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Influence of duty cycle and frequency of the polarizing signal on thickness and protective properties of PEO-coatings on aluminum alloy

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Abstract: Plasma electrolytic oxidation (PEO), also known as micro-arc oxidation, is one of the most effective, though energy consuming, surface treatment methods, which allows one to produce multifunctional coatings for protection of metals and alloys against aggressive media. It still offers challenging topics for researchers to reveal the mechanisms, which underlie the coating formation kinetics and determine their structure and properties. Valve metals and alloys such as aluminum, titanium, magnesium, can be successfully treated by this method. PEO-coatings results from the plasma microdischarges action on the surface of materials and typically consist of oxidized elements of the metal/alloy and the components of the electrolyte. The provided literature data confirm that electrical parameters of the polarizing signal influence significantly (along with the nature of the treated alloy and chemical composition of the electrolyte) the properties of the coatings. Nevertheless, the existing data on the duty cycle influence are often controversial and depend on the electrolyte composition, processed alloy, electrical parameters and frequency of the polarizing signal. The common observation is that decrease in pulse duration can be beneficial to the coatings parameters. The aim of this work was to investigate the peculiarities of the coatings formation on aluminum alloy using 5 μs square wave polarizing signal and its influence on protective properties of the formed oxide layers.

The rectangular plates (20 mm \times 50 mm \times 2 mm) of the wrought aluminum alloy AMg₃ belonging to Al-Mg-Mn-Si system, were used as the samples. Plasma electrolytic oxidation was performed using a transistor power supply equipped with an automated control system with appropriate software. The duration of polarizing pulses was equal to 5 μs . Samples were treated in bipolar mode for 30 and 60 min. In the anodic period the voltage increases from 30 to 360 V at a rate of 65 V/min. Next, the rate of the voltage increase was sequentially reduced down to 2.5 and 1.1 V/min by a total oxidation time of 30 and 60 min, respectively. Thus, the final voltage was 420 V. In the cathodic period, galvanostatic mode with a current density of 0.1 A/cm² was maintained in both cases. To ensure a necessary duty cycle, the pause between the pulses was set as 19 μs ($D=0.21$), 37 μs ($D=0.12$), and 78 μs ($D=0.06$). D was calculated according to equation $D=t_{\text{on}}/(t_{\text{on}}+t_{\text{off}})$, where t_{on} and t_{off} are the durations of pulse and pause, respectively. Morphological features, chemical composition, mechanical, and electrochemical properties of the coated samples were estimated.

The analysis of Fig.1 allows concluding that an increase of thickness and decrease of porosity are in direct relationship with the plasma discharge characteristics during the coating growth process. From Fig.1, it can be found that all of the coatings are bound firmly with the substrate and no cracks or any noticeable discontinuities in the cross-section of the oxide coating were found. All layers appear to be dense and uniform and exhibit morphology without open pores or defects. It is evident that with increase of the duty cycle the relief of the coatings transforms from voids and pancake structures visible on the insets in Fig.1(a,b,d,e) to a more smooth topography with melted pores. Micropores presented in the oxide layers were formed as a result of the plasma microdischarges stimulated the melting of the coating material and gas evolution in the place of the plasma channels. Despite the fact that growth process of the PEO-coatings due to the contribution of plasma-chemical reactions is not obeying the Faraday's law and has non-linear dependence, the typical conclusion is following: the more electricity was spent during the process, the thicker coating will be obtained as a result of the treatment.

Analysis of mechanical tests data shows that both the processes conducted for 30 and 60 min exhibit a tendency to an increase of the microhardness values with the increase of D . The highest microhardness values and the best elastic–plastic characteristics among the studied oxide layers are offered for the coating formed by oxidation for 60 min at $D=0.21$: the values obtained for it exceed the microhardness (950 ± 27 MPa) and elastic modulus (62.4 ± 5.7 GPa) of the metallic substrate in 5.7 and nearly in 2.1 fold, respectively. Increasing the amount of energy consumed for coating growth leads to the formation of thicker PEO-layers, thereby improving their tribological properties. This conclusion is confirmed by the wear data for the coatings. It is worth noting that the roughness factor value R_a for the coatings does not exceed $0.40\ \mu\text{m}$, which indicates that their surface is rather smooth and provides indirect evidence that the coatings have low porosity.

The best results showed the coating formed in the oxidation mode for 60 min at $D=0.21$. The obtained data on mechanical properties and wear behavior are fully conform with the morphological observations and chemical composition of the coated samples. The increase in protective properties is observed with increasing D and oxidation time with subsequent increase in thickness and appearance of hard phases such as molybdenum carbides, having a high microhardness.

The protective coatings on 5754 aluminum alloy possessing better mechanical and anticorrosion properties than the substrate material have been obtained in a mixed electrolyte using microsecond polarizing current pulses. The increase in D and oxidation time lead to the decrease in porosity and increase in thickness, which resulted in improved protective properties.

Increasing the polarizing signal duty cycle leads to a decrease in surface (down to 0.79%) and cross-sectional porosity (down to 6.05%), and a considerable increase in the thickness of the PEO-layers (up to $11.6\pm 1.9\ \mu\text{m}$). Joint analysis of the EDX, XRD, and XPS data disclosed the chemical composition of the samples. The β - and γ -phases of Al_2O_3 are major component of the studied PEO-layers, and aluminum phosphate (AlPO_4), and molybdenum carbides are the minor constituents.

The analysis of electrochemical impedance spectroscopy and potentiodynamic polarization data revealed significant increase of barrier properties of the coated samples in comparison with the bare alloy.

Mechanical properties of the oxide layers demonstrate that an increase in D and oxidation time leads to an increase of microhardness in 2.5-3 fold and of the number of wear cycles in 1.5 fold in comparison with the aluminum substrate.

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Keywords: plasma electrolytic oxidation, protective coatings, chemical composition, aluminum, duty cycle

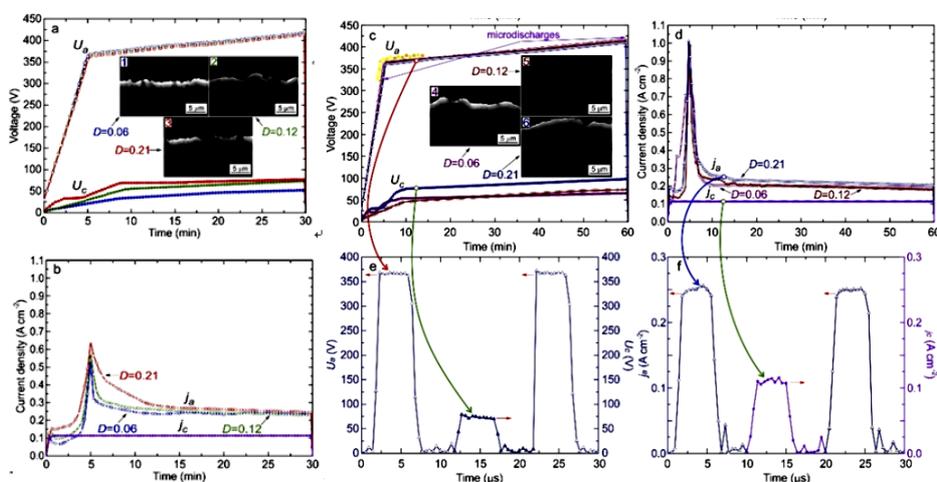


Fig.1 Electrical parameters of the oxidation modes for the 30 min (a,b) and 60 min (c,d) process, and waveforms of the pulses for the 60 min process (e,f), and SEM-images of the cross-sections of the PEO-coatings produced by oxidation for 30 (1–3) and 60 (4–6) min at $D=0.06, 0.12,$ and 0.21

Optical emission spectroscopy as a comprehensive tool for the characterization of micro-arcs during cathodic plasma electrolysis of metals and alloys

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Abstract: The main aspect of plasma electrolytic treatment of metals and alloys is the appearance of spatially and temporally inhomogeneous short-lived micro-discharges (arcs, glow discharges). These micro-discharge events significantly interact with the surrounding gas envelope, electrolyte, and metallic surface, influencing the morphology and composition of deposited layers. Therefore, in order to perform diagnostics of such micro-discharges one needs to employ an appropriate optical measurement technique such as optical emission spectroscopy (OES). In the last seven years, high-resolution OES set-up was used in the frame of plasma electrolytic oxidation (PEO) and cathodic plasma electrolysis (CPE) experiments at the Faculty of Physics Belgrade. In the following text, the brief overview of recent results regarding the spectroscopic investigation of CPE micro-arcs will be presented.

Thin rectangular samples (W, Ni, Zr, Ti, Ta, stainless steel) of dimensions 25 mm×2.5 mm were used as cathode while two platinum plates (40 mm×20 mm) were used as anode. The samples were sealed with insulation resin leaving only active surface with an area of 10 mm×2.5 mm accessible to the electrolyte. For W and Ni cathode experiments, a mixed solution of borax, water and ethylene glycol (6:34:10 in weight) was used as electrolyte. For the experiments with Zr, Ti, Ta and stainless steel samples, the water solution of 30 g/L NaOH was prepared. The experiments were driven with DC power supply and the spectra recorded during flat current-voltage characteristics. Two spectrometers, Czerny-Turner (0.67 m focal length; 0.83 nm/mm inverse linear dispersion in the first diffraction order) and Ebert-Fastie (2 m focal length; 0.74 nm/mm inverse linear dispersion in the first diffraction order) equipped with thermoelectrically cooled CCD camera (2048×512 pixels; 12 μm; pixel width; $T=-10$ °C) were used for CPE spectra recordings. The H I 486.1 nm line, Na I doublet at 588.6 nm and Fe I 538.3 nm line recorded during CPE experiments and the corresponding fitting curves are shown in Fig.1. The presence of several Ni I lines in the vicinity of H I 486.1 nm line proves that the complex line shape of studied spectral lines is not the consequence of the spectrometer imperfections but micro-arc features. For detailed description of developed fitting procedures, see [1] and references therein. It is important to mention that the fitting curve represent the superposition of mutually shifted profiles associated with spatial or temporal regions of micro-arc plasma (in the following text designated with 1, 2 and 3). In conjunction with spectral line broadening theory, the plasma parameters such as electron number density (N_e), density of ground state atoms (N_g) and the mole fraction of CPE plasma constituents (X_i) can be deduced. After the analysis of profiles shown in Fig.1, the following results are obtained: (i) $N_e^1=0.07N^*$, $N_e^2=0.8N^*$, $N_e^3=2N^*$ ($N^*=1 \times 10^{16}$ cm⁻³); (ii) $N_g^1=13N_g^*$, $N_g^2=13N_g^*$, $N_g^3=270N_g^*$ ($N_g^*=1 \times 10^{16}$ cm⁻³); (iii) $X_1=2\%$ (H₂), 34%-42% (Fe), 2% (O), 4% (H), 42%-58% (H₂O); (iv) $X_2=84\%$ -94% (Fe), 2%-5% (O), 4%-11% (H). The influence of cathode material on the results is not significant. Besides the plasma electrolytic technology, the potential applicability of this diagnostics tool is for glow discharge/plasma processes, phenomena in laser-induced plasma and high-pressure light sources.

Keywords: cathodic plasma electrolysis, spectral line shape analysis, plasma diagnostics

Reference:

[1] Jovović J, Stojadinović S, Vasilic R, et al. EPL,2017, 118: 33001.

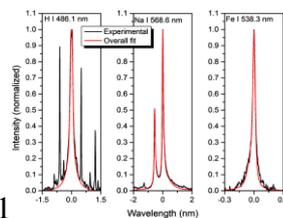


Fig.1

Anodic plasma electrolytic saturation of steels with nitrogen, carbon and boron

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Abstract: The report is devoted to anodic plasma electrolytic treatment, including thermal and electrochemical features of the process, electrolyte compositions for saturation of steels with nitrogen, carbon and boron, the structure and phase composition of the modified layers, and their properties. Plasma electrolyte saturation of metals and alloys with interstitial elements is realized in the system of electrolyte–vapour-gaseous envelope–metal electrode-part. In this case the envelope is a heating and saturating medium. The flux of heat from the envelope to the electrolyte provides the stable solution-vapour interface similar to film boiling of liquids. The heat flux from the envelope to the workpiece results in its heating up to 400-1000 °C. The compounds of nitrogen, carbon or boron contained in the electrolyte solution evaporate into the envelope where they decompose into simpler substances. The nitriding of steels is carried out by adsorption of ammonia or ammonium nitrate, which release atomic nitrogen. Glycerol, acetone, sucrose, and ethylene glycol can be used for the carburising of steels. In this case, carbon monoxide and hydrocarbons are adsorbed on the surface of the steel sample with the liberation of carbon atoms diffusing into the metal. Source of boron can be boric acid which forms with glycerine a complex, diglycerineboric acid, followed by the decomposition into original components at temperatures as low as 50 °C, i.e., near the border with the vapour-gaseous envelope. As a result, an electric field will induce migration of the monobasic hydroxocomplex to the anode, which forms the X-ray-discovered $\text{Fe}_2\text{Fe}(\text{BO}_3)\text{O}_2$ и $\text{Fe}(\text{BO}_2)$, compounds on the anode, as well as boron, which diffuses into the metal per se.

Processes of diffusion saturation, anodic dissolution, and high-temperature oxidation of iron determined the structure and phase composition of the modified layer occur simultaneously on the surface of the steel. The layer thickness, its microhardness and surface roughness, coefficient of friction and wear resistance are considered for nitriding, carburizing, nitrocarburizing and boriding of low-carbon and medium carbon steels.

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Keywords: diffusion saturation, nitriding, carburizing, boriding

Improved corrosion resistance of zinc phosphate-incorporated alumina coating prepared by one-step plasma electrolytic oxidation

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Abstract: Aluminum and its alloys have been used in many fields, including automobile, aerospace and aviation, biomedical, and military industry, due to high strength-to-weight ratio, good casting capability, and so on. However, the intrinsic corrosion resistance of aluminum alloys is poor, especially in the salt solution containing chloride ions. Therefore, improving the corrosion resistance of aluminum alloys is crucial to extend their applications. Plasma electrolytic oxidation (PEO) has been used as a high-efficient and less-polluting method to improve the corrosion resistance of aluminum alloys. Nevertheless, the corrosion resistance of the PEO coatings can be furtherly improved by reducing the cavities in the coatings. Zinc phosphate has been used as environmentally friendly anticorrosive components for protecting steel and Ti alloys. This work fabricated a zinc phosphate-incorporated alumina film on aluminum alloy to improve the corrosion resistance significantly and the selfhealing mechanism of the zinc phosphate to the alumina coating is studied. The composition and morphology of the as-prepared coatings are characterized by X-ray diffractometer (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (SEM). The corrosion resistance of the PEO coatings is evaluated by salt spraying test and Tafel polarization in 3.5% NaCl solution. The results show that non-crystalline zinc phosphate is formed and incorporated into alumina during the PEO process and both the film thickness and porosity increase with the Zn(Ac)₂ concentration. The zinc phosphate-incorporated PEO samples show better corrosion resistance than the as-received Al alloy and undoped PEO sample and the sample prepared in 20 g/L Zn(Ac)₂ (Zn-20) shows the longest lifetime of more than 5000 h for salt spaying test. Polarization test also shows the Zn-20 sample possess the highest corrosion potential and the smallest corrosion current density of the PEO samples, indicating the best corrosion resistance. In conclusion, the MAO coatings with amorphous zinc phosphate show excellent corrosion resistance and are promising to the corrosion protection of aluminum alloys.

Keywords: plasma electrolytic oxidation, aluminum alloy, zinc phosphate, alumina, corrosion resistance

Non-oxidizing trend in plasma electrolytic technologies: mechanism, diagnostics and applications of electrolytic plasma polishing

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Abstract: Plasma electrolytic technologies gain significant interest from the researchers worldwide due to advanced capabilities in surface modification, wide opportunities for deeper understanding of plasma in liquids, and last, but not the least—spectacular sight of microdischarges. The number of papers published every year doubles in the previous 10 years. Among them, more than 60% belong to the oxidizing technologies, primarily, plasma electrolytic oxidation. The others explore electrolytic plasma processes featuring vapour-gaseous envelope (VGE). Such non-oxidizing technologies include anodic and cathodic electrolytic plasma heat treatments resulting in case hardening, cathodic plasma electrolytic deposition resulting in coating formation, and anodic and cathodic electrolytic plasma polishing and cleaning resulting in stripping of undesired surface layers. Anodic electrolytic plasma polishing (EPPo) was patented in early 1980s, and since then, research and industrial applications have been developed primarily for stainless steels and copper alloys. EPPo typically can be applied to valve metals. The mechanism of EPPo is based on the vapour-gaseous envelope concept; the VGE is a result of: (i) oxygen liberation due to water electrolysis, and (ii) electrolyte evaporation due to the highest values of the current density in the anode vicinity. In order to meet these requirements, the treatment must run on the anode, and its surface area must be an order of magnitude less than that of the cathode. Typical current density for the EPPo process is 0.1-1.0 A/cm²; in order to achieve this, the voltage applied should be in the range from 200 to 400 V for aqueous electrolytes. The VGE should have bubble type of boiling and distributed plasma discharge with low intensity. In these conditions the anodic dissolution dominates over the oxides formation on the treated surface, and no electric erosion is caused by the discharge. As a result, mirror-like polished surface can be achieved with R_a as low as 0.05 μm .

The EPPo process diagnostics can be realized via electrical, optical, and acoustical parameters. The optical characteristics, such as optical emission spectroscopy and video imaging, are not as fruitful as those for plasma electrolytic oxidation due to much lower light intensity during the EPPo. The acoustical characteristics can supply information because the noise generated by the process comes from the VGE which action depends not only on the process parameters, but also on the surface properties. For example, it was shown that the acoustic signal has a frequency band from 50 to 5000 Hz with maxima at approximately 500 Hz and 1500 Hz; the position of the second maximum is strongly correlated with the surface roughness. The electrical parameters provide a wide variety of methods; this includes analysis of current-voltage curves (CVC), frequency response (FR) analysis and electric field (EF) analysis. The EPPo process CVC is N-shaped, and the operational conditions belong to the CVC part having negative differential resistance. The FR analysis helps to apply in-situ impedance spectroscopy to the process diagnostics. It was shown that the equivalent circuit of the process is quite complex, and it contains capacitances and inductances, and also positive and negative resistances. The electric field analysis for this nonlinear system helps to understand and optimize the current density distribution along the workpiece, and to assess the voltage drops across the electrolyte and across the VGE.

Current state of the art in the EPPo industrial applications includes polishing of steel, nickel and copper alloy workpieces having complex shape. This can also include coating striping for refurbishing purposes. The most advanced challenges are inner surface polishing and valve metals polishing; with better understanding of the process via diagnostics and modelling, these challenges can be resolved.

The research is supported by RFBR grants 16-53-48008 and 16-38-60062.

Keywords: electrolytic plasma polishing, process diagnostics

Preparation of plasma electrolytic oxidation coating on Mg-Li alloy and its thermal control performance

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Abstract: When the spacecraft runs in orbit, wild temperature swings always affect the inner instruments under strong solar radiation without atmosphere protection. Therefore, the Mg-Li alloy is not suitable as aerospace materials before modified with thermal control coating.

In this work, the plasma electrolytic oxidation (PEO) was employed to prepare thermal control coating on Mg-Li alloy with various Li content (4 wt% and 9 wt%) in silicate-based systems. Briefly, prior to PEO treatment, Mg-Li alloy is polished well by 200, 600 and 2000 sandpaper, and then sonicated in 1% sulfuric acid and acetone for 60 s and 5 min, respectively. The silicate systems was made up with 7-20 g/L sodium silicate, 0.7-2.0 g/L NaF and 0.7-2.0 g/L NaOH, and the PEO parameters are 5 A/dm² of current density, 20% of duty ratio and 20 min of PEO time. The effect of Li content and electrolyte composition on the coating formation and thermal control performance of PEO coating were suited by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), optical emission spectroscopy (OES) and thermal control performance tests.

With the increase of silicate electrolyte concentrations, the coatings of Mg-Li become slightly thicker and rougher, owing to more component from electrolyte participate in the coating formation. SEM and EDS analysis reveal that more nano-particles clusters coating Si and Na element were generated on PEO coating on Mg-4Li alloy, while more micro-protuberances were observed on Mg-9Li alloy, corresponding to the increase of coating roughness. The XRD results show that Mg-4Li alloy are composed of Li_{0.92}Mg_{4.08} (α phase), while Mg-9Li alloy of Li_{0.92}Mg_{4.08} and LiMg(β phase). Nevertheless, the changes of phase compositions in Mg-Li alloy affect little the composition of PEO coating that main composed of MgO and Mg₂SiO₄, and more Mg₂SO₄ are formed with the increases of electrolyte concentration, corresponding to the increase of coating thickness.

Thermal control tests shows that as the electrolyte concentration increases, the obtained PEO coatings of Mg-Li alloy possess lower solar absorptance ($\lambda=0.25-2.5 \mu\text{m}$) and higher emissivity ($\lambda=3-35 \mu\text{m}$), which results from that thicker coating can hinder more solar energy adsorbed by the metal substrate, and more rougher coating provides more surface area for radiating energy.

Furthermore, the spark discharge during PEO process were also characterized by OES. The dominant spark discharge on Mg-4Li is from excitation of Na ions (Na from electrolyte), and the dominant spark discharges on Mg-9Li are Na ions and Li ions (Na from electrolyte & Li the substrate), which are mainly controlled by the phase composition of Mg-Li alloy. Also, the surface morphology were related to the type of spark discharges: due to more Na ions sparks discharge during PEO process, the PEO coatings of Mg-4Li possesses more particles clusters coating than that of Mg-9Li. Therefore, among these results, the Mg-4Li coating of containing more particles clusters has higher absorptance, and the Mg-9Li coating containing more protuberance structure has higher emissivity, showing a good accordance between coating structure and performance.

In summary, the PEO coating prepared on Mg-Li alloy with slightly more Li content in the electrolyte with more concentration has better thermal control performance. The optimal PEO conditions are Mg-9Li alloy, 20 g/L sodium silicate, 5 A/dm² of current density, 20% of duty ratio and 20 min of PEO time, and the obtained coating possesses 0.38 of absorptance and 0.89 of emissivity.

Keywords: plasma electrolytic oxidation, ceramic coating, thermal control property, Mg-Li alloy, optical emission spectroscopy

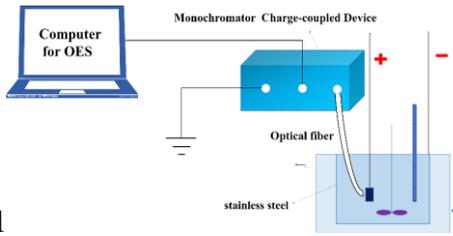


Fig.1

Fig.1 Schematic diagram of plasma electrolytic oxidation (PEO) process and optical emission spectroscopy (OES) apparatus

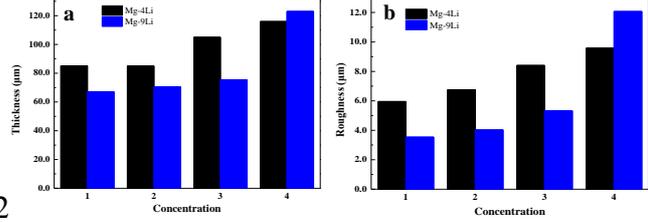


Fig.2

Fig.2 The thickness (a) and roughness (b) of coatings on Mg-4Li alloy and Mg-9Li alloy prepared at the silicate electrolytes with various concentration

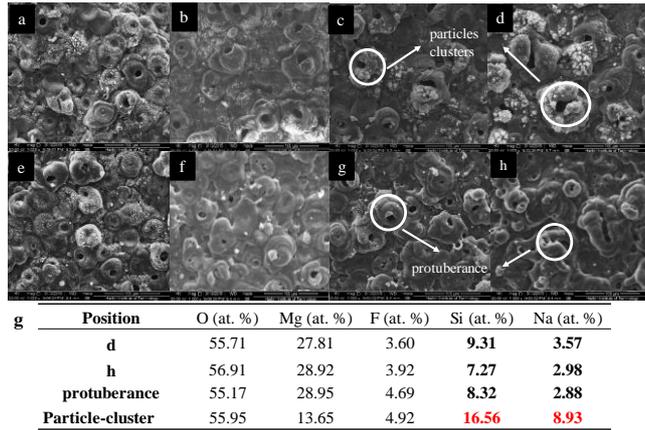


Fig.3 SEM morphologies (a-h) and element distribution (g) of Mg-Li coating: (a) Mg-4Li & 7 g/L NaSiO₃; (b) Mg-4Li & 10 g/L NaSiO₃; (c) Mg-4Li & 15 g/L NaSiO₃; (d) Mg-4Li & 20 g/L NaSiO₃; (e) Mg-9Li & 7 g/L NaSiO₃; (f) Mg-9Li & 10 g/L NaSiO₃; (g) Mg-9Li & 15 g/L NaSiO₃; (h) Mg-9Li & 20 g/L NaSiO₃

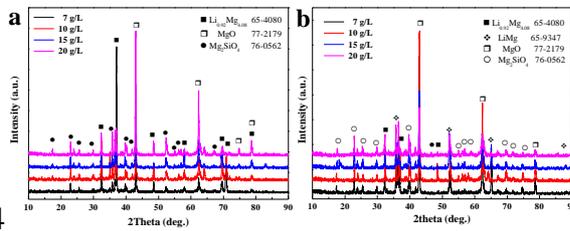


Fig.4

Fig.5

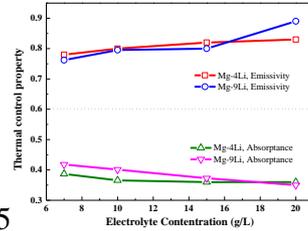


Fig.4 XRD patterns of PEO coatings prepared on Mg-4Li alloy (a) and Mg-9Li alloy (b)

Fig.5 Emissivity and absorptance of PEO coating prepared on Mg-Li alloy in silicate-based electrolyte with various concentration

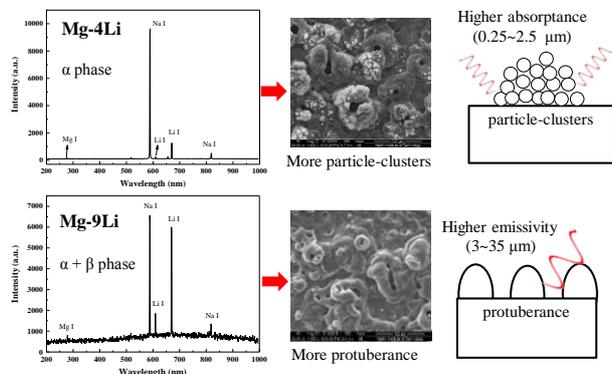


Fig.6 OES on the alloy surface of Mg-4Li and Mg-9Li during PEO process, and the relationships between SEM and thermal control performance of PEO coatings

Evolution of carbon diffusion layer during cathodic plasma electrolysis on steel

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Abstract: In this paper, a thorough research of the cathodic plasma electrolysis process on steel was performed. The evolution of carbon diffusion from the critical voltage to the oxidation voltage was investigated for the first time. The results showed that there was a significant increase of steel surface temperature at the critical voltage, accompanied by a grain refinement near the interface. Above the critical voltage, the substantial carburizing process started. The carbon diffusion coefficient at 380 V was 1.5×10^{-7} cm²/s, which was one magnitude higher than that of the conventional carburizing at the same temperature. As the voltage rising, the activity of oxygen species increased and the carburizing process was replaced by an oxidation process. Meanwhile, the carbon atoms were released from the interstitial sites and aggregated into carbon particles, embedded in the oxide layer on steel surface.

Cathodic plasma electrolysis (CPE) is an atmospheric pressure plasma saturation and deposition process in which plasma is sustained by a continuous discharge in the near-cathode region with abundant activated electrons. Due to its high efficiency and low cost, CPE approach has aroused a wide attention in the application of metal surface modification and pollutant degradation. In the CPE process on steel, active carbon or nitrogen species, decomposed from organic electrolyte are accelerated by electric field to generate an interstitial diffusion into the iron lattice, forming carburized or nitride layer with enhanced wear and corrosion resistance. The physicochemical reactions at the interface of cathode and plasma envelope are complex. However, till now, most of the CPE studies focus on the technological improvement and performance enhancement for modified layer, while the plasma discharge mechanism, the interfacial reactions and evolution of the modified layer during CPE process are rarely investigated systematically.

In this study, we systematically investigated the carbon evolution process during cathodic plasma electrolysis on steel in glycerol aqueous solution. The substrate material was a 2 mm thick carbon steel (0.75-0.84C, ≤ 0.35 Si, ≤ 0.40 Mn, ≤ 0.035 P, ≤ 0.030 S, wt%, Fe balance) sheet with 55 mm \times 15 mm dimensions. The surface temperature of the steel sample and the diffusion coefficient of carbon were evaluated. Optical emission spectroscopy (OES) method was employed to examine the plasma discharge mechanism and the interfacial reactions near cathode. The active species in plasma envelope were determined and the plasma electron temperature was calculated. Meanwhile, the morphology, composition and structural features of CPE treated steel under different discharge voltages were analyzed. The formation process of the modified layers on steel substrate was discussed.

Keywords: cathodic plasma electrolysis, steel, carbon diffusion, oxidation

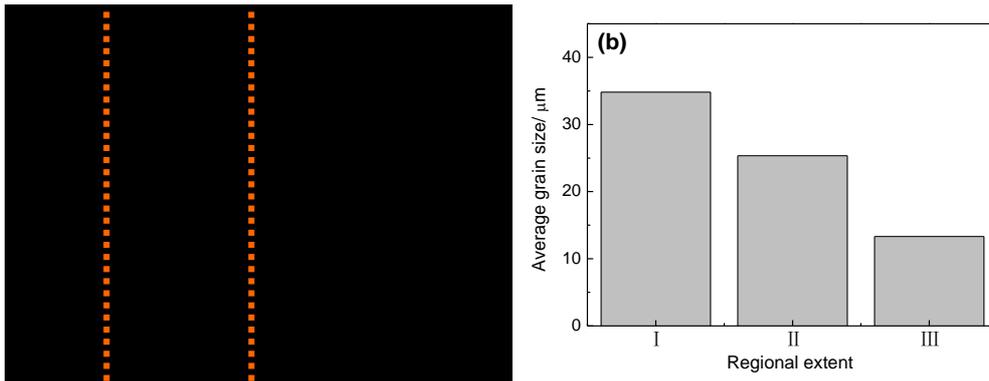


Fig.1 (a) cross-sectional image of CPE treated steel at 340 V, (b) average grain sizes of three typical regions, I: steel matrix, II: transition region, III: surface region

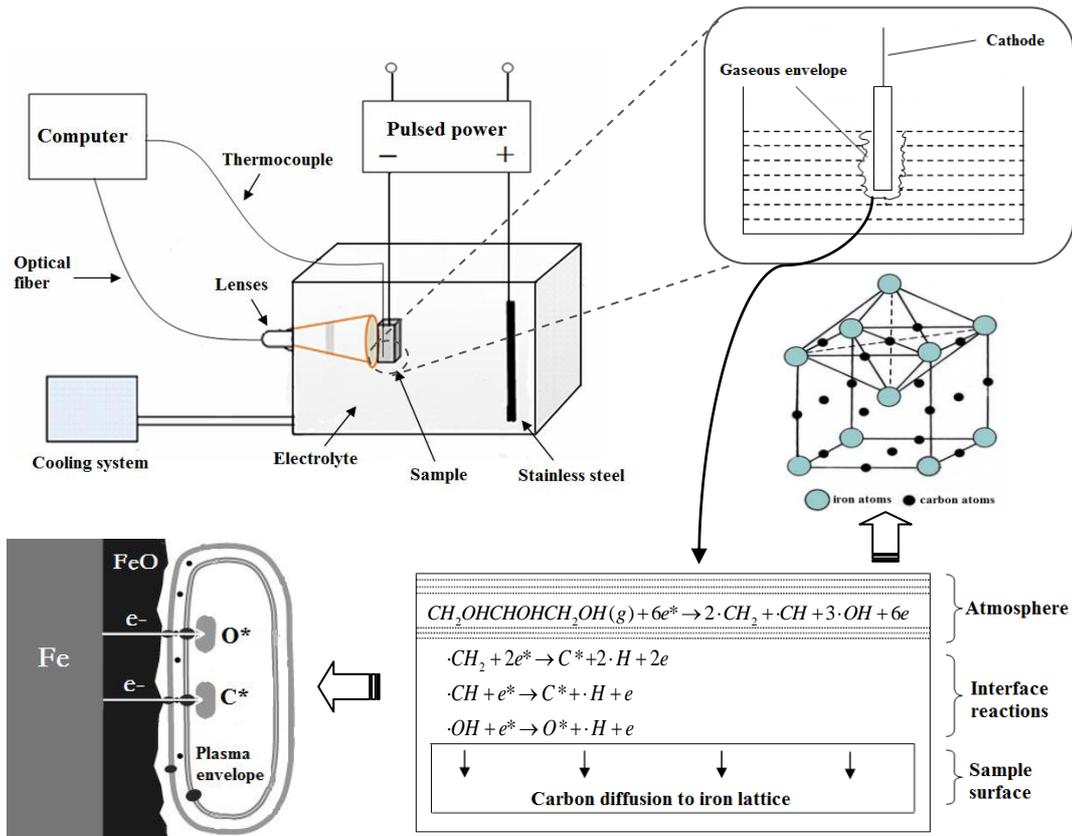


Fig.2 Interfacial reactions and carbon diffusion evolution during CPE process on steel

Increasing corrosion properties of steels by plasma electrolyte treatment

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Abstract: Anodic electrolyte-plasma processes of carburization, nitriding and nitrocarburization of low-carbon steel (0.2%C), stainless steel 20Cr13 and high-carbon steel CrWMn were studied. The treatment was carried out in aqueous electrolytes containing ammonium chloride (10wt%) and saturating components. As sources of carbon, glycerol (8%) or sucrose (10%) was chosen. The source of nitrogen was ammonium nitrate (10%), in addition, carbamide was used, providing a saturating medium with nitrogen and carbon simultaneously. The phase composition of the modified layers was studied with the help of metallographic and X-ray analysis, the surface roughness and corrosion properties of the samples were measured by the potentiodynamic method in a 3% solution of sodium chloride. It was found that the outer layer contains iron oxides FeO and Fe₃O₄, a martensitic layer is observed below as a result of quenching in the electrolyte after saturation of the steel with nitrogen and/or carbon. The possibility of reducing the roughness of steel 20 from the initial 1.0 μm in the control sample to 0.27 μm after cementation in a saccharose electrolyte at 950 °C for 5 min is shown. It is also possible to reduce the roughness of steel 20Cr13 after treatment with urea electrolyte. Nitriding of high-carbon CrWMn steel leads to an increase in its roughness, presumably due to the formation of a loose oxide layer.

Carburizing of low-carbon steel in an electrolyte with addition of sucrose at 750 °C in 5 minutes allows reducing the corrosion current density from 10 μA/cm² to 2 μA/cm² and in the case of electrolyte treatment with the addition of glycerol to 4.2 μA/cm². The nitriding of high-carbon steel at a temperature of 700 °C for 5 minutes and subsequent quenching from 850 °C reduces the corrosion current from 23 μA/cm² to 3.5 μA/cm². The current density of corrosion of steel 20Cr13 after quenching from the furnace from 1050 °C and removal of the oxide layer is 25 μA/cm², and after additional tempering at 650 for 30 minutes to 18 μA/cm². Nitriding at a temperature of 600 °C in 5 minutes makes it possible to reduce the corrosion current density to 3 μA/cm², and nitrocarburization in a solution with the addition of urea at the same temperature up to 6 μA/cm². The mechanical removal of the oxide layer by the 1200 sandpaper before partial surface clarification reduces the corrosion current density in the first case to 1.5 μA/cm², and in the second case to 1 μA/cm².

Acknowledgements: This work was financially supported by the Russian Science Foundation (Contract No. 18-79-10094) to the Kostroma State University.

Keywords: plasma electrolyte treatment, corrosion resistance, steel

Influences of processing factors on corrosion resistance and calcium content of anodic coatings developed on AZ31B magnesium alloys

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Abstract: Magnesium appears to be the most promising degradable metal due to its excellent property. However, the too rapid initial degradation rate in body fluid is the biggest challenge for clinical applications. The developed coating on magnesium alloy with excellent corrosion resistance and rich in calcium element has become the research focus. In this study, the influences of processing parameters including NaOH concentration, sodium phytate (Na_{12}Phy) concentration, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ concentration and treating time on the corrosion resistance and calcium content of micro-arc oxidation (MAO) coatings on AZ31B magnesium alloy were systematically investigated by using an orthogonal experiment of four factors with three levels. The affecting factors on the formation of micro-cracks on the surface of MAO coating in this electrolyte system were further studied. The process was optimized to prepare MAO coating with high corrosion resistance and calcium content. Scanning electron microscope (SEM), X-ray energy dispersive spectroscopy (EDS), X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize MAO coatings. The corrosion resistance of MAO treated samples was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy in simulated body fluid (SBF). The results show that the rank of influencing factors on corrosion resistance of the MAO treated samples is treating time > Na_{12}Phy concentration > $\text{Ca}(\text{H}_2\text{PO}_4)_2$ concentration > NaOH concentration. The developed micro cracks on the surface of MAO coatings, which are resulted from the synergy effects of prolonged treating time, excess high NaOH and Na_{12}Phy concentration, play an important role in the corrosion resistance of MAO samples. The order of influencing the calcium content is $\text{Ca}(\text{H}_2\text{PO}_4)_2$ concentration > Na_{12}Phy concentration > NaOH concentration > treating time, demonstrating that calcium ions enter into MAO coatings mainly by diffusion. The increased $\text{Ca}(\text{H}_2\text{PO}_4)_2$ concentration in the electrolyte can improve the calcium content in MAO coatings. It is found that with the increase of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ concentration, the fabricated MAO coatings exhibit decreased porosity with increased pore size and rougher surface. When $\text{Ca}(\text{H}_2\text{PO}_4)_2$ concentration is 8 g/L, the prepared MAO coating achieves the best corrosion resistance.

Keywords: magnesium alloy, micro-arc oxidation, calcium, corrosion resistance, orthogonal test

Effect of surfactants on morphology and wear resistance of TiO₂/hBN composite ceramic coatings formed by microarc oxidation on Ti6Al4V alloy

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Abstract: The effect of four different types of surfactants on the morphology and wear resistance of the composite microarc oxidation (MAO) coatings containing hexagonal boron nitride (hBN) solid lubricating particles are studied in order to get composite microarc oxidation coatings with good wear resistance on titanium alloy. A certain amount of different surfactants are added respectively to the electrolyte consisted of 20 g/L of Na₂SiO₃, 6 g/L of (NaPO₃)₆ and 2 g/L of NaOH in distilled water with 2 g/L hBN particles. During the MAO process, the electrolyte is continuously stirred in order to improve the dispersity of the particles. The effect of surfactants on the voltages during microarc oxidation are recorded. The thickness, surface roughness, surface and cross-sectional morphologies of the composite microarc oxidation coatings are investigated by eddy current thickness gauge, profile meter and SEM respectively. The tribological performance of the coatings is evaluated under dry conditions at room temperature, by using an HT-1000 ball-on-disc tester. The results show that the surfactants have a significant effect on wear resistance of the composite microarc oxidation coatings. The surfactants influence the wear resistance of composite microarc oxidation coatings mainly from the four aspects: the surface morphology of MAO coatings, the porosity of MAO coatings, the content of hBN particles in MAO coatings and the dispersity of hBN particles in MAO coatings. Cationic surfactant cetyl trimethyl ammonium bromide (CTAB) decreases the content of hBN in the coating and weakens the coating/substrate bond strength, which is not conducive to the improvement of the wear resistance of the coating; Nonionic surfactant absolute ethyl alcohol (ethanol) makes the decline in the density of the coating due to its strong volatility, thus reducing the wear resistance of the coating; Anionic surfactant sodium dodecyl benzene sulfonate (SDBS) has little effect on the morphology and wear resistance of the coating; Anionic surfactant sodium carboxymethyl cellulose (NaCMC) is effective in improving the dispersity and content of hBN particles in the electrolyte, thereby improving its complex and uniform distribution in the coating, thus significantly improving wear resistance of the composite microarc oxidation coating.

Keywords: composite microarc oxidation, surfactant, titanium alloy, microstructure, wear resistance

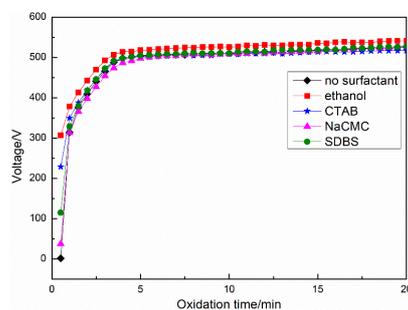


Fig.1 Voltage-time response of MAO process in electrolytes with addition of different surfactants

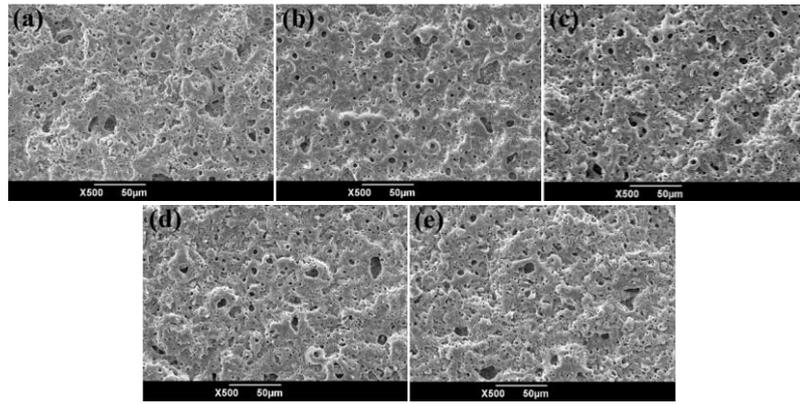


Fig.2 Surface morphology of MAO coatings prepared in electrolytes with addition of surfactants (a) no surfactant; (b)CTAB; (c)ethanol; (d)NaCMC; (e)SDBS

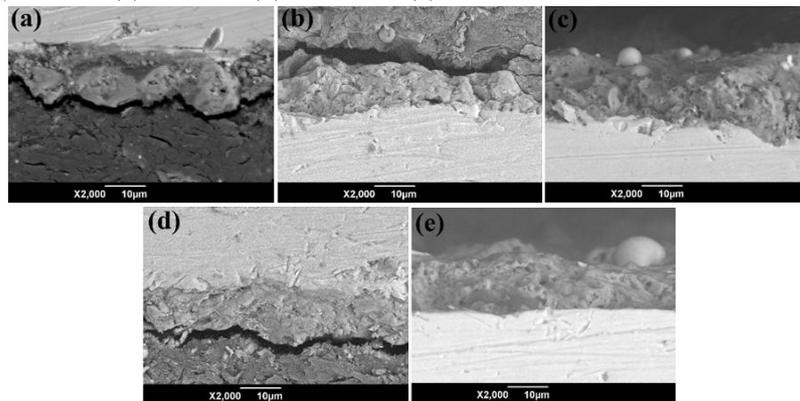


Fig.3 Cross-sectional morphology of MAO coatings prepared in electrolytes with addition of surfactants. (a) no surfactant; (b)CTAB; (c)ethanol; (d)NaCMC; (e)SDBS

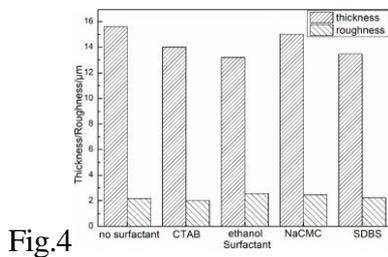


Fig.4

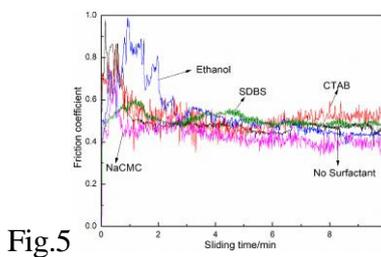


Fig.5

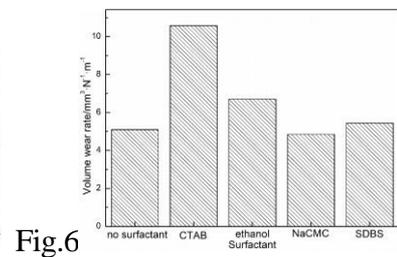


Fig.6

Fig.4 Thickness and roughness of MAO coatings prepared in electrolytes with addition of surfactants

Fig.5 Friction coefficient of MAO coatings prepared in electrolytes with addition of surfactants

Fig.6 Volume wear rate of MAO coatings prepared in electrolytes with addition of surfactants

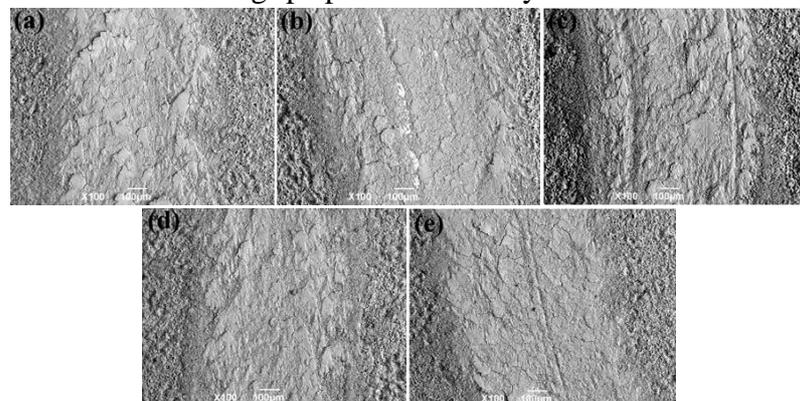


Fig.7 Worn surface of MAO coatings prepared in electrolytes with addition of surfactants

Can free state W exist in plasma electrolytic oxidation (PEO) coatings?

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Abstract: There is a point of view that free state W exists in the coatings produced on aluminum alloy by plasma electrolytic oxidation (PEO) using a electrolyte containing sodium tungstate, which was supported by the presence of W peaks in X-ray diffraction (XRD) pattern of the coatings. However, the extremely high temperature in the PEO discharge channels seems to disfavor the formation of free state elements. Further, a previous study reported that free state W was not found in the PEO coating by X-ray photoelectron spectroscopy (XPS). Hence, it is interesting to clarify whether or not free state W really exists in PEO coatings. Here, PEO of 8090 aluminum alloy was carried out in a mixed electrolyte containing sodium tungstate and sodium silicate. The PEO coatings were first analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), and the results showed that the W species were mainly enriched at the interface of the coating and the substrate. According to the XRD patterns of the sample, there were obvious characteristic peaks that coincide with free state W. In order to trace the exact existing states of W species in the PEO coatings, XPS and transmission electron microscopy (TEM) were employed to characterize the coatings. XPS analyses have been performed on the surface, inner layer (exposed by grounding) and bottom of the coating. The bottom side of the coating was exposed by dissolving the substrate metal with an electrochemical method. Most of the XPS analyses did not detect the presence of free state W, only a small amount of free state W has been found to be presented in the XPS spectrum of the coating inner layer. Finally, a transmission electron microscope (TEM) sample was prepared by focused ion beam (FIB) from the interface between coating and substrate, where W species was enriched. Selected area electron diffraction (SAED) and EDS have been employed to examine the TEM sample. The results of the SAED showed that the PEO coating was a heterogeneous mixture, which mainly consisted of a large number of amorphous and grains in different sizes. Numerous fine grains ranging from several to tens of nanometers have been found to be embedded in an amorphous substrate. The nano sized grains are possibly free state W according to an EDS elemental mapping. In summary, the answer to the question of whether free state W exists in the PEO coatings is, YES, it exists but is limited to a very small amount. Most of W species should exist in oxide forms according to XPS. The free state W is possibly presented in the form of nanocrystalline particles, however, the W oxides may exist in the form of amorphous state since it was not detected by XRD.

Keywords: plasma electrolytic oxidation, aluminum alloy, interface, free state W

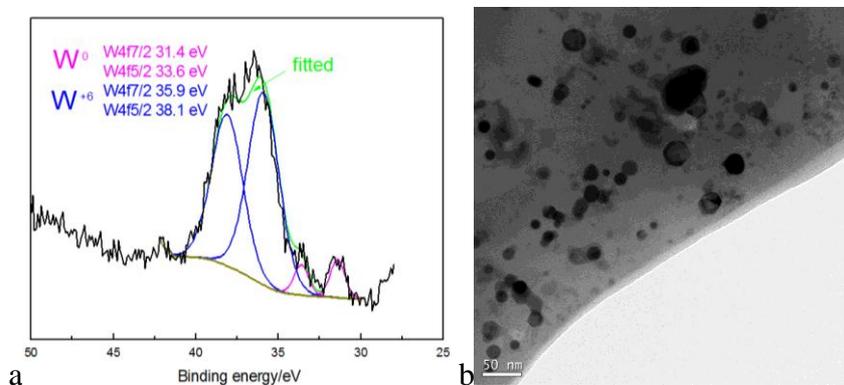


Fig.1 (a) XPS of the inner coating (polished sample) showing the presence of free state W; (b) TEM of the region close to coating/substrate interface, showing the W-containing crystalline nano grains (the black particles)

Entrance formation of calcium and magnesium elements into microarc oxidation coatings developed on Ti6Al4V alloys

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Abstract: Titanium alloys are widely used as metallic implants due to the combination of their outstanding characteristics such as high strength, low density, high immunity to corrosion and good biocompatibility. However, as bio-inert materials, titanium alloys can not form osseointegration with the surrounding bones in vivo and the resultant implant loosening and failure remains one of the major challenges in orthopaedics and dentistry. It is thus necessary to develop proper surface treatment methods to enhance biological property of implant materials. Micro arc oxidation (MAO) is a surface treatment technology, which can fabricate ceramic membrane by in situ formation on the surface of titanium alloys. The composition and concentration of the used electrolytes have great influences on the coating performance. Macro elements such as calcium and magnesium play an important role in bone growth, but its entry mechanism is not clear. The optimal ranges of processing parameters on the magnesium and calcium content of MAO coatings on Ti6Al4V were achieved by using an orthogonal experiment of four factors with three levels. The effects of treatment time, NaOH concentration, EDTA-MgNa₂ concentration, EDTA-CaNa₂ concentration on the properties of MAO coatings were studied. The microstructure and constituents of the obtained coatings were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Results show that the growth mechanism as well as magnesium and calcium content in MAO coatings are greatly influenced by electrolytes. The effect order of factors on the magnesium content is ranked as treatment time > NaOH concentration > EDTA-MgNa₂ concentration > EDTA-CaNa₂ concentration. In the solution containing 5 g/L NaOH, 10 g/L EDTA-MgNa₂, 5 g/L EDTA-CaNa₂ with treatment time 3.5 minute, the MAO coatings achieve the highest magnesium content. It should be noted that the magnesium content in coatings is mainly affected by treating time, indicating that magnesium ions enter into MAO coatings mainly by electric migration. With the increasing KOH concentration, the magnesium content in the coatings continually increases from Level 1 to Level 2 but decreases from Level 2 to Level 3. With the gradual increase of EDTA-MgNa₂ concentration, the magnesium content in the coatings increases. The sequence on the calcium content is EDTA-CaNa₂ concentration > treatment time > EDTAMgNa₂ concentration > NaOH concentration. With the increase of EDTA-CaNa₂ concentration, the calcium content in the coatings gradually increases, indicating that calcium ions enter into MAO coatings mainly by diffusion. It can be seen that the content of magnesium and calcium content in the coatings influences each other. These results clarify the entrance mechanism of magnesium and calcium elements and will provide the important theoretical foundation and experimental data for the development of bioactive coatings on medical titanium alloys.

Keywords: micro-arc oxidation (MAO), titanium alloys, calcium, magnesium

A kinetic model of plasma electrolytic oxidation for Mg-1Ca alloy

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Abstract: New generation magnesium alloys, e.g. Mg-1Ca, are promising in implant applications since they can be used for bioresorbable device design. Magnesium has mechanical properties close to that of a human bone. Mg and Ca are non-toxic, and they play important roles in human metabolism. However, magnesium alloys have a serious drawback: they quickly dissolve in the body. This disadvantage can be eliminated if the implant is coated with a protective film, e.g. using plasma electrolytic oxidation (PEO) method. Complex electrochemical and electrophysical processes occur during PEO of magnesium alloys; their mechanisms need deeper investigation, e.g. by applying well-established electrochemical approaches to analysis of high voltage PEO data. Therefore, the purpose of this research is to study the film growth mechanism during plasma electrolytic oxidation of Mg-1Ca alloy having coarse grained (CG) and ultrafine grained (UFG) structure.

Disk samples (diameter 10 mm and thickness 1 mm) were used for the experiments. The UFG structure was developed via high pressure torsion (HPT) technique. The PEO process was performed in a 6 liter tank at the electrolyte temperature of 20 ± 1 °C. The treatment time was up to 10 min. The electrolyte was composed of 12 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and 2 g/L $\text{Ca}(\text{OH})_2$; the electrolyte volume was 4 litres. The PEO process was realized using 50 kW automated equipment providing PC process control and data acquisition for voltage, current and electrolyte temperature. The PEO process was used in pulsed unipolar mode. The amplitude of voltage pulses was kept at $U_p=470$ V, duty cycle $dp=10\%$, and frequency $f=500$ Hz.

Experimental dependences of current density on time t were analysed using MATLAB. Since the PEO was performed in voltage control mode, the current density curves show gradual decay which is considered as a relaxation region. This happens due to a transition of the system to a new stationary state which is accompanied by the growth of the oxide film. The current density transients were approximated using Curve Fitting Toolbox and a kinetic model which contains two terms, the first for Mg dissolution, and the second for 3D crystallization of precipitate products: $i=i_0 e^{-(t/\tau)+4836.5 \cdot \sqrt{D/t}} (1-e^{-(t/\tau)})$, where i_0 —initial dissolution current density; D —mobility of Mg species in the film; τ —time constant of 3D crystallisation. As a result of the approximation, these coefficients were estimated. The goodness of the fit was evaluated using coefficient of determination R^2 which was 0.98 and better.

The estimated values of the diffusion coefficient belong to the range $(2.55 \dots 3.63) \times 10^{-5}$ cm²/s; the diffusion coefficient is higher for the PEO of the UFG magnesium alloy. The estimated values of the time constant of 3D crystallization belong to the range $(17.0 \dots 30.0)$ s⁻¹; the time constant of 3D crystallization is smaller for the PEO of the UFG magnesium alloy. As a result, this quantitative kinetic information shows that PEO process for Mg alloy is controlled by the competing dissolution and 3D crystallization processes, and the film growth rate is limited by the rate of the precipitation products formation. Finally, the chosen kinetic model was successfully applied to the mechanism study of the PEO film growth, since it adequately describes the current density transient. The results can be used for the process control of plasma electrolytic oxidation for Mg-1Ca alloy.

This research is supported by Russian Science Foundation, grant No. 17-79-10144.

Keywords: plasma electrolytic oxidation, kinetic model, magnesium alloy

The effect of NaOH on the plasma electrolytic oxidation of A356 aluminium alloy in a concentrated aluminate electrolyte

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Abstract: According to our previous study, ceramic coatings with high corrosion resistance and wear resistance can be obtained by plasma electrolytic oxidation (PEO) of aluminium alloys in moderately concentrated sodium aluminate electrolytes. However, the stability of the concentrated electrolytes decreases, which will impede the practical application of the aluminate electrolyte. In this study, plasma electrolytic oxidation of (PEO) a cast A356 aluminium alloy was carried out in 32 g/L sodium aluminate with addition of different concentrations of sodium hydroxide (NaOH). It is found that the stability of sodium aluminate electrolyte has been greatly enhanced by increasing the concentration of NaOH. However, the increasing of the NaOH concentration leads to corresponding changes in the PEO behaviour. A thicker precursor coating should be employed for the treatment in electrolytes with higher concentrations of NaOH. Our results also demonstrated that the optimal concentration of sodium hydroxide is 5 g/L, which has increased the electrolyte stability to ~35-40 days and allows the formation of high performance coatings.

Specimens were cut from a cast A356 aluminium alloy automotive wheel, and then the specimens were mounted in epoxy resin to provide working areas of 10 mm×20 mm. A 5 kW power supply was used for the PEO. A cooling system with magnetic stirring was employed to cool the electrolyte temperature below 40 °C. Pulsed bipolar constant current regimes, using average positive and negative current densities of ~0.108 and -0.056 A/cm² respectively, a frequency of 1000 Hz and a duty cycle of 20% are used. Coatings are obtained by PEO in a 32 g/L NaAlO₂ electrolyte with the addition of 1, 5 and 10 g/L NaOH. The effect of NaOH on the stability of the aluminate electrolyte and the PEO behaviour was investigated. For the PEO of the alloy in aluminate electrolytes, precursor coatings should be employed by PEO treatment of the alloy in 2 g/L NaAlO₂+1 g/L NaOH electrolyte. The precursor coatings are formed for durations between 2 and 8 min, which depend on the NaOH concentration in the electrolyte. Wear performance of the resultant coatings was tested by a CETR UMT-3 tribometer (20 N load, WC ball and sliding time of 30 min). Coatings were characterized by SEM, EDS, and profilometer. The stability of the PEO electrolyte with different NaOH concentrations has been tested by the observation of the appearance of the electrolytes which were kept at 25 °C in a thermostat. The electrolyte with the addition of 1 g/L NaOH begins to decompose after a standing of ~24 hours. In contrast, the addition of 5 g/L NaOH has drastically improved the stability of the electrolyte to ~35 to 40 days.

The addition of NaOH affects the precursor coating required for the treatment in the concentrated aluminate electrolyte. For the PEO in the electrolytes with 1 and 5 g/L NaOH, a precursor coating formed for 2 min in the dilute electrolyte can be used. However, a precursor coating with a longer formation time of 10 min should be employed for the PEO treatment in 32 g/L NaAlO₂ + 10 g/L NaOH.

Wear performances of three different coatings, formed in 32 g/L NaAlO₂ electrolyte with the addition of 1, 5 and 10 g/L NaOH, with thicknesses of 34.5, 37.3 and 30.0 μm respectively, have been measured by reciprocating ball-on flat tests. The coating formed in 5 g/L NaOH displayed the best performance. Fig.1 shows the cross-section depth profiles of the respective wear scars. The coating generated from the 32 g/L NaAlO₂+5 g/L NaOH electrolyte shows the narrowest wear scar width of ~0.79 mm and the wear scar depth is about 13 μm. However, the uncoated specimen (the substrate) and the other two coating specimen have been worn out after 30 min sliding against the WC ball.

Keywords: PEO, wear resistance, sodium aluminate, sodium hydroxide, A356 alloy

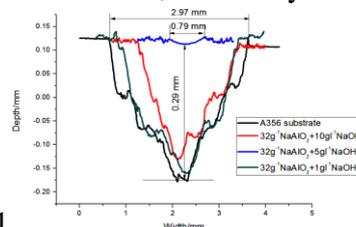


Fig.1

The role of cathodic current in plasma electrolytic oxidation of aluminium: kinetic aspects

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Abstract: Plasma electrolytic oxidation (PEO) is an electrochemical surface treatment technique carrying out under higher anodic overpotentials (up to 1000 V) on the valve metals (Al, Ti, Mg, Ta, Zr etc.) in dilute aqueous solutions. In such conditions, anodic oxidation of substrate material is accompanied by local breakdowns of the forming film. Changes caused by plasma assisted reactions, sintering and calcination of the coating materials under breakdown conditions lead to formation of new materials with unique protective properties. PEO of aluminium and its alloys allows one to obtain extremely hard and dense coatings enriched with α -alumina. It is considered that additional negative (cathodic) polarization (alternating with positive one) is the key factor in the formation of α -alumina in PEO of Al. However, such alternating polarisation causes increase in number of the process parameters (positive and negative current densities, timings of pulses and pauses). Therefore, optimisation of the process to either certain results or technologies requires multiple complex experiments. Reduction of experiment complexity can be achieved with additional information about the phenomenological model of the soft PEO process. It was assumed that cathodic current causes decreasing of potential barrier in EDL on the oxide-electrolyte interface and narrowing the non-conductive part of the coating located at metal-oxide interface (so-called active zone, where the main voltage drop occurs). Such an effect reduces activation energy in the processes of charge and mass transfer in anodic oxidation during PEO coating formation that can be considered as “electrocatalysis”. It was also suggested that highly conductive state of the coating is caused by injection of the protons under cathodic polarisation and their following neutralisation yielding hydrogen atoms stabilised with surrounding oxygen sublattice.

This work is devoted to study the time resolved kinetic aspects of the formation and disappearance of above mentioned highly conductive state of the coating caused by prior cathodic polarisation. Self-decay of the highly conductive state was also under investigation in types of experiment with opened and closed pauses. The experimental technique included application of positive and negative pulse series with variable timings and amplitude by programmable power supply Titan-1500. Delays between negative and positive diagnostic pulses were 50-800 ms. Direct application of such delays causes considerable increase in total process duration, therefore special polarisation conditions were applied. The current mode includes alternation of six steps: a) one second of bipolar current polarisation ($R=0.8-1.2$) producing coating; b) depolarising pulse of positive voltage; c) exciting pulses of negative current; d) open or closed delay; e) diagnostic positive current pulses; f) pause up to two seconds (Fig.1a,b).

It was found that longer delay between negative and positive polarisation pulses causes appearance of additional highly conductive state (Fig.1d) in the coating (anodic hysteresis), in respect conventional soft sparking mode (Fig.1c).

Keywords: plasma electrolytic oxidation, soft sparking, aluminium

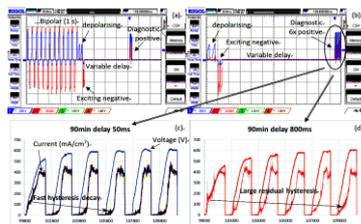


Fig.1 Structure of the complex polarisation conditions (a, b) and voltage, current oscillograms during diagnostic pulse train at different delays: 50 ms (c), and 800 ms (d). A2024 alloy, $R = 1.0$. $J_{AC,BIPOLAR} = 100 \text{ mA/cm}^2$, KOH (2 g/L) and Na_2SiO_3 (10 g/L)

Effects of second phases on microarc oxidation process of magnesium base materials

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Abstract: The effects of second phases on microarc oxidation (MAO, also named plasma electrolytic oxidation-PEO) behavior of Mg base materials were investigated and the related mechanism was discussed. The formation of barrier layer and its influence on sparking discharge behavior were characterized and analyzed on the base of systematic selecting and designing substrate materials. The variation of second phases at the early MAO stage was observed and analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS), and then the effect mechanism of second phases on MAO behaviors was revealed. Voltage evolution trend during MAO were recorded to study the formation state of the barrier layer on the different Mg base materials. According to the growth mechanism of MAO film, the film growth process can be simplistically considered as a repeated breakdown and reconstruction process of a capacitor. Accordingly, the growth process of MAO film on multiphase metal materials and the effects of second phases were discussed.

The results show that different second phases in substrate materials have different effects on formation process of MAO films, depending on their own characteristics. For the second phases which have the characteristics of valve metals, although selective sparking discharge occurs at the early stage of MAO, the second phases will not hinder the growth of MAO film since barrier layer can form on the second phases, and they will not induce structural defects into the film-substrate interface. If the second phases have not the characteristics of valve metals, their conductivity property will be an important influencing factor to affect the MAO behaviors. For the elecinsulating second phases which have not the characteristics of valve metals, sparking discharge just occurs on Mg matrix in the substrate, while doesn't occur on the second phases; the second phases exist in the MAO film as heterogeneous phases, do not react in MAO process, and will not hinder the growth of MAO film. For the semi-conductive second phases which have not the characteristics of valve metals, they delay the growth of MAO film because they destroy the integrity of barrier layer. For the electroconductive second phases which have not the characteristics of valve metals, they seriously hinder the growth of MAO film.

Keywords: metal matrix composite, second phase, microarc oxidation, barrier layer

A new understanding of plasma electrolytic oxidation from the treatment of a non-valve metal (carbon steel)

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Abstract: It is normally considered that plasma electrolytic oxidation (PEO) is confined to the treatment of valve metals (Al, Mg, Ti, Zr, etc). However, there are a few reports that PEO coatings could also be fabricated on a non-valve metal—the carbon steel. The mechanism of PEO of non-valve metal should be different from that of the typical valve metals. Unfortunately, the understanding of the mechanism of PEO of carbon steel is seriously lack. In this study, PEO of Q345 carbon steel has been carried out under pulsed unipolar regimes in an aluminate-based electrolyte with the addition of NaH_2PO_4 to understand the coating formation and plasma generation mechanisms on carbon steel. Real time imaging, optical emission spectroscopy (OES), gas collection, scanning electron microscopy (SEM) assisted with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) have been adopted to characterize the PEO processes. The results show that the PEO of the carbon steel displays some unique aspects from the conventional PEO of valve metals. It has been found that the voltage-time responses during the PEO process have been affected by the surface roughness of the carbon steel and the electrolyte agitation, which are not encountered in PEO of valve metals. The addition of the NaH_2PO_4 is also critical to the formation of thick PEO coatings on carbon steel. Although plasma discharges have been observed during the PEO of the steel in pure aluminate electrolyte, thick coatings can not be formed at all on the samples. Further, an “oscillation” of the intensity of plasma discharges has been observed during the PEO in pure aluminate electrolyte. The duty cycle has also some effect on the integrity of the PEO coating. The plasma discharges for the PEO in 8 g/L NaAlO_2 +2 g/L NaH_2PO_4 contain Fe lines, whereas only Na and H_α was found in the plasma discharges in pure aluminate electrolyte. It is supposed that the formation of a thin initial layer of the AlPO_4 , which is a product of the reaction between aluminate and the phosphate, plays an important role for the plasma generation and hence PEO coating formation on carbon steel. The observed changes in the cell voltage-time responses are associated with the stability of the AlPO_4 layer.

Keywords: Q345 carbon steel, plasma electrolytic oxidation, mechanism, AlPO_4 layer

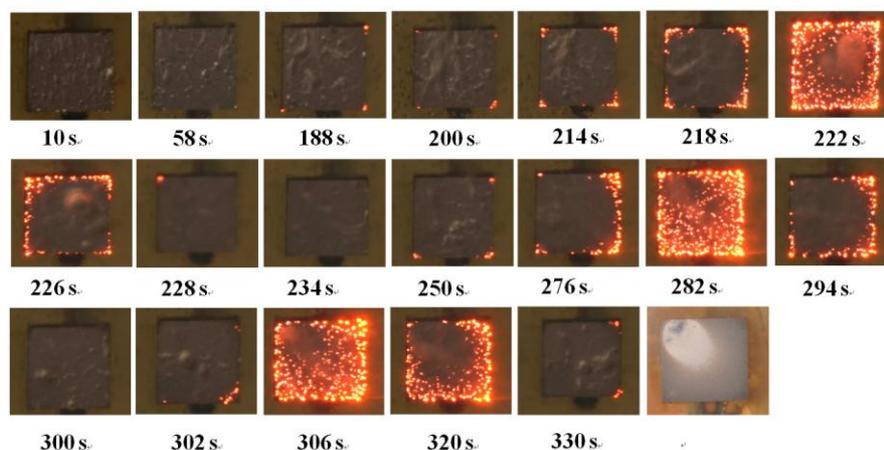


Fig.1 An “oscillation” of the intensity of plasma discharges during the PEO of carbon steel in pure aluminate electrolyte

PEO-coatings for biodegradable nanostructured Mg-2Sr implants

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Abstract: Medical implants for osseosynthesis are highly demanded for recovering human musculoskeletal system due to increase of traumatism. A significant part of the implants act as temporary devices which require extraction after recovering of bone tissue due to a fracture. Therefore, development of biodegradable implants that do not require extraction from the body is a topical research direction.

In this research we used a new generation material for the implant applications—nanostructured Mg-2Sr alloy. The choice of this material is based on a number of advantages. This alloy contains nontoxic elements that play significant role in human metabolism. Nanostructuring increases the implant strength and makes its mechanical characteristics close to that of a human bone.

The goal of this research is controlling the rate of magnesium implant degradation by forming plasma electrolytic oxidation (PEO) coating. Ca-, P- containing coatings obtained by PEO have good adhesion, high surface area and substances beneficial for the bone regeneration. The experiments were performed using samples having coarse-grained (CG) and ultrafine-grained (UFG) structure. All the experiments were carried out at temperature of 20 °C in electrolyte consisting of aqueous solution of 12 g/L Na₃PO₄•12 H₂O and 2 g/L Ca(OH)₂ (pH=12.6). The treatment time was 10 min. The PEO process was used in a pulsed unipolar mode under voltage regulation. Corrosion properties of the coated and uncoated samples were assessed using both weight loss and electrochemical techniques. The samples were immersed into 50 mL of Ringer's solution (0.86% NaCl, 0.03% KCl, 0.033% CaCl₂, pH 7.4) for 32 days at 37±2 °C; periodically, the samples were taken out and weighted. The electrochemical tests were carried out in Ringer's solution using P-5X (Elins, Russia) electrochemical system which was programmed to run consecutive tests: open circuit potential recording, electrochemical impedance spectroscopy and potentiodynamic polarisation test.

The thickness of the PEO-coatings is 12.0±1.5 µm and porosity is near 20%. The results of corrosion tests and electrochemical impedance spectroscopy of the PEO coating on a magnesium alloy Mg-2Sr with different grain size (≈40 µm, ≈1 µm, ≈100 nm) show that corrosion current for CG uncoated samples is 5.4×10⁻⁴ A/m², for UFG uncoated sample is much less 1.1×10⁻⁴ A/m². The PEO coating decreases corrosion current to the values (0.7...0.8×10⁻⁴ A/m²). Also, corrosion resistance was calculated after fitting of the EIS results; these values are in line with the corrosion currents.

Finally, the study shows that the grain size reduction significantly increases corrosion resistance of the Mg-2Sr alloy in Ringer's solution. Moreover, formation of the PEO coating reduces the corrosion rate by more than a half. These results confirm the good prospects of choosing nanostructured magnesium alloy Mg-2Sr with PEO-coating for biodegradable implant applications.

Keywords: bioresorbable magnesium alloy, plasma-electrolytic oxidation, nanostructuring

A significant improvement of the wear resistance of Ti6Al4V alloy by a combined method of magnetron sputtering and plasma electrolytic oxidation (PEO)

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Abstract: Titanium alloys own a series of advantages such as low density, high specific strength, and biocompatibility. However, the poor wear resistance of titanium alloys impedes their wide applications in industry. In this study, we show that the wear resistance of the Ti6Al4V alloy can be greatly improved by a combined method of magnetron sputtering and plasma electrolytic oxidation (PEO). An about 10 μm pure aluminium layer was first applied on the Ti6Al4V alloy by magnetron sputtering and then PEO was employed for the second step treatment of the Ti6Al4V alloy. The PEO of the Al coated Ti6Al4V was carried out in aluminate (32 g/L) and silicate (16 g/L) electrolytes respectively. Ball-on-disc tribological tests with an applied load of 10 N and 62 HRC Cr steel ball were used to evaluate the wear performances of the samples. For the PEO of the magnetron sputtered alloy in aluminate electrolyte, about 15 μm dense oxide coating has been formed for a short time of 4 min. However, only about 10 μm coating was formed on the sputtered alloy in silicate for a PEO duration of 15 min. The aluminate coating shows superior wear performance, which sustained 30 min under 10 N against the steel ball. The wear rates of the aluminate coating, the silicate coating and the Al-coated Ti6Al4V are about $7.13 \times 10^{-7} \text{ mm}^3/(\text{N m})$, $7.26 \times 10^{-6} \text{ mm}^3/(\text{N m})$ and $6.15 \times 10^{-6} \text{ mm}^3/(\text{N m})$ respectively. The superior wear resistance of the aluminate coating is due to its excellent homogeneity in microstructure. An examination of the cross section of the PEO coatings formed in aluminate electrolyte shows that the coating grows from about 8.5 to 15.0 μm during the duration between 1 to 4 min, however, only about 1.5 μm substrate has been consumed during the same duration. The result shows that the ratio of the outward to the inward growth rate for the aluminate coating is 10:3, which implies that coatings are mainly grown by decomposition of electrolyte species.

Keywords: Ti6Al4V alloy, magnetron sputtering, plasma electrolytic oxidation, aluminate, wear

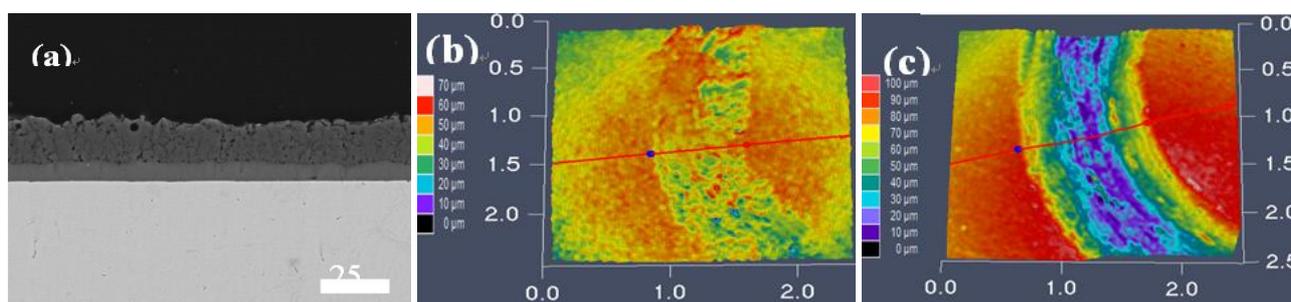


Fig.1 (a) The cross section of the coating formed by PEO of the magnetron sputtered Ti6Al4V alloy in 32 g/L NaAlO₂ for 4 min. (b) and (c) 3-D display of the wear scars on the magnetron sputtered Ti6Al4V alloy following PEO treatment in 32 g/L NaAlO₂ for 4 min and the magnetron sputtered Ti6Al4V alloy. 10 N load and 30 min sliding time are used for the wear tests

Study on the chromogenic mechanism and optical absorption properties of black ceramic coating of magnesium alloy micro-arc oxidation

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Abstract: Magnesium alloys are the light and high specific strength metals which is expected to be applied in aerospace field, but the corrosion resistance and optical absorption performance is poor, so the surface treatment is needed. In this paper, the high absorption micro-arc oxide black ceramic coating was prepared on the surface of the magnesium alloy by the use of the asymmetric bipolar pulse micro arc oxidizing power and adding coloring additives to the electrolyte system of sodium silicate. The chromaticity of the ceramic coating is evaluated by X-rite 530 spectrophotometer. The morphology, structure, composition and corrosion resistance of the black ceramic coating were analyzed by X ray diffraction (XRD), energy dispersive spectroscopy (EDS), X ray photoelectron spectroscopy (XPS), and the chromogenic mechanism of the black ceramic coating of magnesium alloy was discussed. Finally, UV absorbance and corrosion resistance of black ceramic coating were tested by ultraviolet visible spectrophotometer and electrochemical workstation.

The results show that: black ceramic coating has good absorption effect, which main component is magnesium oxide, chromogenic mechanism depends on the substitutional solid solution formed by copper oxide and magnesium oxide, which reduces the band gap of MgO ceramic coating, thus increasing the light absorption range of ceramic coating. The higher the solid solution content of CuO, the better the black degree of ceramic coating. At the same time, the surface roughness and pore distribution of the black ceramic coating also affect the light absorption of ceramic coating. The color value of the black ceramic coating can reach 23, and the absorption rate of visible light in the range of 380-780 nm is as high as 96%; In addition, the formation of solid solution does not reduce the corrosion resistance of ceramic coating, In 3.5wt% NaCl aqueous solution, the impedance of the black ceramic layer $3.8 \times 10^5 \Omega$, is 3 orders of magnitude higher than the impedance of the AZ31 magnesium alloy, corrosion current of $6.7502 \times 10^5 \text{ A/cm}^2$, reducing by 3 orders of magnitude. To sum up, magnesium alloy microarc oxide black ceramic coating has good absorption and corrosion resistance.

Keywords: micro arc oxidation, magnesium alloy, black ceramic coating, coloration, absorbance

Influences of processing factors on the corrosion resistance and calcium content of micro-arc oxidation coatings on AZ31B magnesium alloys in a neutral solution

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Abstract: As a new type of biodegradable metal, magnesium and its alloys have obvious advantages in repairing and replacing damaged tissues, such as low elastic modulus, similar density to natural bone, in vivo degradation via corrosion obviating the requirement of a second surgery for implant removal and so on. However, despite these advantageous properties, magnesium alloys display a high corrosion rate under physiological conditions. This represents one of the key disadvantages that restrict their usefulness. Micro-arc oxidation (MAO) is an electrochemical method that can efficaciously improve the corrosion resistance of magnesium alloys. Because calcium and phosphorus are the main components of human bones, it is desirable to fabricate MAO coatings with good corrosion resistance and high calcium content). Currently, the used MAO solutions on magnesium alloys are generally strongly alkaline), resulting in a large pore diameter layer. Herein in a neutral solution, we report the influences including phytic acid concentration, phosphoric acid concentration, EDTA-CaNa₂ concentration and oxidation time on properties of anodic coatings formed on AZ31B magnesium alloy by an orthogonal experiment with four factors and three levels. Surface morphology, chemical composition, phase structure and elemental state were examined by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). The corrosion behavior of the treated sheets was verified by potentiodynamic polarization. The results show that the order of the four factors on the calcium content is phytic acid concentration > oxidation time > EDTA-CaNa₂ concentration > phosphoric acid concentration. The order on the corrosion resistance is phytic acid concentration > EDTA-CaNa₂ concentration > phosphoric acid concentration > oxidation time. With the increase of phytic acid concentration, the corrosion resistance of the oxide film first decreases and then increases, while the calcium content slightly increases and then increases significantly. With the extension of the oxidation time, the corrosion resistance of the oxide film first decreases and then increases; while the calcium content in the oxide film first decreases and then increases. With the increasing EDTA-CaNa₂ concentration, the calcium content in the oxide film increased first and then decreased. Therefore, we can pick out a conclusion that the mechanism of calcium ions entering the oxide film is electro migration. In the course of MAO treatment, phytic acid can improve the calcium content of coatings by its chelating action and is hydrolyzed into lower myo-inositol phosphate esters and inorganic phosphate radicals due to spark discharge. In this study, it can be concluded that increasing the calcium content of the coating helps to improve the corrosion resistance of the magnesium alloy. The research results in this paper lay a foundation for preparing oxide film with good corrosion resistance and calcium content in neutral solution, which achieves an important research significance.

Keywords: magnesium alloys, micro-arc oxidation, corrosion resistance, calcium element

Biomedical and heat dissipating applications of Mg alloys coated by microarc oxidation

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Abstract: To explore the new performances of Microarc oxidation (MAO) coated magnesium alloys for functional applications still remains increasing attractions. Herein we reported the two latest developments of MAO coated degradable magnesium alloys for bone defect healing, MAO coated magnesium alloy radiator for heat dissipating of large power electronic devices. For bone defect healing application, to adjust the degradation rate of Mg stent implant, the MAO coatings mainly composed of MgO, MgSiO₃, Mg₂SiO₄, CaSiO₃ and Mg₃(PO₄)₂ phases were fabricated in silicate based electrolyte. 10 μm and 20 μm MAO coated magnesium stent samples and uncoated bare magnesium samples were implanted into the New Zealand white rabbits employing a bone trauma defect model. The X-ray and μ-CT results revealed that abundant bone callus appeared in 8 weeks postoperatively of all the groups and the uncoated groups grew more, which is mainly due to the released Mg²⁺ that promoting new bone formation. However, the uncoated magnesium implant was completely dissolved in 8 weeks in vivo, while the 20 μm thick MAO coated implant still existed to maintain the mechanical integration in 12 weeks which showed excellent corrosion resistance. For heat dissipating application of large power electronic devices, MAO coated magnesium alloy radiator with promoted infra emissivity exhibits better heat dissipating performance. MAO coated Mg alloys in silicate electrolyte exhibit a high emissivity up to 0.8 within 8-20 μm wavelength range, while the values are only 0.1-0.3 for the Mg substrate. Compared with the uncoated magnesium radiator, the MAO coated samples enable the junction temperature of LED to drop approximately at 7.3 °C. MAO method is expected to be a promising candidate for heat dissipation applications.

Keywords: magnesium, microarc oxidation, corrosion, bone defect, in vivo degradation, emissivity, heat dissipation

What can we learn from plasma diagnostics of the PEO processing of light metallic alloys?

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Abstract: Plasma electrolytic oxidation (PEO) also known as Micro-Arc Oxidation (MAO) is a powerful process to grow protective oxide coatings on light metallic alloys (e.g. Al, Mg, Ti...). However, PEO is a quite complex process involving chemistry, electrochemistry, plasma physics, material science & engineering. Complexity of the process is emphasized because of the multiple interfaces it has to face with: ceramic/metal, liquid/gas, liquid/solid, gas/solid, while considering the plasma surface interaction as well.

Over the last 30 years, there has been an abundant scientific literature dedicated to PEO. However, since there is a huge industrial demand, the published works mostly deal with the performances and properties of the processed materials, and only few of them rely to the process and the mechanisms underlying the material conversion. One way to progress in the understanding of underpinning mechanisms of PEO consists in deeply investigating the discharges that result from the dielectric breakdown under the applied voltage or current. Plasma diagnostics can indeed provide us with essential parameters that can bring useful information in the description of the growth mechanisms, or in the coating structure properties. As examples, plasma diagnostics can access the gas temperature that can be related to the material phase transformation; micro-discharge behavior can be correlated with the coating thickness and evenness.

The presentation will review plasma diagnostics studies that have been carried out to get new insights into the PEO process. A particular attention will be paid to optical emission spectroscopy and to fast video imaging. From the plasma characterization, growth mechanisms will be inferred. In view of the presented results, related energetic issues will be discussed as well.

Keywords: plasma electrolytic oxidation, plasma diagnostics

Non-electrode plasma electrolysis: principle and application

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Abstract: The plasma electrolysis typically includes two processes, i.e. anodic plasma electrolysis and cathodic plasma electrolysis, where the working part is served as the anode and cathode, respectively. In this case, only conductive specimens including metals, alloys, semiconductors and/or their composites can be successfully applied in the plasma electrolysis process. In the present paper, we have successfully developed a novel non-electrode plasma electrolysis process, where the formed plasma directly affects on the working part, the working part is not an electrode and can be conductors and insulators. In this case, nano- or submicro- coatings are rapidly deposited on the working parts under the mechanical impact, thermal effects and physical/chemical effects of the plasma. The non-electrode plasma electrolysis was presently applied to prepare ceramic nano-coatings on carbon fiber, quartz fiber and graphite. The coated carbon fiber, quartz fiber and graphite exhibited superior tensile property and oxidation resistance in high temperatures. We believe that the non-electrode plasma electrolysis will find a wide range of applications in surface/interface modifications for conductors and insulators.

Keywords: non-electrode, plasma electrolysis, carbon fiber, quartz fiber

Metal oxide nanostructured catalysts fabricated by PEO method for efficient CO oxidation

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Abstract: The stringent environmental contamination and the urgent demanding for clean atmosphere require an efficient and low-cost solution to the environmental problems like CO emission. In this talk, we report the in-situ integration of non-noble Ni₅TiO₇ whiskers and its Co-doped (Ni_{1-x}Co_x)₅TiO₇ nanostructures on Ti substrate using conventional plasma electrolyte oxidation (PEO) method and their utilization for efficient CO oxidation. It was found that the dimensional size of Ni₅TiO₇ whiskers can be selectively tailored by controlling the concentrations of Ni(NO₃)₂ impregnating solution and the size of the Ni₅TiO₇ nanowires reducing from 4 μm to 50 nm leads to a significant decrease of maximum CO conversion temperature from 550 °C to 440 °C. The introduction of Co dopant further decreases the CO conversion temperature to 326 °C at an optimized Co content of $x=0.16$ and the continuous 20 hour catalytic test of (Ni_{1-x}Co_x)₅TiO₇ nanostructures at 326 °C suggests that these in-situ grown metal oxide catalyst nanostructures have a superior thermal stability. In addition, the Co/Ni ratios in the original electrolyte precursors directly result in the different dimensional size and morphology evolution. All these Ni₅TiO₇ and (Ni_{1-x}Co_x)₅TiO₇ nanostructures prepared by PEO technology show decent single crystal nature, large surface area, excellent CO catalytic capability and strong substrate adhesion, which exhibits competitive advantage compared with rare-earth or noble metal based catalysts and the PEO technology will also open up more opportunities in CO oxidation ranging from autovehicle exhaust to chemical gas emission processing in industry.

Keywords: PEO, metal oxide, in-situ growth, CO oxidation

Growth mechanism and tribological behaviors of plasma electrolytic carbonitriding layer on pure iron

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Abstract: In this paper, the carbonitriding (PEC/N) hardening layers were prepared on pure iron by plasma electrolytic treatment in glycerin and urea solution under 360 V for 1-10 min. Influence of discharge time on morphology, structure and microhardness of PEC/N layer were analyzed. The tribological performance of the PEC/N layer, growth mechanism and diffusion process during PEC/N treatment were investigated on pure iron. The thickness of PEC/N layer grows to 48 μm for 10 min treatment and the highest microhardness is 811 HV, which is much higher than that of iron substrate. The PEC/N layer consists of α-Fe, Fe₂₋₃N, Fe₄N, Fe₃C, Fe₅C₂ phases and a little FeO phase. The wear rate of the PEC/N layer is about 1/6 of the iron substrate and the surface of the wear track of the 10 min PEC/N sample is much smoother. The fitted temperature close to the surface inside the sample under 360 V is 801 °C, and the diffusion rate of C and N in pure iron by plasma electrolytic discharge at 360 V reaches 4.09 × 10⁻¹² m²/s. The PEC/N layer displays a very good wear resistance and the higher diffusion rate makes plasma electrolytic carbonitriding a very effective technique for surface modification of iron.

Keywords: plasma electrolytic carbonitriding, pure iron, diffusion

The way to save energy and reduce consumption of micro-arc oxidation

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Abstract: Aiming at the engineering problem of high energy consumption in micro-arc oxidation treatment, a new method was proposed on the basis of boundary conditions of OH⁻ compound consumption or oxygen discharge on Al/Mg anode surface. By using the inhibition of OH⁻ compound consumption on oxide film and modulating sequence state of interelectrode peak current, this method realized the initial induction of oxygen ionization, and thus provides oxygen plasma for the process of ceramic transformation on Al/Mg alloy surface. On these basis, an environment-friendly preparation technology of ceramic layers on Al/Mg alloy surface can be developed, which only consumes OH⁻ ions from water electrolysis. The optical communication synchronizer, free of electromagnetic interference, supported by high-speed DSP core operation, was used to realize the synchronized switching of multiple high-power IGBT switching power supply. Hence, the electronic control system can be developed with pulse height of each unit pulse current overlapping, peak value equal to the product of current peak of a single power supply and unit number, and power factor during micro-arc induced process always higher than 85%. Power usage effectiveness in the process of micro-arc oxidation was lifted from 375 kW output (2500 A effective peak) to 160 kW output (3200 A effective peak). According to gradually increasing from low to high evolution rule of electrode voltage during micro-arc induced process, the constant power control mode had the ability to transform power margin at low-voltage stage before arcing to current increment by conversion. Therefore, the single processing area during micro-arc induced process at rated power was increased by 30%, compared to that in constant peak current control mode.

Keywords: micro-arc oxidation, save energy, reduce consumption, oxygen plasma, power supply

Influence of frequency on the behaviors of HA-containing ceramic coatings on

AZ31 Mg alloy by micro-arc oxidation

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Abstract: There remains growing interest in magnesium (Mg) and its alloys as a class of biodegradable metallic biomaterials. The major obstacle to the clinical use of magnesium alloys is their fast degradation behaviors. In this study, Ca-deficient hydroxyapatite (Ca-def HA) coatings were directly prepared on AZ31 Mg alloy by micro-arc oxidation to improve its corrosion resistance and biocompatibility. Effects of applied frequency on the microstructure, phase composition and corrosion resistance of the coating were studied by SEM, XRD, EDS and potentiodynamic polarization tests. Micro-arc oxidation (MAO) treatment could significantly improve the corrosion resistance of Mg alloy. The pore size of the discharge channels decreased significantly as applied frequency increased, resulting in a compact coating layer. The thickness of the MAO coating decreased with increasing applied frequency. And coating formed at 2000 Hz demonstrated the highest polarization corrosion resistance.

Keywords: magnesium, hydroxyapatite, micro-arc oxidation, bonding strength, corrosion resistance

The effect of rapidly increasing negative voltage on the high frequency plasma electrolytic oxidation coatings of ADC12 alloy

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Abstract: Environmental friendly ceramic coatings on the surface of ADC12 aluminum alloy were obtained using a plasma electrolytic oxidation process (PEO) employing a pulsed alternating current (AC) power mode in an alkaline electrolyte with a high frequency above 800 Hz, which was referred as high frequency plasma electrolytic oxidation (HiPEO). In this paper, the influence of the negative voltage on the morphological and structural properties of ceramic coatings were evaluated by scanning electron microscopy (SEM). It was found that the negative voltage increased immediately in the process of HiPEO, which was beneficial for the coating thickness, density and porosity. The rapidly increasing negative voltage could also change the status of discharge. The negative voltage mutation could increase the growth rate and density of coatings by 3-5 times for producing sufficient power to break the channel of discharge in local region where contains higher content of silicon than others. However, the density and porosity in the outer layer was not changed obviously.

Keywords: plasma electrolytic oxidation coating, negative voltage, ADC12 alloy, engine block

High-temperature tribological properties of microarc oxidation coatings on 7075 aluminum alloy

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Abstract: Microarc oxidation (MAO) was employed to produce ceramic coatings on 7075 Al-Zn-Mg-Cu alloy in silicate electrolyte. The high-temperature tribological properties of bare 7075 aluminum alloy and MAO coatings were evaluated under dry sliding against ZrO₂ ceramic ball at different environment temperatures up to 300 °C. Friction coefficients and wear rates before and after PEO treatment were measured, and the morphology of wear tracks was observed. Furthermore, their wear mechanism during the wear process at different temperatures was discussed. It was found that the MAO coatings could maintain a low wear rate and stable wear performance at high temperature. The friction coefficients of MAO coatings were low and stable, and their wear rates slightly increase with environment temperature. The wear rate of the MAO coatings was about two orders of magnitude lower than that of the aluminum substrate at ambient temperature. The wear mechanism of the aluminum substrate was mainly abrasive wear, and oxidation wear at high temperature. However, the wear mechanism of MAO coatings was mainly adhesive wear at ambient temperature, and abrasive and adhesive wear at high temperature.

Keywords: high-temperature wear, microarc oxidation, 7075 aluminium alloy, wear mechanism

Mechanism of anodic film formation on Mg alloys in aqueous solution

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Abstract: In this presentation, anodic oxide formation mechanism on Mg alloys will be discussed, based on the experimental results obtained, in view of ionic migration through anodic film, dissolution or breakdown of anodic film, arc generation and anodic film formation/growth under the application of high anodic electric field in various electrolytes. The effects of alloy composition, electrolyte composition and form and magnitude of the applied anodic current on the formation behavior of anodic films on Mg alloys will be also discussed by analyzing in-situ observation of arc generation behavior, voltage-time curves, and morphological observation of the PEO (plasma electrolytic oxidation) films. Electrolytes containing various anions of OH^- , SiO_3^{2-} , CO_3^{2-} , BO_2^- and WO_4^{2-} are employed for the formation of anodic films on Mg alloys. Three different arcing behaviors was observed to occur on the Mg alloy surface. First, small size micro-arcs were generated randomly over the entire surface, producing relatively uniform PEO film thickness and lower surface roughness. Second, large size group arcs were observed to travel first along the edges and then over the remaining surface, called linear discharges, which leaves thicker and more porous PEO films. Third, generation of large size arcs at the same site, which is called as local burning, occurred when breakdown of the anodic films becomes easier. Various arcing and PEO film formation mechanisms during the PEO treatment of Mg alloys will be discussed in more detail.

Keywords: plasma electrolytic oxidation, anodic oxide

Corrosion behaviour and biological activity of pure magnesium with puerarin coatings

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Abstract: In order to improve corrosion resistance and biological activity of micro-arc oxidation (MAO) coating on magnesium alloy, a puerarin-loaded (PL) coating was prepared and coated on MAO coating by dip-coating method. Chemical and morphological characterizations of the coatings were examined by using scanning electron microscope (SEM) and fourier transform infrared spectroscopy (FTIR). Corrosion properties of the coatings were studied by potentiodynamic polarization technique and electrochemical impedance spectroscopy in simulated body fluid (SBF). To evaluate the biological activity of a PL coating in vitro, the cell culture test were performed and evaluated the effect of PL coating on osteoblast. In addition, magnesium implants were analyzed in early repair of mandibular defects of rabbit in vivo. The coatings exhibited high corrosion resistance with detectable change in the drug-loaded concentration than MAO coating. Besides, In vitro, the PL coating exhibited good biocompatibility and promoted adhesion and growth compared to MAO group. In vivo, we observed new bone gradually formed at 2 weeks and 4 weeks, but the PL coating induced more new bone and reduced inflammatory compared to MAO. The results indicate that MAO coating loaded with puerarin achieve high efficacy to corrosion resistance for concentration of puerarin. Furthermore, PL coating may accelerated the healing process in early stage of bone healing.

Keywords: magnesium, micro arc oxidation, puerarin, corrosion, bone repair

Enhanced corrosion resistance and optical emission spectroscopy of cathodic plasma electrolytic oxidation film on Q235 low carbon steel

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Abstract: In this paper, we reported a novel method to prepare oxide film on low carbon steel which served as cathode during plasma electrolysis process in organic solution. The oxide films up to 110 μm thick on Q235 low carbon steel were prepared by cathodic plasma electrolytic oxidation (CPEO) in glycerol electrolyte within 9 minutes. The morphology and composition of composite films were analyzed. Their phase components and microhardness profiles were measured. Their corrosion behaviors were evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The sample temperature close to surface was measured by a thermocouple. Furthermore, the optical emission spectroscopy was collected and the electron temperature in plasma discharge region was calculated. It was found that the composite films mainly contained FeO phase and Fe_2O_3 phase with maximum hardness of 615 HV, meanwhile some carbon particles disperse in the films. The plasma discharge region contained many active carbon and oxygen species with a high electron temperature.

Keywords: cathodic plasma electrolytic oxidation, corrosion resistance, optical emission spectroscopy, Q235 low carbon steel

Effect of NaOH concentration on formation behavior of plasma electrolytic oxidation films on Al1050 alloy

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Abstract: In this study, effect of NaOH concentration in SiO_3^{2-} containing solution on the formation behavior of PEO films on Al1050 alloy was investigated by in-situ observation of arc generation behavior, voltage-time curves, surface roughness, film hardness and morphological observation of the PEO films. The PEO films were formed in 0.3 M Na_2SiO_3 solution containing various concentrations of NaOH by the application of a constant current density. Three different arc generation behaviors was observed with NaOH concentration. Under 0.2 M of NaOH concentration, random generation of micro-arcs was observed on the whole surface with high breakdown voltage. With increasing NaOH concentration, breakdown voltage decreased and size of the micro-arcs increased. In NaOH concentrations between 0.2 M and 0.45 M, there observed group arcs consisting of a number of arcs at a specific area that are initiated at the edges and travelled along the edges first and then across the central region of the surface. Moving speed of the group arcs decreased with increasing NaOH concentration. In more than 0.45 M of NaOH concentration, arcs were generated at a specific site continuously, called as local burning, resulting in highly rough surface. Characteristics of the PEO films formed by random arcs, group arcs and local burning was examined in terms of PEO film thickness, surface roughness, hardness and morphologies.

Keywords: plasma electrolytic oxidation, Al alloy, silicate ion, sodium hydroxide

Tribological properties of MAO coating on zirlo alloy formed in phosphate electrolyte

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Abstract: Zirconium alloys are widely used in various industrial application, especially in nuclear fission energy systems. In modern technological application such as an increase burn up and higher reactor temperature, wear and corrosion resistance of zirconium alloys exhibit substantial influence on their industrial application. Thus, it is important to improve the wear and corrosion resistance of Zr alloy. In this paper, the MAO ceramic coatings were prepared on Zirlo zirconium alloy to improve its wear and corrosion resistance.

In addition, surface morphology, cross sectional micro-structure and phase components of MAO ceramic coatings were analyzed by scanning electron microscope (SEM) with energy dispersive X-ray spectrometer (EDS) and X-ray diffraction (XRD). The coatings up to 18 μm contain a thin outer porous layer and an inner dense layer. Tribological properties of the MAO coatings were evaluated by a ball-on-disc friction and wear tester in dry sliding against GCr15 ball at ambient temperature, and the wear mechanism was also discussed. Compared to bare zirlo alloy, the MAO coatings have a relatively high wear resistance, gradually increasing with the increase of voltage. The lowest wear rate is below 4.596×10^{-6} mm³/Nm, which is only about 1/60 of bare zirlo alloy at the same wear condition. In addition, the polished coatings have a lower volumetric wear rate and higher wear resistance than those unpolished coatings. The wear mechanism of MAO coatings is mainly the adhesive wear while the wear mechanism of bare Zirlo alloy is mainly the abrasive wear. Therefore, the MAO treatment could significantly influence the friction coefficient and improve wear resistance.

Keywords: microarc oxidation, zirlo alloy, tribological performance

Mechanism of Al₂O₃ particles in improvement of plasma electrolytic

oxidation coating on AM60B alloy

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Abstract: Al₂O₃ particles were added into coatings of AM60B magnesium alloy using plasma electrolytic oxidation (PEO) method to improve the properties of the alloy. The mechanism of improvement of Al₂O₃ particles was investigated using Raman spectra and EDS analysis. The results indicate that the enhancement of Al₂O₃ particles on the coatings depended on the applied voltage. The Al₂O₃ particles were adsorbed on the surface of samples at low voltage, and then embedded into the coating with increased voltages. The formation of MgAl₂O₄ and disappearance of Al₂O₃ particles analyzed by XRD analysis confirmed that the additive of Al₂O₃ particles improved the properties of PEO coatings on magnesium alloy.

Keywords: plasma electrolytic oxidation, Al₂O₃ particle, mechanism, magnesium

Preparation and corrosion resistance of Ti-containing composite coatings on biomedical magnesium alloys

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Abstract: Medical metal materials play an important role in the repair and replacement treatment of injured or damaged bone tissue. Magnesium-based metal can be used as for its biodegradability and beneficial mechanical properties, e.g. degradable bone fixation screws and plates or cardiovascular stents. However, the high degradation rate and associated evolution of hydrogen gas under physiological conditions which severely limit its clinical development. Alloying can be an efficient method to improve the mechanical properties of magnesium alloys. The results showed that the addition of Sr can significantly improve mechanical properties of ZK40 magnesium alloy, and can meet the mechanical properties of stents. However, the corrosion resistance of this Sr-contained ZK40 magnesium alloy was not significantly improved. Ti and its alloys are widely used as biomedical materials for good biocompatibility and corrosion resistance. Since the advantages of Mg and Ti, this work first injected titanium on the surface of ZK40-0.4Sr by ion implantation, and then prepared a coating consist of MgO and TiO₂ on the surface of the base material by using micro-arc oxidation to obtain better surface corrosion resistance. We focused on the amount of titanium injected and the effect of micro-arc oxidation on the microstructure and properties of the MAO coatings. On this basis, the corrosion resistance of the MAO coatings under simulated physiological conditions was further studied. This research combines ion implantation and micro-arc oxidation technology, which is conducive to expanding the application of magnesium alloy materials in the field of biomedical materials. It can also be used as a reference for the design and preparation of new surface functional films.

Keywords: medical magnesium alloy, ion implantation, microoxidation, microstructure, corrosion resistance

Effect of phosphate-based sealing treatment on PEO coated AZ91 Mg alloy

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Abstract: The effect of phosphate-based sealing treatment on PEO coated AZ91 Mg alloy was investigated. PEO coatings were fabricated in a silicate electrolyte under a constant current mode. Various concentrations of NaH₂PO₄ were used as treatment bath to seal the porous layer and corrosion inhibitors were added to further increase the corrosion performance of the composite coatings. The influence of applied post-treatment parameters on the microstructure, phase composition and corrosion resistance of the composite coatings was evaluated using SEM, EDS, XRD and XPS, Polarization and EIS. Electrochemical corrosion tests and salt spray test showed that the corrosion resistance of PEO coatings was increased by the sealing treatment process. Addition of corrosion inhibitors contributes to the improvement of corrosion performance and formation of superior protective coatings.

Keywords: phosphate-based sealing, AZ91 Mg alloy

Fabrication and bio-corrosion resistance of MAO/CaO-HA-GO composite coatings on TC4 alloy through micro-arc oxidation and solgel methods

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Abstract: In these years, Hydroxyapatite (HA) has been widely used in biomedical material due to its function to elevate activity of cells, which can increase biocompatibility of materials. Graphene oxide (GO), as a kind of two-dimension structural carbon material, has been found that it has ability to enhance biomineralization. Therefore, in this study, MAO/CaOHA-GO composite coatings had been fabricated by a process of micro-arc oxidation in silicate solution and subsequent sol-gel dip-coating in sol containing HA and CaO. Then the control groups of MAO/CaO-HA and MAO had also been fabricated. The microstructure of surface, elemental composition, component and functionalized group had been characterized by Scanning electron microscope, Energy Dispersion Spectrum, Grazing Incidence X-ray diffraction (GIXD) and Raman spectra. Then bio-corrosion behavior had been evaluated by potentiodynamic polarization test in simulated body fluid (SBF). The results shew that the icorr of MAO, MAO/HA and MAO/HA/GO were $1.71433 \times 10^{-3} \mu\text{A}/\text{cm}^2$, $3.17832 \times 10^{-4} \mu\text{A}/\text{cm}^2$ and $8.66746 \times 10^{-4} \mu\text{A}/\text{cm}^2$.

Keywords: hydroxyapatite, graphene oxide, micro-arc oxidation, TC4 alloy, bio-corrosion resistance

Influences of anion deposition on plasma electrolytic oxidation of valve metals

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Abstract: Plasma electrolytic oxidation (PEO) is an advanced technique for the formation of multifunctional ceramic coatings on valve metals. The name of the technique delivers the information that it is an “oxidation” process. However, the deposition of electrolyte anions, which is a process different from substrate oxidation, plays an important role in PEO and determines the properties of the resultant coatings. This presentation discusses the similarities and differences of the deposition of several electrolyte anions such as SiO_3^{2-} , AlO_2^- and WO_4^{2-} in the PEO of valve metals of Al, Zr, Mg, Ti and their alloys. In general, deposition rate of the anions accelerates with the concentration of the anions in the electrolyte, leading to a higher coating growth rate and more homogenous microstructure. The deposited anions possibly exist in the form of oxide due to the sintering effect of the high temperature plasma. PEO discharges will also be affected by the anion deposition process. In dilute electrolyte, strong plasma discharges, with the presence of substrate species in the plasma spectra, are found with the PEO processes. Only very weak plasma discharges, like those of “soft sparking” are found with the PEO in concentrated electrolytes with heavy anion deposition. The optical emission spectra at the latter case are also unique. All the above mentioned anions can be significantly deposited on the different valve metals and become the main source of coating materials. However, it has been found in the PEO of Al in tungstate electrolytes that high amount of fine WO_3 particles can be generated and dispersed into electrolyte due to the lower melting point and the sublimation of the tungsten oxide.

Keywords: plasma electrolytic oxidation, anion deposition, valve metals

The 'local over-growth' characteristic of MAO coating extending into substrate and its response to in-situ tensile behaviors

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Abstract: Microarc oxidation (MAO) coatings fabricated on 6061 aluminum alloy under different oxidized time (10, 30 and 50 min) were used to investigate the 'local over-growth' characteristic extending into substrate, further explore its effect on in-situ tensile fracture behaviors. The intact interface structure of the 'over-growth' patterns was presented perfectly by both microdischarge-sculpted substrate side 'pits' and electrochemically detached coating side 'protrusions'. The patterns demonstrate that the over-growth 'pits' and 'protrusions' gradually grow up with increasing oxidized time, which is attributed to the larger discharge channels and molten pools caused by the increased size and intensity of plasma discharges. The tensile properties of bare and MAO coated aluminum alloy were investigated. Tensile test shows that MAO treatment decreases tensile strength and elongation of aluminum substrate, while enhances the elastic modulus slightly. With the oxidized time prolonging, the exfoliated area ratios of the outer layer of the coating increase under the same elongation. The real-time crack initiation and propagation behaviors were recorded by in-suit SEM tensile test. The results indicate that cracks initiate at the bottom of over-growth regions between the coating/substrate, which implies the cracks initiation is sensitive to high residual stress concentration caused by the over-growth regions. The thicker MAO coating induces the earlier crack initiation. The cracks propagate into aluminum alloy rather than the interface of coating and substrate implies that the ceramic coating has good adhesion with aluminum alloy substrate.

Keywords: aluminum alloy, microarc oxidation, local over-growth, in-suit SEM tensile

Properties of boride layer on plasma electrolytic boro carbonitriding of Q235 low-carbon steel

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Abstract: Q235 low carbon steel was treated by plasma electrolytic boro carbonitriding (PEB/C/N) technique in borax solution with glycerinum and carbamide additive. At different treatment time, the structure and morphology of boro carbonitriding layer on Q235 low-carbon steel were investigated. The electrochemical corrosion properties of the Q235 steel treated by PEB/C/N were evaluated, and the growth mechanism of boride layer in the PEB/C/N process was analyzed. The results show that the Q235 low-carbon steel forms a compact boride layer about 25 μm thick after 30 min PEB/C/N treatment at 300 V. The boride layer mainly consists of Fe₂B phase, and the maximum hardness of boride layer can reach to 2200 HV. The PEB/C/N treatment significantly improves the corrosion and wear resistance of Q235 steel.

Keywords: plasma electrolytic boro carbonitriding, Q235 low-carbon steel, corrosion, wear

Synergic effects of antioxidation ability and amorphous phase on the surface structure and corrosion resistance of the modified micro arc

oxidation coating on titanium surface

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Abstract: The surface chemistry and topological structure of MAO coatings surface after microwave hydrothermal treatment are affected by the corrosion resistance and phase compositions of as-formed MAO coating. Thus in this work, the pure Ti and Ti2448 plates are studied. After MAO treatment, the phase compositions of MAOed Ti coating are anatase phase and Ti phases, while that of MAOed Ti2448 are amorphous phase and Ti phase. Moreover, the corrosion resistance of pure Ti and Ti2448 plates after MAO treatment have been improved. Meanwhile, the surface structure on the MAOed Ti coating are sodium titanate and HA nanorods, while that on the MAOed Ti2448 coating is HA nanorods. Thus the relationship between the corrosion resistance and phase compositions of MAO coatings and surface structure could be build, which could offer the theoretical guidance for the surface modification technology.

Keywords: antioxidation ability, micro arc oxidation, microwave hydrothermal treatment, surface structure

Fabrication of hard plasma electrolytic oxidation coatings on Ti alloys for tribological applications

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Abstract: Titanium (Ti) and its alloys are used in many fields such as aerospace, marine, biomedicine and so on, due to their high strength-to-weight ratio, good corrosion resistance and excellent biocompatibility. Nevertheless, the low hardness and poor wear resistance of Ti alloys have seriously restricted their extensive applications. Plasma electrolytic oxidation (PEO) is an effective surface treatment to greatly improve the hardness and wear resistance of Ti alloys by producing ceramic coatings. However, in some tribological applications with high loads or velocities, the PEO coatings could not provide sufficient wear resistance to the substrate due to the unsatisfied hardness and adhesion of the coatings.

In our work, the PEO coatings on Ti alloy were prepared in different electrolytes. The influences of electrolytic composition on the structure, composition, adhesion and wear resistance of PEO coatings were systematically studied. In addition, the correlations between the growth mechanism and properties of PEO coatings were discussed. Results showed that the electrolytic composition played a key role on the properties of the PEO coatings. The PEO coatings prepared from the electrolyte containing aluminate exhibited higher hardness and better wear resistance. Based on the results, hard PEO coatings on Ti alloys were prepared by using adapted electrolytes. The coating has now been successfully applied on Ti alloy components in aerospace industry.

Keywords: Ti alloy, plasma electrolytic oxidation, tribology

In-situ fabrication of nano-sized ceria via plasma electrolytic oxidation method in silicate electrolyte on GR1 Ti

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Abstract: Cerium is the most abundant among the so-called rare earth elements. The oxide of cerium, ceria, owns excellent redox property and high oxygen storage capacity (OSC), which is widely utilized today in the field of catalysis. In this study, cerium is successfully injected into the PEO (plasma electrolytic oxidation) film in silicate electrolyte. The atomic percent of Ce at the top-most layer reaches up to 23%, demonstrating a strong chelating ability of EDTA-2Na. The PEO film shows a double-layer morphology: volcano-like Ti-rich first layer and coral-like Ti-poor second layer. Annealing treatment in air ambient gives driving force for crystallization of Ce species, which mainly existed in the PEO film in an amorphous form. During annealing process, amorphous Si species in PEO film restrains the size enlargement of ceria and leading to formation of nano-sized CeO₂. After a simple erosion treatment, the catalytic capability of as-synthesised CeO₂ nanoparticles is triggered, mainly due to the exposure of active sites. CO oxidation test is used to measure the catalytic performance of in-situ fabricated CeO₂ nanoparticle layer and the cut-off curve shows the T50 located at 360 °C. This study opens up an efficient way for in-situ preparation of metal-supported ceria based catalysts, which will probably possess considerable prospects for application in CO oxidation, TWCS, SCR, etc.

Keywords: PEO, ceria, catalysts, CO oxidation

Preparation and properties of ceramic coating on tantalum alloy by plasma electrolytic oxidation

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Abstract: A Ceramic coating was successfully prepared on tantalum alloy by plasma electrolytic oxidation (PEO) technique. The morphology, elemental and phase composition, corrosion behavior and thermal stability of the uncoated and coated samples were studied by scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), X-ray diffractometer (XRD), electrochemical corrosion test, high temperature oxidation test and thermal shocktest. The results showed that the composite ceramic coating was composed of Ta₂O₅ and TaO_x. After PEO treatment, the corrosion potential of tantalum alloy was increased and the corrosion current density was significantly reduced. Besides, the coated tantalum alloys also showed excellent high temperature oxidation resistance and thermal shock resistance.

Keywords: tantalum, plasma electrolytic oxidation

Effects of micro arc oxidation and multiple treatments on corrosion fatigue behaviors of aluminum alloy

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Abstract: Micro arc oxidation (MAO) treatment can produce wear-resistant and corrosion-resistant coatings for aluminum alloys, however, MAO treatment often results in fatigue performance deterioration of base materials. In this paper, multiple treatments were adopted to improve the fatigue properties of MAO treated samples. Results show that MAO treatments with different thickness reduced the corrosion fatigue life of 7A85 aluminum alloy. The corrosion fatigue life of samples with thin MAO coatings (10 μm -thick) is decreased for the localized corrosion induced by micro pores and cracks in the coating. The corrosion fatigue life of samples with thicker MAO coatings (35 μm -thick) is reduced for the bad fatigue properties of oxide coatings. The corrosion fatigue performance of combined shot peening and MAO treated samples is improved for the residual compressive stress field induced by shot peening. The corrosion fatigue life of shot peening, surface polishing, MAO treated, consequently, samples is further improved for the decreasing of equivalent notch effect.

Micro arc oxidation (MAO) technique can produce hard, dense, corrosion-resistant, wear-resistant and well-adherent oxide coatings for light metals such as aluminum, magnesium, and titanium. Generally, MAO treatment results in fatigue property deterioration of base materials. The fatigue performance of MAO coating is concerned increasingly with the extensive study and application of MAO technique. Many methods such as parameters optimization, multiple treatments etc. have been tried to improve the fatigue performance of MAO coatings. Though there are many previous studies, the understanding of MAO treatment on corrosion fatigue behaviors of base materials remains elusive. This paper investigated the corrosion fatigue performance of MAO coatings with different thickness. Furthermore, the effect of combined shot peening and MAO treatment on corrosion fatigue behaviors of 7A85 aluminum is studied. 7A85-T7452 aluminum alloy is used as base material in this research. MAO treatment is performed in an alkaline silicate solution (NaOH 1 g/L, Na₂SiO₃ 15 g/L) with additions of (NaPO₃)₆ 10 g/L and NaAlO₂ 1 g/L. A pulsed bipolar current supply is used with frequency of 1 kHz and current density of 0.6 mA/cm². Fig.1 shows the MAO process photo of corrosion fatigue samples. Shot peening parameters are: glass shots, 100% surface coverage, 0.15 mmA Almen intensity. Axial fatigue tests in laboratory air and aqueous 3.5wt% NaCl solution are conducted on SDS-100 electrohydraulic servo-fatigue test machine, with a load ratio of 0.1, frequency of 10 Hz and maximum cyclic stress of 182 MPa. As shown in Fig.2, special Plexiglas cell is fabricated for the corrosion fatigue test. The cell encloses the gage section of the specimen in a fully submerged condition during corrosion fatigue test.

Fig.3 shows the fatigue life of 7A85 aluminum alloy with different surface treatments in laboratory air and aqueous 3.5wt% NaCl solution. In laboratory air, the fatigue life of base material samples (BM) and samples with 10 μm -thick MAO coating (10MAO) both exceed 5×10^6 cycles, but the fatigue life of samples with 35 μm -thick MAO coating (35MAO) is only 4.4×10^5 cycles. This suggests that thin MAO coating (10 μm -thick) has less effect on fatigue performance of base material, but thick MAO coating (35 μm -thick) dramatically reduces the fatigue life. In aqueous 3.5wt% NaCl solution, the fatigue life of BM and 10MAO samples is evidently decreased compared to that in laboratory air. This means that 7A85-T7452 aluminum alloy is very sensitive to corrosion fatigue, and 10MAO treatment cannot improve its

corrosion fatigue performance. 35MAO treatment also cannot enhance the corrosion fatigue property of aluminum alloy for its bad fatigue resistance.

As can be seen from Fig. 4, multiple treatments improve the corrosion fatigue life of aluminum alloy. The corrosion fatigue life of combined shot peening and micro arc oxidation (SP+MAO) samples is increased above that of BM samples for the residual compressive stress field induced by shot peening. The corrosion fatigue life of samples treated by shot peening combined polishing, micro arc oxidation (SP+P+MAO), consequently, is further improved for the decreasing of equivalent notch effect induced by shot peening crater and local oxide coating overgrowth.

MAO treatments with different thickness reduced the corrosion fatigue life of 7A85 aluminum alloy. The corrosion fatigue life of 10MAO samples is decreased for the localized corrosion induced by micro pores and cracks in the coating. The corrosion fatigue life of 35MAO samples is reduced for its bad fatigue properties.

The corrosion fatigue life of SP+MAO samples is increased above that of BM samples for the residual compressive stress field induced by shot peening. The corrosion fatigue performance of SP+P+MAO samples is further improved for the decreasing of equivalent notch effect.

Keywords: micro arc oxidation, shot peening, corrosion fatigue



Fig.1

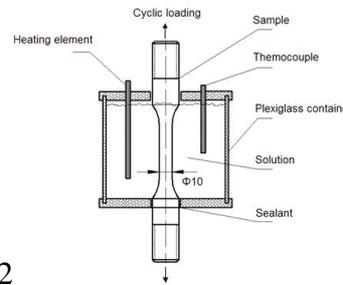


Fig.2

Fig.1 MAO process of corrosion fatigue samples

Fig.2 Schematic drawing of the corrosion fatigue sample and device

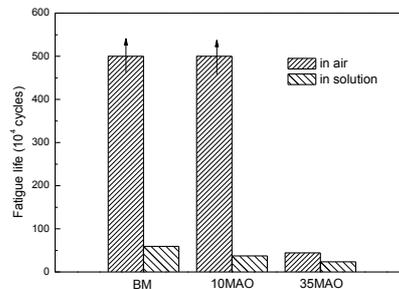


Fig.3 Fatigue life of MAO treated aluminum alloy with different thickness

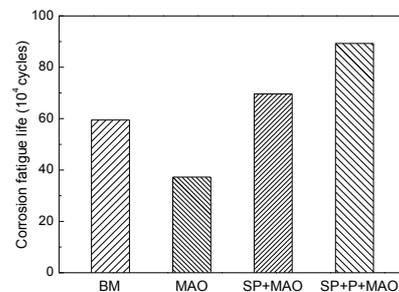


Fig.4 Corrosion fatigue life of samples with different surface conditions

Corrosion behavior of ceramic coatings formed by microarc oxidation on 7N01 aluminium alloy

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Abstract: In this paper, ceramic coatings were prepared on 7N01 Al alloy in alkaline sodium aluminate solution using micro-arc oxidation (MAO) technique. The surface morphologies, microstructure of MAO-treated samples were investigated using a Quanta200 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS). Fig.1 shows SEM morphology of coatings formed on 7N01 Al alloy samples at different concentrations of NaAlO₂. The electrochemical corrosion behaviour of coatings was evaluated by the electrochemical polarization method. The potentiodynamic polarization curves in 3.5wt% NaCl solution were carried out by a LK2005 electrochemical workstation with a three-electrode cell system. Fig.2 shows the polarization curves of the 7N01 Al and its coated samples. The results showed that the corrosion potential of 7N01 Al alloy moves to a more positive potential after MAO treatment. The corrosion current density of the coated 7N01 Al alloy was reduced several orders of magnitude.

Keywords: micro oxidation, 7N01 Al alloy, corrosion behavior, ceramic coatings

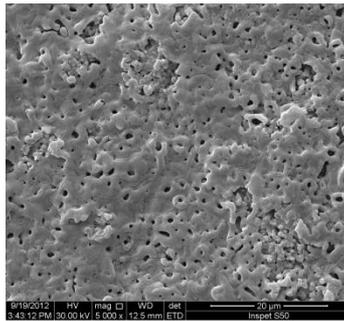


Fig.1 SEM morphology of MAO coatings

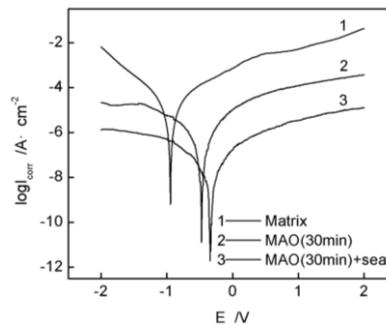


Fig. 2 Polarization curves of 7N01 alloy and MAO coatings

Evaluation of environmental performance for electrolytic plasma processes

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Abstract: Electrolytic plasma processes (EPP) belong to a branch of electrochemical treatments which usually utilize aqueous solutions of salts, acids and alkali with low concentration (3%...20%), and high voltages (100...600 V). In the majority of the cases, the electrolytes are non-toxic. At the same time, high voltages and elevated electrolyte temperatures (50...90 °C) can cause environmental performance problems for the EPPs. For example, high temperature of the electrolyte during electrolytic plasma polishing can promote ammonium salt decomposition and consequent evolution of ammonia. Another important issue is the necessity to utilize the spent electrolyte and reaction products.

This investigation is devoted to two types of electrolytic plasma processes: one characterized by dissolution of the surface layer (electrolytic plasma polishing and electrolytic plasma coating stripping), and the other characterized by formation of an oxide coating (plasma electrolytic oxidation). For the both types of the EPPs, we analyzed environmental performance, having polishing of stainless steel, stripping of chromium coating and oxidation of aluminum, titanium, zirconium and magnesium, as typical processes. For the EPP experiments, the following electrolyte components were used: ammonium sulphate and chloride, sodium phosphate and silicate, potassium hydroxide. According to International standard family ISO 14000, parameters of the environmental performance were estimated. The first group of the parameters includes coefficients of contamination for the electrolyte as waste water, and for air of the working area. These parameters take into account the threshold limit value for contaminants in the electrolyte and pollutants in the air of the working area. The pollutant concentrations in the air were estimated using partial pressures of the electrolyte components. The second group of the parameters stands for toxicity and includes class of dangerous goods for the electrolyte and vapor components. The third group of the parameters includes energy consumption for running the EPP, taking into account the consumption for providing required current density on the workpiece and consumption for maintaining the required electrolyte temperature. The fourth group is the time of personnel exposure to harmful and dangerous factors was determined using experimental data and mathematical models. The parameters were convolved into a cumulative environmental performance indicator using expert analysis of the significance.

We compared the environmental performance parameters for the selected EPPs and their classical chemical alternatives. The cumulative coefficients of contamination both for the electrolyte and the air of the working area are quite large for the both alternatives. However, the toxicity parameters of the electrolyte and vapor for the EPPs are better than that for the chemical alternatives. The energy consumption of for the EPPs is higher than that for the chemical alternative; however, the difference is not dramatic. The time of personnel exposure to harmful and dangerous factors is better for the EPPs, because the chemical alternatives are significantly longer. Analysis of the cumulative environmental performance indicator shows the advantage of the EPP processes.

Therefore, an approach to assess the environmental performance of electrolytic plasma processes have been developed in accordance with the requirements of ISO 14000 family. It was demonstrated that the cumulative environmental performance indicator of EPPs exceeded that for chemical alternatives by 6% ... 40%.

The research is supported by RFBR grant 16-38-60062.

Keywords: environmental performance, electrolytic plasma processes, chemical process

Anode plasma electrolyte nitrocarburising of titanium alloy VT-6 in aqueous solution containing glycerol and ammonium nitrate

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Abstract: Titanium alloys are actively used in engineering, aircraft building, medicine, etc. Due to alloying additives, the alpha- and beta-titanium alloy VT-6 has higher heat resistance, ductility and strength in comparison with other materials. But other mechanical properties remain rather low. Anodic plasma electrolyte diffusion saturation can improve the surface properties of alloys, while slightly affecting the properties of the core of parts.

The purpose of this work is to determine the effect of anode plasma electrolyte nitrocarburising on the mechanical and electrochemical properties of the titanium alloy VT-6. Samples of the titanium alloy VT-6 were processed for 5 minutes. The composition of the electrolyte is glycerol (10wt%), ammonium nitrate (5wt%), ammonium chloride (10wt%). The treatment temperature varied from 800 to 950 °C in 50 °C steps. After saturation, the samples were cooled in the electrolyte from the saturation temperature. The study of the friction characteristics was carried out on the UMT-01 tribometer using the “ball-on-disk” scheme. A ball of bearing steel (diameter 9.5 mm) served as a counter body. The normal load is 51 N, sliding speed is 0.24 m/s. The sliding distance for all samples is 100 m. Corrosion tests were carried out using potentiostat-galvanostat P-45X in Ringer’s solution like an analog of human body liquid. The friction coefficient of a titanium alloy does not depend significantly on the temperature of nitrocarburising.

Average weight loss of samples nitrocarburised at 900 °C and below is 0.4 mg after wear testing. The weight loss increases to 2 mg as the processing temperature rises up to 950 °C. The weight loss of untreated sample is 6.6 mg. This fact can be explained by the formation of the brittle layer of titanium oxide rutile on the sample surface at 950 °C.

The current density of corrosion for nitrocarburised samples drops from 1.27 mA/cm² to 0.3 mA/cm² with increasing of the saturation temperature. The minimum value of corrosion rate is comparable with the results of electrochemical tests of an untreated sample (0.25 mA/cm²). A decrease in the corrosion current density can be associated with a reduction of the surface roughness of the sample from 0.827 µm (800 °C) to 0.534 µm (950 °C) during its processing.

The formation of the oxide film is confirmed by X-ray diffraction analysis. X-ray patterns of the processed samples had additional peaks of titanium oxide–rutile. The thickness of the oxide film was calculated by decreasing the intensity of the titanium peaks. Its thickness increases with the temperature rise and reaches up to 10 µm at 950 °C. Also, the growth of the sizes of the coherent scattering blocks was found when the saturation temperature rises.

Thus, it was established that increasing the nitrocarburized temperature has a positive effect on the mechanical and electrochemical properties of VT-6 titanium alloy.

Keywords: nitrocarburising, titanium alloy

Prospects of improving properties of low-carbon steels by plasma electrolytic treatment

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Abstract: Plasma electrolytic anodic treatment is often used to improve the functional properties of the material by formation a thick coatings up 500 microns^[1]. The microhardness, corrosion resistance and wear resistance of low-carbon steel containing 0.1% of carbon (M1010) after plasma electrolytic carburizing, borading, nitriding were compared.

Plasma electrolytic was carried out using following electrolytes: 10wt% NH₄Cl+5% NH₃ (for nitriding), 10wt% NH₄Cl+3% H₃BO₃ (for borading) and 10wt% NH₄Cl+10% glicerol (for carburizing). Temperature of treatment was changed in the range of 700-1050 °C. The investigation of corrosion behavior of the obtained samples was carried out in 3.5% sodium chloride solution. A ball-on-disk configuration was applied to evaluate friction coefficient of the untreated and treated samples at dry conditions (5 N normal load, 0.2 m/s sliding speed and 240 m sliding distance). The corundum ball having 6, 35 mm in diameter was serving as counterbody.

Plasma electrolytic nitriding give the possibility to obtain the thicker coating, while the highest hardness were achieved by electroplasma borading. Besides, coatings obtained by plasma electrolytic carburizing were demonstrating improved wear resistance than nitrided and boraded coatings Fig.1.

Keywords: plasma electrolytic anodic treatment, carburizing, borading, nitriding

Reference:

[1] Belkin PNA, Yerokhin A, Kusmanov S A. Plasma electrolytic saturation of steels with nitrogen and carbon [J]. Surf Coat Technol, 2016, 307: 1194-1218.

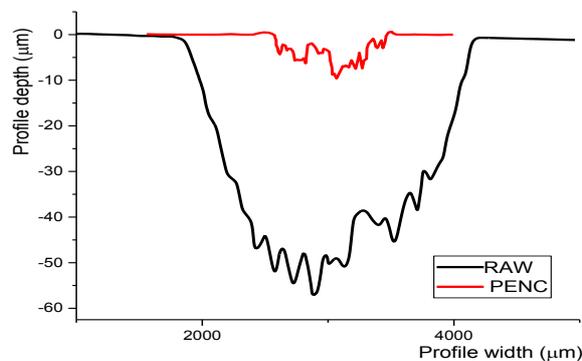


Fig.1 Profile of wear tracks for carburized and raw M1010 samples against Al₂O₃ ball at 5 N load for 0.2 m/s sliding speed

Additives on structure and anticorrosion of micro arc oxidation on AZ31B magnesium alloy

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Abstract: To know the effects of some additives on the anti-corrosion of coating, micro-arc oxidation (MAO) coatings were developed on AZ31B magnesium alloy via constant voltage method using Na_2SiO_3 -KOH as a base electrolyte system, and with the addition borax, sodium citrate, and disodium EDTA as additives. The surface morphology and corrosion resistance of MAO coated samples were evaluated by scanning electron microscopy (SEM) and neutral salt spray test (NSS). The MAO coating with crater shape was unobserved under 260 V of constant voltage in single component sodium silicate because of its high arc voltage, and shows poor anti-corrosion of Mg alloy. The sample treated by MAO in the electrolyte solution containing potassium hydroxide showed good corrosion resistance, which can be attributed to the low arc voltage and fast discharge role of OH^- . The selfsealing MAO coated samples prepared in the electrolyte solution containing borax displayed higher corrosion resistance, especially pitting corrosion resistance. Inversely, these samples produced in the electrolyte solution containing sodium citrate, and disodium EDTA demonstrated poor corrosion resistance though exhibited smaller micro porous with uniform distribution.

This work was supported by Science and Technology Planning Project of Sichuan Province (2016JZ0032), and Talent Introduction Fund of the Sichuan University of Science and Engineering (2017RCL15).

Keywords: magnesium alloys, micro-arc oxidation, additive, corrosion resistance

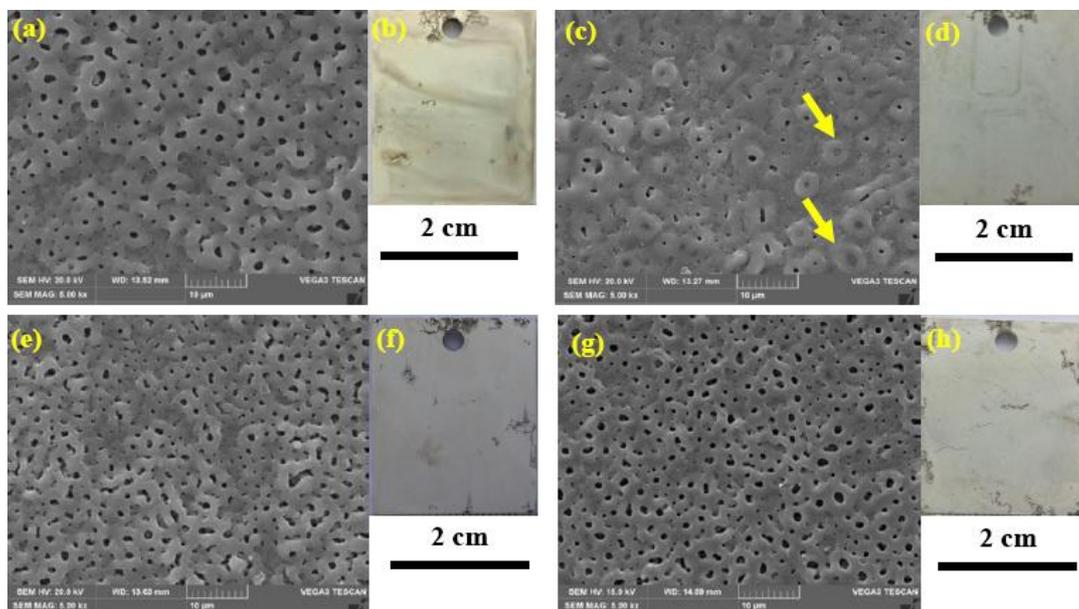


Fig.1 Surface morphology of MAO coating, and its corrosion appearance after NSS test: (a) Na_2SiO_3 -KOH; (b) Na_2SiO_3 -KOH- $\text{Na}_2\text{B}_4\text{O}_7$; (c) Na_2SiO_3 -KOH- $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$; (d) Na_2SiO_3 -KOH-EDTA Fund

Formation mechanism analysis of isolatedly oxidized regions underneath plasma electrolytic oxidation coating of magnesium alloy

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Abstract: Plasma electrolytic oxidation (PEO) can form a dense coating on magnesium alloy substrate with the suitable soft sparking regime^[1]. However, there often appeared isolatedly oxidized regions underneath the PEO coating when the processing parameters are not coupled well, as shown in Fig.1. It can be seen that the isolated oxidation islands lie under the porous layer with almost sphere form.

The PEO sparks usually have different types at the different processing phases: noise sparks and soft sparks. Noise sparking often can last on several minutes, which caused the porous layer formation. The heat transfer from magnesium substrate to the electrolyte solution was hindered by decreased thermal conductivity of this porous coating. The thermal barrier layer initialized the sequential soft sparks appearance with the voltage decreasing.

The isolatedly oxidized regions usually lie in the constituent segregation in the magnesium alloy substrate. During the heating process, chemical composition segregation regions have the lower melting point compared with that of the surrounded bulk materials, and can be partial liquidation^[2], and then decay into sphere oxidation areas. The partial oxidation regions can combine with the interface of porous layer/magnesium alloy when the interface penetrates inward to the substrate. The effective liquidation in constituent segregation adjacent to the interface is the key point to get the PEO dense layer.

Keywords: plasma electrolytic oxidation, magnesium alloy

Reference:

[1] Lippold J C. Welding Metallurgy and Weldability[M]. John Wiley & Sons, Inc., 2015.

[2] Tsai D S, Chou C C. Review of the soft sparking issues in plasma electrolytic oxidation [J]. Metals - Open Access Metallurgy Journal, 2018, 8(2): 105.

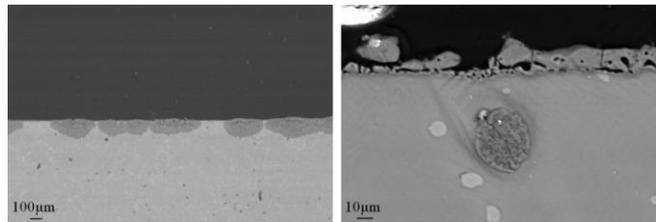


Fig.1 Isolatedly oxidized region under the PEO porous layer

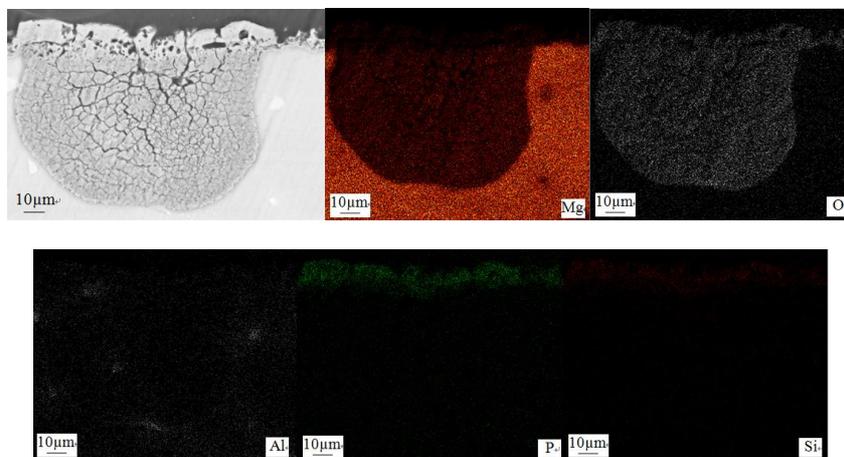


Fig.2 EDX mapping for a single oxidized region of PEO coating

Effect of L-Ornithine acetate on morphology and corrosion performance of anodic coatings on AZ31 magnesium alloy and its mechanism

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Abstract: Anodic oxide coatings were prepared on AZ31 magnesium alloy by anodizing in an environmentally friendly alkaline NaOH-Na₂SiO₃ solution with and without the addition of 0-0.09 mol/L L-Ornithine acetate (C₇H₁₆N₂O₄). The effects of the concentration of L-Orn on the voltage response, microstructure, morphology, composition and corrosion properties of the coatings were studied by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Fourier transform infrared, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), respectively. The results show that L-Orn can not change the chemical composition and microstructure of the oxide coating.

However, the anodized growth process, surface morphology, thickness and corrosion resistance of the anodized films were strongly dependant on the concentration of the L-Orn. When the L-Orn concentration was 0.03 mol/L in the electrolyte, a thick, compact anodized film with excellent corrosion resistance was obtained. Moreover, the mechanisms of L-Orn on the process of anodizing were also approached, which were combined effect of inhibition, arc suppression, and surfactant by absorption on the surface of magnesium alloy substrate.

Keywords: L-Ornithine acetate, anodizing, AZ31 magnesium alloy, corrosion resistance

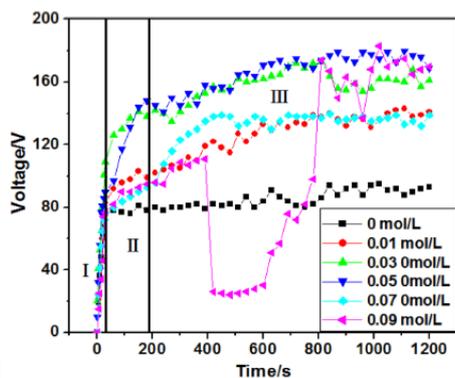


Fig.1

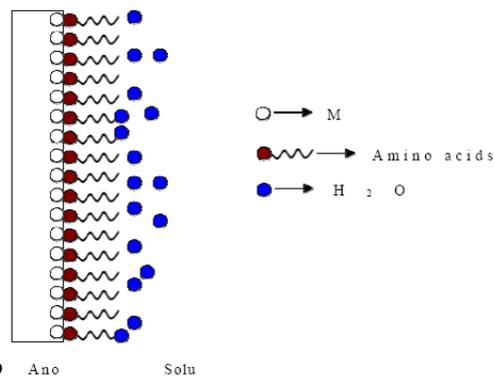


Fig.2

Fig.1 Effect of the concentration of L-Orn on the voltage of anodizing films forming

Fig.2 The schematic model for the surface adsorption of additives over AZ31 magnesium alloy

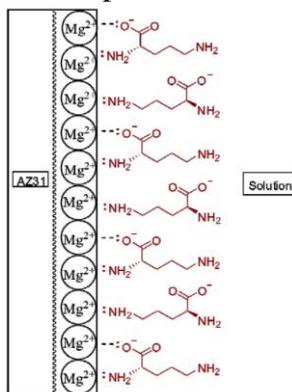


Fig.3 The adsorption model of L-Orn molecular on magnesium alloy surface

Effect of electrolyte composition on protective properties of PEO coating on zirconium alloy Zr-1Nb

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Abstract: Zirconium has high corrosion resistance and excellent neutron transparency; therefore, its alloys are extensively used in nuclear power plants for fuel cladding applications. However, zirconium suffers from waterside corrosion and erosion during prolonged operation in pressurized and boiling water reactors. One of the major concerns is connected with the hydrogen pickup resulting from the cathodic corrosion half-reaction; formation of ZrH₂ phase makes the Zr alloy brittle, and this may lead to the fuel cladding failure. Application of protective oxide coatings can serve as a good option to natural zirconia appearing on the cladding surface during the waterside corrosion. Plasma electrolytic oxidation (PEO) is an advanced environmentally friendly technology which can serve this task.

This research is devoted to the effect of electrolyte composition on protective properties of PEO coating on zirconium alloy Zr-1Nb. The following properties were considered when assessing the surface: corrosion current density i_{corr} , corrosion potential E_{corr} , coating porosity, hydride orientation coefficient. For the PEO experiments the following electrolytes were used: 1 g l-1 KOH+2 g l-1 Na₂SiO₃+2 g l-1 Na₄P₂O₇ (APS), 1 g l-1 KOH+2 g l-1 Na₄P₂O₇ (AP) and 1 g l-1 KOH+2 g l-1 Na₂SiO₃ (AS). The PEO treatment was carried out using flat samples 20 mm×20 mm×0.8 mm in a 6 liter vessel at constant temperature 20±1 °C for 10 min. Pulsed unipolar mode was used at frequency 500 Hz, duty cycle 50% and current density 10 A/dm². Electrochemical corrosion tests were performed in 0.1 M LiOH solution using P-5X potentiostat. Corrosion current density i_{corr} and corrosion potential E_{corr} were calculated via Tafel analysis. The surface topography was assessed with ImageJ software using SEM images obtained with JEOL JSM-6490LV. Hydrogen pickup test was performed for samples cut from the fuel cladding tubes ø10 mm, in Midiclave autoclave at 400 °C for 60 hrs in vapor, using 20% LiOH solution. The hydride orientation coefficient was calculated using sample crosssections as a ratio of hydrides length having 45-90 degrees angle towards the surface, to the overall length of hydrides.

All the PEO coatings show typical porous structure; the porosity is highly influenced by the electrolyte composition. The least porosity appears for APS electrolyte (3%), the highest – for AS (20%). Analysis of E_{corr} (vs Ag/AgCl) shows that the most passive coating is formed in APS electrolyte (–370 mV) compared to the other electrolytes (–460 mV both) and the substrate (–440 mV). The corrosion current for all the electrolytes appears to be the same within the experimental error ($0.9...1.2 \times 10^{-4}$ A/m²) showing improvement compared to the substrate (5.8×10^{-4} A/m²).

The hydrogen pickup test was performed for the coatings obtained in APS electrolyte. Compared to the uncoated sample, the hydrides network appears to be shorter; moreover, the length of radially oriented hydrides was smaller. The overall value of the hydride orientation coefficient is 0.18 ± 0.05 for the PEO coated sample and 0.31 ± 0.07 for the uncoated sample.

Finally, it was shown that PEO coating formation in APS electrolyte increases corrosion resistance and decreases the hydrogen pickup; therefore, this technology can be recommended for the surface treatments of Zr alloys used in nuclear power industry.

The research is supported by RFBR-Indian DST grant No. 16-53-48008.

Keywords: plasma electrolytic oxidation, zirconium alloy, fuel cladding

Effects of phosphate on structure and thermal shock resistance of

PEO ceramic coatings on Ti6Al4V alloy

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Abstract: There has been a great interest in plasma electrolytic oxidation (PEO) because of the promising application prospects of this technique in the surface treatment of metals. Among the important factors, electrolyte and electrical source influence the composition, structure and performances of the prepared ceramic coatings. As the common sole component electrolyte in the PEO process, phosphate is also widely used as an auxiliary component in many systems to improve the quality of the coating forming.

Therefore, a novel bi-polar pulsed source (with constant power output) was adopted to conduct PEO process on Ti6Al4V alloy in silicate system, and the phosphate was selected as an additive during the preparation of PEO coatings. Briefly, plate samples of Ti-6Al-4V alloy with a reaction dimension of 20 mm×10 mm×6 mm were used as working electrode and the electrolyser made of stainless steel served as the counter electrode. The electrolyte used in the experiments was Na₂SiO₃ solution with the concentration of 40 g/L and different concentrations of Na₃PO₄. A home-made high power pulsed bi-polar electrical source with power of 10 kW was used for plasma electrolytic oxidation under the current densities of 10 A/dm² for both pulse and the working frequency of 3000 Hz for 30 min. The effects of auxiliary phosphate concentration on the phase composition, structure, and thermal shock resistance of the ceramic coatings were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively. The thermal shock resistance of the coated samples was evaluated by the thermal shock tests. The results show that the coating was mainly composed of rutile TiO₂ and anatase TiO₂, as well as a large amount of amorphous silica oxide. Increasing the concentration of phosphate, the content of TiO₂ and the thickness of the coating increased first and then decreased. When the concentration of Na₃PO₄ was 20 g/L, the content of TiO₂ was the most and the thickness reached the maximum. SEM analysis shows that with improving the concentration of Na₃PO₄, the micro pores and the micro cracks of the coating increased gradually. The coatings were of double-layer structure, the outer layer was porous and the inner layer was comparatively dense. Furthermore, the distribution of the elements changed greatly within a few micrometers from the interface; otherwise, the coating is basically uniform all throughout the main coating and at the outer part of the coating the distribution of the elements also changed much because of the porosity and the roughness of the coatings. When the concentration of Na₃PO₄ increased, the micro pores and the micro cracks of the coatings were increased. The distribution of the elements changed greatly within a few micrometers from the interface and at the outer part of the coating. Otherwise, the coating is basically uniform: with the Ti and Si contents remaining at 30wt% or so and the O content remaining at 40wt% or so all throughout the main coating. The thermal shock resistance was mainly attributed to the surface state under the similar composition and thickness of the coatings. Increasing the concentration of Na₃PO₄, the thermal shock resistance of the coatings reduced greatly due to the increase of the residual discharging channels and the micro cracks. When the concentration of Na₃PO₄ was 6 g/L, the thermal shock resistance of the coatings was the best in the experimental conditions.

Keywords: plasma electrolytic oxidation, ceramic coatings, phosphate, thermal shock resistance, Ti6Al4V alloy

Lotus leaf clusters-like organic-free super-hydrophobic Al₂O₃ coating prepared by one-step plasma electrolytic oxidation

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Abstract: Inspired by water-repellent phenomena in nature, super-hydrophobic surfaces have attracted a great deal of interest in bionic research and practical applications. Most of the super-hydrophobic surfaces despite the methods and substrates usually have two common features: low surface free energy and micro/nano structures. Generally, modification by low surface energy materials contributes to generating a hydrophobic surface and control of micro/nano surface structure modulates the surface roughness and helps realize super-hydrophobicity. Previous reports also construct some special structures which can repel water without any modification, such as mushroom, T-shape structure. However, the preparation is difficult and costly, which hampers the practical application. In this work, a lotus leaf clusters-like organic-free super-hydrophobic Al₂O₃ coating are fabricated on aluminum alloy by one-step plasma electrolytic oxidation in the electrolyte composed of sodium tripolyphosphate and sodium hydroxide with a constant current density for 5 min. The coating is mainly composed by clusters of randomly distributed nail structure which looks like a pond filled with clusters of lotus leaves by an average distance of about 1200 nm with some porous structures planted among them. The as-prepared sample giving a water (2 μ L) contact angle of around 150 ° and a slide angle (10 μ L) of about 10 °. The XRD and XPS results show that the coating is mainly composed of alumina. To clarify the formation process of the super-hydrophobic surface, simulation is carried out by MATLAB software and a simplified 2D model is built for the convenience of calculation. The results suggest that the unique structure of the sample surface is formed due to a synergetic effect of formation and dissolution of alumina in the electrolyte. In conclusion, a novel and simple method to fabricate super-hydrophobic surfaces on aluminum alloy without any modification by low surface energy materials is proposed, which not only provides a possibility for industrial production with high throughputs but also new insights into the design of super-hydrophobic surfaces on other new materials.

Keywords: plasma electrolytic oxidation, lotus leaf clusters-like, alumina, super-hydrophobic

Thermophysical features of anode heating

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Abstract: Anode electrolytic heating is a complex of thermophysical and electrochemical processes occurring on the anode surface, associated with local liquid boiling due to electrocaloric effect. In view of specific features of the process, newly formed VGE performs current-carrying functions, acting as a heating element in a three-phase system (anode-VGE-electrolyte) at the same time. Emitted heat allows to maintain a steady inter-phase boundary between the electrolyte and the VGE, as well as to heat the electrolyte and the anode. Heat flux distribution in the VGE is essentially dependent on qualitative and quantitative characteristics of electrolyte, heating voltage, the mode of heating organization as well as on hydrodynamic conditions for electrolyte flow. Knowledge about energy-balance in the system “anode-VGE-electrolyte” allows to construct more adequate models of anode temperature pattern which would enable to work out modes of thermochemical treatment of anode electrolytic heating.

Development of various thermophysical models with their subsequent experimental verification, allows for better understanding of the mechanism of ongoing physical processes in the VGE. Up to now, all the models have been built by analogy with film boiling, i.e. vapour layers at rest or in motion between the anode and electrolyte solution have been under consideration. Under the assumptions made, there is a qualitative consistency with the experimental data: increasing temperature-voltage and decreasing current-voltage characteristics. Quantitative consistency would be possible in the case of investigating physical aspects of current flow through the VGE. Alongside solving the energy equation, models, considering vapour motion in the envelope, imply solving the equation of vapour flow with various boundary conditions. This would facilitate obtaining envelope profile and specify temperature-voltage and current voltage characteristics. This is not a question of experimental verification, as determination of VGE thickness involves certain difficulties.

Keywords: heat exchange at phase transitions, plasma electrolytic treatment PET, vapour gas envelope VGE

First-principles calculations and narrow band gap energy of WO₃/TiO₂ composite films on titanium prepared by microarc oxidation

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Abstract: The porous WO₃/TiO₂ composite films were in-situ prepared by microarc oxidation (MAO) process on pure titanium in sodium tungstate electrolyte at different voltages. Morphology, phase structure, chemical composition and optical property of films were characterized by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-vis spectra. The results showed that the porous composite films prepared at positive voltage of 400-450 V had many pores with larger size and lower density, and the film at 400 V had lowest electron hole recombination rate. The WO₃/TiO₂ composite films as n-type material consisted of anatase TiO₂, rutile TiO₂ and WO₃ phases. It was found that the flat band potential was in the range of 0.38 V to 0.86 V, and the doping density value varied between 1.62×10¹⁷ cm⁻³ and 6.84×10²² cm⁻³. The band gap energy of WO₃-TiO₂ composite films prepared at different applied voltages was 2.23 eV - 2.61 eV. The first-principles calculations for analyzing the band structure of films demonstrated that the WO₃/TiO₂ films fabricated by MAO process could reduce the gap width between conduction band (CB) and valence band (VB) of anatase phase in WO₃/TiO₂ films due to the appearance of the W doping, oxygen vacancy, titanium vacancy and so on. That resulted in a red-shift of optical absorption. Furthermore, the WO₃/TiO₂ composite films could extend the optical absorption threshold and enhance the utilization of solar light.

Keywords: microarc oxidation, WO₃/TiO₂ composite film, pure titanium, first-principles calculations

Degradation mechanisms of micro-arc oxidation composite coatings on biomedical Mg-(Li)-Ca alloys for orthopaedic implants

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Abstract: Intermetallic compounds and porosity have significant impact on the formation of micro-arc oxidation (MAO) coating on Mg-(Li)-Ca alloys. Polymeric coatings (poly(L-lactic acid (PLLA) and chitosan (CS)) have been utilized to seal the pores. The second phase Mg₂Ca on formation and biodegradation mechanism of the MAO coating and its composite coatings on Mg-1Li-1Ca alloy have been investigated by means of optical microscopy, electron probe X-ray microanalysis, scanning electron microscopy, nano-scratch tests, mass loss, electrochemical potentiodynamic polarization, hydrogen evolution and pH measurements. Results reveal that pitting and filiform corrosion occur on bare Mg-1Li-1Ca alloy in Hank's solution. MAO coating significantly improve the corrosion resistance of alloy at the initial stage. The results indicated that the MAO/PLLA or CS composite coatings significantly enhanced the corrosion resistance of the Mg-1Li-1Ca alloy. MTT and ALP assays using MC₃T₃ osteoblasts indicated that the MAO/PLLA coatings greatly improved the cytocompatibility, and the morphology of the cells cultured on different samples exhibited good adhesion. Hemolysis tests showed that the composite coatings endowed the Mg1Li-1Ca alloys with a low hemolysis ratio. The plate-counting method designates that MAO/CS coating enhances the antibacterial growth activity. The increased solution pH resulting from the corrosion of magnesium could be tailored by the degradation of PLLA and CS. The in vitro degradation mechanisms of MAO coating and MAO/PLLA or CS on Mg(Li)-Ca alloy has been discussed.

Keywords: magnesium alloy, micro-arc oxidation, polymer coating, intermetallic compounds, degradation

Promising orthopedic implant material with enhanced osteogenic and antibacterial activity: Al₂O₃-coated aluminum alloy

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Abstract: Better orthopedic implants improve the life quality of patients and elderly people. Compared to Ti and Mg alloys commonly found in bone implants, Al alloys have merits such as high specific strength, excellent casting capability, and low cost. However, the poor wear resistance, corrosion resistance, and insufficient biocompatibility have hampered their application in orthopedic implants. In this study, well structure designed and excellent adhered Al₂O₃ coating, which has been widely used as orthopedic implant materials, especially dental and bone replacement for its good wear resistance, intrinsic wettability, chemical stability and biocompatibility, is fabricated by plasma electrolytic oxidation (PEO) on Al alloys to improve the wear resistance and corrosion resistance and inhibit release of potentially harmful Al ions from the Al alloy substrate. Elements such as Zn, Ca, and Fe are incorporated into the Al₂O₃ coatings in situ to obtain the favorable biological functions by PEO in special modified electrolyte. The prepared Al₂O₃ coatings have good adhesion strength and double-layer structure which improve the anti-abrasion and anti-corrosion performance and avoid the leaching out of toxic Al ions. Biological assessment demonstrates that the Al₂O₃ coating significantly improves the cytocompatibility of Al alloy samples. In particular, the Zn-doped Al₂O₃ coating delivers outstanding osteogenic performance and the antibacterial rates against E. coli and S. aureus are $99.5 \pm 0.56\%$ and $98.77 \pm 0.52\%$, respectively. The biological mechanism of the PEO coating is discussed at last. The Al₂O₃-coated aluminum alloys with good biocompatibility and enhanced osteogenic and antibacterial activity have great potential in the development of novel kinds of bone substitute biomaterials in orthopedics.

Keywords: plasma electrolytic oxidation, aluminum alloy, orthopedic implant, antibacterial, osteogenic, aluminum alloy, orthopedic implant, antibacterial, osteogenic

Formation and properties of Ca-doped barium titanate based coatings produced by plasma electrolytic oxidation

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Abstract: In this paper, (Ba,Sn)TiO₃ (BST) coatings were synthesized using a plasma electrolytic oxidation (PEO) technology on a Ti6Al4V alloy. The coating's formation mechanism, wear and corrosion resistance, and piezoelectric property were carefully investigated. The results indicated that during the PEO preparation process, Ti-O layer was firstly formed and then it reacted with Ba(OH)₂/NaSnO₃ electrolyte to form the (Ba, Sn)TiO₃ coatings. The main phase of as-synthesized coatings is tetragonal BT, which accounts for the coating's ferroelectric character. It is also found that the BT coating presents lower friction coefficient and higher wear and corrosion resistance than the uncoated Ti alloy.

Keywords: barium titanate, plasma electrolytic oxidation, tribological properties, corrosion resistance

Investigation on electrochemical behavior of TA2 alloy treated by micro-arc oxidation

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Abstract: In this paper, two kinds of micro-arc oxidation (MAO) coatings on TA2 with different thickness were prepared by control of oxidation time, and were characterized for its composition, crystalline structure, and surface morphology. The effect of MAO treatment on electrochemical behaviors of TA2 in 3.5%NaCl solution were studied by the electrochemical tests including measurement of open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization. The results indicate that the electrochemical behavior of MAO coating is related to the coating structure. OCP can be used to evaluate the porosity of MAO coating, and the more positive OCP indicates the coating with lower porosity and larger resistance obtained from EIS. The MAO treatment can significantly enhance the corrosion resistance of TA2, but the increase of thickness of MAO coating cannot bring out the further enhancement of corrosion resistance. In addition, because of the increases of effective surface area, the MAO treatment may enhance the cathode action of TA2 when the galvanic cell is composed of TA2 and other more negative metal, and promotes the corrosion of negative metal.

Keywords: micro-arc oxidation, porosity, open circuit potential, electrochemical impedance spectroscopy, polarization

Corrosion behavior of plasma electrolytic oxidation coatings on Mg alloy

produced in an electrolyte containing SiO₂ particles

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Abstract: In this study, nano-sized SiO₂ particles were in-situ incorporated into phosphate-based coatings and the effect of these particles on the microstructure, composition and properties of the coatings was investigated. The particles of nano-sized SiO₂ were separated the colloidal particles on the surface of the negatively charged particles in the electrolyte. It could be effective to enter into the ceramic coatings during plasma electrolytic oxidation process. The number of holes decreased on magnesium oxide ceramic surface and ceramic coatings surfaces become dense more. With the increment of nano-sized SiO₂ powder to add, the thickness of the ceramic layer was thickened obviously. The corrosion resistance of the ceramic coating had a larger increase in the modified electrolyte. The corrosion current density of the ceramic coating dropped from 3.882×10^{-5} to 1.266×10^{-9} A/cm². Impedance value of the composite ceramic coating increased from $2.909 \times 10^5 \Omega$ to $1.28 \times 10^7 \Omega$. Noise resistance of the composite ceramic coating increased two orders of magnitude. The corrosion resistance of the composite ceramic coating was enhanced significantly.

Keywords: magnesium alloy, PEO coatings, corrosion, electrochemical impedance spectroscopy

Thermal damage of magnesium alloys ceramic coating by micro arc oxidation surface treatment

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Abstract: The energy of the breakdown discharge in the process of micro arc oxidation (MAO) is released by heating the material around the discharge channel instantaneously, the result of heating is that oxide coating and the surrounding metal matrix in the discharge channel is melted and vaporized. Coupled with the subsequent cold quenching, it is inevitable to cause thermal effect to ceramic coating, and thermal damage to ceramic coating is caused under the condition of repetitive breakdown. Based on this, the damage mechanism is revealed of MAO ceramic coating, through which the microstructure of ceramic coating under different thermal effect were studied in this paper.

The results are shown: With the increase of ceramic coating thickness as well as the increase of dielectric breakdown energy, the single arc size and energy of the specimen surface increases, and the pore size and thermal crack of ceramic coating surface increases. So the impedance of ceramic coating increases first and then decreases with the increase of thickness, and the maximum can be reached $2.324 \times 10^6 \Omega \cdot \text{cm}^2$. It is proved that the bulk density of ceramic coating is decreased and the thermal damage is formed with the increase of dielectric breakdown energy. The corrosion resistance of magnesium alloy samples decrease treated by MAO treatment.

The thermal damage of ceramic coating caused by MAO treatment can be reduced under bipolar pulse mode by regulation of negative and positive discharge energy ratio. When the electric quantity of positive is constant, the thermal damage of the ceramic coating can be reduced and the corrosion resistance of the magnesium alloy can be improved by increasing the negative electric quantity. However, the MAO ceramic coating can not grow normally and the local exfoliation and abnormal thickening appear, when the negative pulse power is too large when the negative pulse power is too large. The corrosion resistance of magnesium alloy samples decrease treated by MAO treatment.

Keywords: micro arc oxidation, magnesium matrix, ceramic coating, bipolar pulse, thermal effect

Effect of electrolyte system on the structure and corrosion resistance of plasma electrolyte oxidation (PEO) coating on 1060 aluminum alloy

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Abstract: The PEO coatings were prepared under the constant current density mold on 1060 aluminum alloy in silicate electrolyte, phosphate electrolyte and silicate-phosphate mixed electrolyte, respectively. The growth mechanism of PEO coating was discussed based on the structure and corrosion resistance of PEO coating prepared in different electrolytes. The coating growth mechanism was considered that there is a molten zone connecting the substrate to the surface adjacent surrounding each plasma discharge. The deposition of silicate oxides under plasma causes a PEO coating with rough surface, porous structure and poor corrosion resistance in silicate electrolyte. On the contrary, the coating prepared in phosphate electrolyte has the good corrosion resistance because its dense and smooth structure. The combination of silicate and phosphate electrolyte can effectively improve the corrosion resistance of the coating.

Keywords: plasma electrolyte oxidation, corrosion resistance, growth mechanism, aluminum

The cavitation stripping mechanism of micro-arc oxidation system and the follow-up finishing design of 3D titanium alloy parts

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Abstract: Due to the high roughness of 3D titanium alloy parts, titanium alloy surface contact polishing can cause abrasive damage and non-contact chemical polishing technology will introduce elemental contamination and other processing problems. This study is based on the low-value shunt law of electron flux and the principle of small curvature convergence of electric field strength. In an electrochemical system using titanium alloy 3D as the anode, based on the mechanism of convergence of the field intensity by the peak height of the small curvature and the low-resistance shunting mechanism of the microporous titanium oxide film obtained by the electrochemical conversion of the anode surface. The surface of titanium alloy gets enhanced by nano-micro-beam discharge oxidation and the oxygen plasma environment of cavitation jet effect is set up by regulating the peak current and the continuous state of the inter-polar current. Studying conversion film material properties, micropore structure, peak and continuous current between electrodes, electrolyte flow field characteristics, geometric deformation to the law of electric field feedback, cavitation jets on the anode surface and the corresponding crystal integrity. To reveal the physicochemical mechanism of the plasma oxidation enhancement and cavitation jet induced and corresponding temporal and spatial characteristics of the electrochemical system and the physical properties of the jet product and summary the boundary conditions of nanoscale cavitation jet induced and product stripping. Finally, the physical properties of the conversion film, the electric field distribution between the electrodes, and the distribution characteristics of the flow field were used to polish the titanium alloy 3D to $R_a < 0.05 \mu\text{m}$.

Keywords: microarc oxidation, cavitation, titanium alloy, 3D printing, polishing

Influence of circular workpieces configurations on temperature field of vacuum heating process

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Abstract: The configurations of workpieces determines the view factors between workpieces surfaces, which affects the radiation heat transfer between surfaces of the loads. Vacuum heating processes of workpieces with two typical shape, round bar and disc shape, are studied. In order to achieve high-efficient and uniform radiation heat transfer, finite element method has been applied to calculate the temperature field of the loads with different arrays. The effects of arrays of workpieces on the heating rate and temperature uniformity are investigated. The results indicated that under the same heating process, round bar in aligned arrangement and the disc in vertical arrangement can effectively reduce radiation dark zone, improve heating uniformity and increase heating efficiency. The simulation results have directive significance for the configurations of circular workpieces, such as gears, shafts, bearings and nozzles, in the heating zone of vacuum furnace.

Keywords: circular workpieces, loads configurations, vacuum heating, finite element method, temperature field

A novel energy management method for micro-arc oxidation

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Abstract: The problem of excessive energy consumption in micro-arc oxidation (MAO) process has become the key to restricting development. In the pre-arcing stage of MAO, a Faraday discharge process was taken place, and a high impedance coating was formed and dissolved. the impedance between the samples and the electrode is small before the high-impedance ceramic layer is formed. If a high voltage applying to them will cause a large current overshoot, and the current density even can be 10 A/dm² or more. The constant current control is adopted to limit the current overshoot usually. But the voltage will increase slower to reach the arcing stage at a lower current density, especially in large area. Therefore, the pre-arcing stage has hardly effect on the growth of the ceramic layer, but also limit the maximum area of micro-arc oxidation that can be performed by a single power supply under rated power conditions. A cross-stage-mode method based on anode gradually immersed is proposed for improving the problem of excessive energy consumption in micro-arc oxidation (CSM-MAO) using pulse power source. In the proposed method, power supply output voltage will be controlled above the arcing voltage, and the sample connected to positive electrode will immersed electrolyte at a certain speed. The immersed area of sample will be conducted with cathode and arc rapidly to form ceramic layer. All of the sample will arc with the immersing process. The experimental results indicate that the energy consumption before arcing, the critical current density and the time required for the arc initiation process are effectively reduced, and the performance of the ceramic layer is not changed. In addition, the technology has been successfully applied to the mass production of magnesium alloy wheels.

Keywords: micro-arc oxidation, energy consumption

Anti-corrosive microarc oxidation film modified with layered double hydroxide on 6061 Al alloy

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Abstract: In this study, layered double hydroxide (LDH) was in-situ synthesized on the MAO film to realize its porosity reduction on 6061 Al alloy. The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests were used to evaluate the anticorrosion performance of the LDH modified MAO film. The testing results show that, by comparing with the neat MAO film, the LDH modified MAO film can significantly improve the long term anti-corrosion property of the 6061 Al alloy when exposed to NaCl solution environment. The microstructure of the LDH was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), X-ray diraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) to demonstrate the growth mechanisms and morphology evolution of the LDH on the MAO film. It was observed that the porosity of the MAO film can be largely reduced due to the precipitation of the LDH nanoplates in the MAO pores. In addition, it was found that the growth behaviors of LDH on various areas of MAO film are distinctively different because of their specific surface area, chemical composition, and phase structure. This method not only provides an effective approach to improve the anti-corrosive performance of MAO film on Al alloys, but also shed a light on how to mitigate the porosity problem in various porous inorganic films.

Keywords: layered double hydroxide, microarc oxidation, aluminum alloy, corrosion resistance

Quasi two-dimensional CePO₄ and its self-lubrication in Al₂O₃ coatings

prepared by one-step plasma electrolytic oxidation

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Abstract: Aluminum alloys possess many mechanical and physical properties that make them attractive to aerospace and automotive applications. However, the intrinsically poor wear resistance and high friction coefficient severely hinder their further use. Plasma electrolytic oxidation (PEO) is always used to improve the mechanical and tribological properties of aluminum alloys by producing alumina coating which usually has a high friction coefficient. Many reports tried to incorporate graphite particle or graphene into the coating, however, some special additives should be used and a long-termed stable oxidation seem not easy to realize. This work discovers a new quasi two dimensional material (CePO₄) by structure calculation and CePO₄ is successfully incorporated into the alumina coating by a one-step PEO in an additive-free electrolyte. The composition and morphology of the coatings are analyzed by X-ray diffractometer (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (SEM), and transmission electron microscopy (TEM) And the friction and wear properties are investigated by sliding the disk samples against Si₃N₄ balls under dry condition. The results show that CePO₄ and Al₂O₃ mainly compose the coating and higher elemental concentration of Ce and P can be observed with the increase of Ce³⁺ concentration in the electrolyte. CePO₄ enriches in the upper layer of coatings in term of nanocrystals. The coatings with a high concentration of CePO₄ has the best wear performance with low friction coefficient (approximately 0.15) and low wear rate for a long-time testing. The tribological mechanism of the Al₂O₃/CePO₄ coating is also discussed.

Keywords: plasma electrolytic oxidation, CePO₄, self-lubrication, aluminum alloy

Plasma electrolytic polishing of steel after diffusion saturation

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Abstract: The paper shows the possibility of plasma electrolytic polishing of the steel surface after its chemical-thermal treatment in a single technological process. Positive results of the plasma electrolytic polishing are obtained for carbon steel after its treatment in borid acid, nitrate and ammonium chloride solution. In the process of PET, three processes simultaneously occur on the steel surface: oxidation, diffusion saturation with nitrogen and boron, and anodic dissolution of steel. An oxide layer is formed on the surface of the steel as a result of oxidation. Under the oxide layer, the diffusion layer is detected, which is the result of nitrogen and boron diffusion with the formation of iron nitrides and a solid solution of nitrogen and boron. The formation of surface topology is shown to determine by the competition between two processes: oxidation and anodic dissolution. The uneven formation of the oxide layer occurs during oxidation. On the contrary, anodic dissolution promotes smoothing of the surface. The reduction of the surface roughness and corrosion current density of plasma electrolytic treated steel by plasma polishing using mode of current interruption for 2 min without changing the structure of the diffusion layers is shows.

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Keywords: plasma electrolysis, polishing, steel, corrosion resistance, surface roughness