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Phase Formation in Ceramic Coatings During Plasma Electrolytic Oxidation of Aluminium Alloys

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Abstract: Phase formation in oxide ceramic coatings on aluminium alloys during plasma electrolytical oxidising has been studied. The theoretical interpretation was based on a model that considers two mechanisms of oxide formation: electrochemical surface oxidation and plasma chemical oxide synthesis in the discharge channels. Thermodynamic calculations were carried out for both the formation of reaction products, as well as heating and cooling of the discharge channel. The divergence of the calculated and experimental results was estimated to be less than 20%. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Plasma electrolytic oxidising (PEO) of aluminium alloys is an advanced technique for routine anodising.[1–3] The PEO process operates at potentials greater than typical breakdown voltages of the original oxide films (typically 400–600 V). Breakdown of the film is manifested as multiple sparking on the treated surfaces. Oxide ceramic coatings (OCC) with structures similar to those of sintered oxide ceramics are formed on the surfaces due to the local thermal action of the sparks. The coating composition can be modified considerably because the anionic components of the electrolyte, as well as the aluminium cationic alloying elements, are incorporated in the film.[4–6] OCCs are often superior to the original anodic oxides in mechanical characteristics and superior to plasma sprayed ceramic coatings in adhesive strength.[7,8] Consequently, not only researchers studying the fundamentals of this process but also surface engineers, who deal with the exploitation of the parts treated by PEO, attach great importance to the study of OCC phase formation.

Multi-component chemical interactions taking place at the sample surface during oxide layer formation, accompanied by arcing, are generally quite complicated. Consequently, typical experimental approaches to the determination of the phase assemblage in OCCs are quite difficult and tedious.[1,4,5–7,9–12] At present there are no works in the literature that provide a theoretical approach allowing even an approximate prediction of OCC phase composition during the design of the PEO parameters.

The principal aim of the present work was to develop a theoretical model that will provide a representation of the phase formation of OCCs suitable for the estimation of the coating phase assemblage at the PEO design stage.

2 GENERAL PRINCIPLES

It is clear that the development of the model should incorporate consideration of the contribution of the processes occurring in the coating discharge channels to the formation of the OCC phase assemblage. Physico-chemical processes in the discharge channels can be appropriately described using the model of the PEO process,[13] which is based on the general theory of the breakdown of a metal/dielectric/liquid system in a strong electric field.[14]

Three main steps can be discerned in the breakdown process. In the first step, the discharge

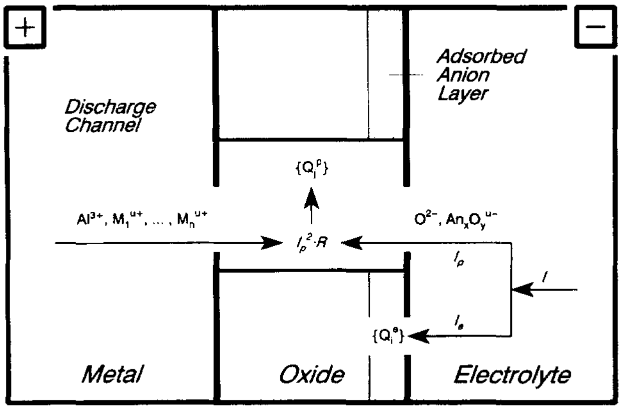

Fig. 1. Current distribution in a metal/oxide/electrolyte system during plasma electrolytical treatment.

channel is formed in the oxide layer as a result of the loss of its dielectric stability in a region of elevated conductivity. This region is heated by generated electron avalanches up to temperatures of $\sim 10^4$ K.[15] Due to the strong electric field (of the order of $\sim 10^6\,V{\cdot}m^{-1}$), the anionic components of the electrolyte are drawn into the channel. Concurrently, owing to the high temperature, aluminium and alloying elements are melted out of the substrate and enter the channel. Thus, a plasma column (*plasmoid*) is formed as a result of these processes.

In the second step, plasma chemical reactions take place in the channel. These lead to an increase in pressure inside the channel, so the plasmoid expands to balance it. At the same time, separation of oppositely charged ions occurs in the channel due to the presence of the electric field. The cations are ejected from the channel into the electrolyte by electrostatic forces.

In the last step, the discharge channel is cooled and the reaction products are deposited on to its walls.

According to Snezhko and Tchernenko,[16] the duration of a single arc impulse, t_i, is estimated to be $\cong 10^{-4}$ to 10^{-5} s and the current passing through the arc, I_i, is $\cong 2\text{–}4 \times 10^{-3}$ A. Since the minimum current density I is set at $\sim 100\text{–}250\,A{\cdot}m^{-2}$, then the time density of arcing, d_a, should be $\sim 0.5\text{–}4.0 \times 10^6\,m^{-2}{\cdot}s^{-1}$. It can be calculated that the total current passing through the arcs, I_p, accounts for $\sim 10\text{–}15\%$ of I. Raising I leads to the share of I_p of the total current passing through the cell being increased.

Since I_p is substantially less than I, it is possible to consider a schematic of the case when an electric current passes through a metal/oxide/electrolyte system during the PEO process. This is shown in Fig. 1.

According to eqn (1), the total current passing through the system (I) consists of the current passing through the oxide layer (I_e) and the current by-passing it (I_p). Thus:

$$I = I_e + I_p \qquad (1)$$

Consequently, there are two parallel processes for OCC formation: the electrochemical and the plasma chemical mechanisms.

The electrochemical formation of surface oxide layers can occur through different mechanisms. If standard strong electrolytes — sulphuric, oxalic, salicilic acids and their salts, etc. — are used, then the alumina layer grows as a result of mutual diffusion of metal and oxygen ions through the oxide lattice.[17,18] However, such electrolytes are not widely used in the PEO technique, where aqueous solutions of inorganic polymers — silicates, aluminates, phosphates, etc. — show the best results.[7,9,12,19–21] Unfortunately, there are few studies of the electrochemical formation of surface oxide layers in these electrolytes.

It has been proposed that these layers are formed by the polycondensation of adsorbed anionic complexes of an electrolyte due to dehydration under the action of an electric field.[22,23] Therefore, the processes associated with ionic diffusion can be ignored, so the coating composition can be formed only from the anionic complexes of an electrolyte when considering the electrochemical formation of oxides in such electrolytes.

To calculate the composition of the products formed through the plasma chemical mechanism, it is necessary to know the reactions taking place in the coating discharge channel, as well as their kinetics. However, this is extremely difficult because the discharge phenomenon is a multi-step, multi-component and heterophase process.

Therefore, the probability of formation of a product must be estimated using thermodynamic calculations of high-temperature processes in the channel. These are based on the principle of maximum entropy summed over all phases in the multicomponent heterophase system.[24]

The following preliminary restrictions must be imposed on the system to undertake the calculations:

1. The initial conditions of the system must be defined.
2. The final conditions are equilibrium.
3. There is no mass exchange with the external environment.
4. Two of the five basic thermodynamic parameters of the final condition of the system — temperature, pressure, volume, total energy and enthalpy — must be determined.

While restrictions 1, 2 and 4 can be assumed without concern, restriction 3 is not satisfied throughout the breakdown process because some of the components are ejected into the electrolyte during the second step. At the same time, the suggestion that the discharge channel can be considered as a closed system during heating (i.e. before the cations are ejected into the electrolyte) and cooling (i.e. after the ejection) can be assumed.

In this case, the calculations must be separated into several steps because the final conditions of the system after heating will differ from the initial conditions before cooling.

Consequently, thermodynamic estimation of the composition of the products condensed in the discharge channel requires the development of a specialised model.

Thus, the model should account for the two main mechanisms — the electrochemical surface oxidation and the plasma chemical oxide synthesis in the discharge channels — concerning OCC phase formation during PEO. Additionally, consideration of the second mechanism calls for the development of a specialised model of the processes taking place in the coating discharge channel.

3 ASSUMPTIONS

Several assumptions based on the general principles discussed above must be made:

1. The current I_p, as well as the current I_e, causing OCC formation through the two parallel mechanisms are constant.
2. The processes of mutual diffusion during the electrochemical formation of the oxide layer can be ignored.
3. The discharge channel is considered to be a closed heterophase system during heating and cooling.
4. The final conditions of the system for each step during the discharge process are at quasi-equilibrium.
5. The energy loss from heat absorption by the environment is negligible.

4 MODEL OF OCC PHASE FORMATION

Based on eqn (1) and the above assumptions, the phase assemblage of the OCC can be represented as the sum of sets of oxides formed by electrochemical $\{Q^e\}$ and plasma chemical $\{Q^p\}$ mechanisms:

$$Q = Q^e + Q^p \tag{2}$$

where

$$Q^e = Q_1^e,\ Q_2^e \dots Q_i^e \dots Q_m^e \tag{3}$$

$$Q^p = Q_1^p,\ Q_2^p \dots Q_j^p \dots Q_n^p \tag{4}$$

Here, Q_i^e and Q_j^p are the fractions of oxides of the ith and jth type formed by the electrochemical and plasma chemical mechanisms, respectively.

According to Faraday's ratio and eqn (2), the total amount of the oxide of the kth type can be calculated from the following:

$$Q_k = Q_k^e + Q_k^p = (k_k^e I_e + k_k^p I_p)t \tag{5}$$

where k_k^e and k_k^p are the coefficients corresponding to the formation of the kth oxide through the electrochemical and plasma chemical mechanisms, respectively, and t is the oxidation time.

The coefficients have the same dimensions as the electrochemical equivalents but may be different in value due to the side processes of various types occurring in the arcs and the remainder of the surface.

Consequently, the summarised coefficients k^e and k^p, corresponding to the formation of sets $\{Q^e\}$ and $\{Q^p\}$, may be different too. If the coefficients k^e and k^p have been determined and the function $I_e = f(I)$ has been established, then the ratio Q^e/Q^p for the total amounts of oxides, formed by the different mechanisms, can be estimated. So, the relative amounts of the oxides containing the sets $\{Q^e\}$ and $\{Q^p\}$ can be determined to estimate the OCC phase assemblage.

On the basis of Assumption 2, the composition of the oxides containing $\{Q^e\}$ can be defined by the anion (An) composition of the electrolyte, so:

$$Q^e = Q^{An} \tag{6}$$

The set of oxides formed by the plasma chemical mechanism is derived from the n types of oxides deposited during each arc. Taking into account Assumption 1 for the oxide of the jth type formed during plasma chemical reactions:

$$Q_j^p = d_a q_j^p t \tag{7}$$

where q_j^p is the amount of oxide of the jth type formed in an arc.

Thus, the determination of the phase assemblage of oxides formed as a result of the plasma chemical reactions is reduced to the search for the set $\{q^p\}$ formed in a single arc.

A thermodynamic model of the processes taking place in the discharge channel of the oxide film was developed to solve this problem. The goal was to simulate the composition of the channel when it is heated to temperatures appropriate for the discharge channel and then cooled. Taking into account the breakdown process discussed above, three steps for the calculation are used in the model.

In the first step, the heating of the discharge channel is simulated. According to Assumption 3, the channel is considered to be a closed heterophase system. The system's initial composition is set by the components of the electrolyte and aluminium alloy combined in various proportions. The system's final condition corresponds to the moment when the heated plasmoid has already been expanded but cations still have not been ejected. In accordance with Assumption 4, the final condition of the system can be considered to be at quasi-equilibrium. Then, the following two thermodynamic parameters for the final condition, temperature T and pressure P, can be determined. Here, T corresponds to the temperature in the discharge channel[15] and P is the atmospheric pressure and the hydrostatic pressure of the electrolyte added together. However, the latter can be ignored because the immersion depth of the sample during the PEO usually does not exceed 10 cm. Thus, the final composition of the heated system is determined according to the following equation:[24]

$$S = S_s + S_l + S_g = S_{\max}|_{T,P} \qquad (8)$$

where S is the entropy of the system and the subscripts refer to solid (s), liquid (l) and gaseous (g) sub-systems.

In the second step, the ejection of positively charged ions into the electrolyte is simulated. For this purpose, the set of substances taken from the result of the calculation for the first step must be corrected. The cations are neglected and the proportions of the remaining substances then are recalculated. Thus, the initial set for the calculation of the condensed products in the discharge channel can be generated.

In the final step, simulation of the channel cooling is carried out in a manner similar to the calculations for the first step. However, the coating's final temperature is set at room temperature owing to Assumption 5. The components of the plasmoid are condensed as various oxides, the amounts of which generate the unknown set $\{q^p\}$.

Table 1. Calculated plasma composition during heating of the discharge channel

Component	Content (mol·kg^{-1})
H^{1+}	48.006
O	25.909
Al	17.714
Mg	1.311
Si	0.346
Na^{1+}	0.243
P	0.242
Mn	0.063
e^- gas	0.019
H_2^{1+}	0.011
Ti	0.005
OH	0.002
Na	0.001
AlH	0.001

5 AGREEMENT OF CALCULATED AND EXPERIMENTAL RESULTS AND DISCUSSION OF MODEL

A closed reaction system consisting of AlMg6.0Mn1.0 aluminium alloy in a solution containing $Na_6P_6O_{18}$ (50 g·litre^{-1}), SiO_2 powder (0–64 g·litre^{-1}) and Al_2O_3 powder (100–0 g·litre^{-1}) was selected for the estimation. The phase assemblage of the coating formed on the alloy was calculated using the developed model and compared to experimental results obtained by Bakovets *et al.*[25] by X-ray microprobe analysis. The plotted profiles of the main elements, including P, Si and Al, were converted to the simple oxides P_2O_5, SiO_2 and Al_2O_3, respectively.

The sets $\{Q^e\}$ and $\{Q^p\}$ were calculated for the estimation of the OCC phase assemblage. According to eqn (6), it was established that the set $\{Q^e\}$ consists of the oxides P_2O_5, SiO_2 and Al_2O_3, the proportions of which correspond to concentrations of $P_6O_{18}^{6-}$ anion, SiO_2 and Al_2O_3, respectively, in the electrolyte.

Computer simulation of the formation of set $\{Q^p\}$ was carried out using the software *Astra 4*,[26] which allows simulation of high-temperature transformations in mixed-phase systems on the basis of the principle of maximum entropy.

According to the developed model, the composition of the heated discharge channel was simulated in the first step of the calculations. Based on the results of earlier work,[27] the initial composition of the system was held to consist of 50% alloy components and 50% electrolyte. The parameters of the system's final condition corresponded to the temperature 10^4 K reached in an arc[15] and the pressure 10^5 Pa, as defined by the model. The equilibrium composition of the system at the final condition was calculated using the thermodynamic properties of the individual substances, which were part of the database of the software.

The principal results from the simulation of the composition of the heated discharge channel for coatings formed in the phosphate electrolyte solution are given in Table 1 for the case when 42.0 g·litre^{-1} SiO_2 and 33.3 g·litre^{-1} Al_2O_3 are added to the electrolyte. Analysis of the calculation shows that the products of the thermal decomposition of the electrolyte (H, O, Al, Si, Na, P) and the substrate (Al, Mg, Mn) form the bases of the components of the discharge channel. The presence of ionic components and electron (e^-) gas indicates that the substance in the channel is under plasma conditions.

The initial composition of the system during the channel cooling was obtained from subsequent calculations. The ions Na^{1+}, H_2^{1+} and H^{1+} were assumed to be ejected from the channel. Thus, they were expelled from the set and disregarded in the further calculations.

The results for the calculation of the condensed products from the plasma chemical reactions during discharge channel cooling, which give the set $\{q^p\}$, are shown in Table 2. It is clear that Al_2O_3 is the basis of the products condensed in the discharge channel. The fact that Al_2O_3 predominates over all other components is explained by its presence in the electrolyte and by the oxidation of the substrate material. As might be expected, Si and Mn form simple oxides. However, P forms only complex oxides with Na and Mg.

To estimate the OCC phase composition completely, the ratio Q^e/Q^p must be determined. This ratio was not estimated for the PEO in phosphate solutions. The calculations carried out for solutions of $Na_6P_6O_{18}$ showed that Q^e/Q^p is approximately 1/1 for a wide range of I when electrolyte concentrations of 30–60 g·litre^{-1} are used.[28] From this, it is assumed that the ratio Q^e/Q^p is similar to 1/1 for the PEO in phosphate electrolytes with a concentration of 50 g·litre^{-1}. Then, according to eqn (2), the set $\{Q\}$ can be determined from the summation of the data from Table 2 and the $\{Q^e\}$ in equal proportions.

Re-calculation according to the molecular weights of P_2O_5, SiO_2 and Al_2O_3 was done using the set $\{Q\}$ to compare with experimental data,[25] as shown in Fig. 2. The agreement between the theoretical and experimental data is relatively good. In the case of Al_2O_3, the divergence reaches 20% for high-Al_2O_3 concentrations. This divergence is probably associated with the absence of experimental data for MgO and MnO in the coatings. While the ratio Q^e/Q^p can also be determined somewhat inaccurately, a separate experimental estimation would be required.

Table 2. Calculated condensation products during cooling of the discharge channel

j	q_j^p (mol·kg^{-1})
Al_2O_3	0.220
MgP_2O_6	0.040
SiO_2	0.014
$Mg_2P_2O_7$	0.004
$NaPO_3$	0.001
MnO	0.001

6 CONCLUSIONS

A model of OCC phase formation during the PEO of aluminium alloys, including electrochemical and plasma chemical oxidising mechanisms, has been developed.

Thermodynamic simulation of the plasma chemical processes showed that the formation of complex oxides, as well as oxides of the substrate alloying elements, is possible in the coating discharge channels. Being in small concentrations, these phases are difficult to analyse experimentally. However, they can have a significant influence on the coating's protective properties and, consequently, should be considered.

Agreement between the calculated and experimental data is relatively good, with a divergence of less than 20%. The divergence may be caused by the inaccurate determination of the contribution of the various mechanisms in OCC formation, which requires separate consideration. Nevertheless, the results indicate that the model is adequate for estimation of the coating phase assemblage at the PEO design stage.

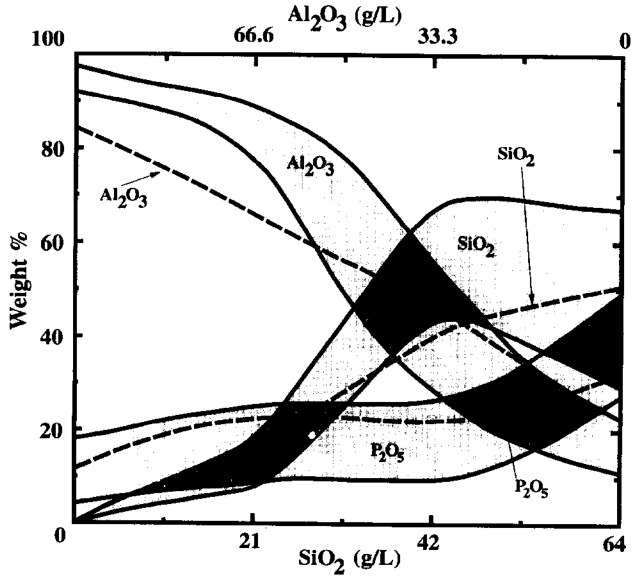

Fig. 2. Calculated (dashed lines) and experimental (shaded regions) compositions of the OCC produced with a phosphate electrolyte containing additions of SiO_2 and Al_2O_3.

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