

PLASMA ELECTROCHEMICAL NONCONTACT METHOD TO OBTAIN COATINGS ON VALVE METALS AND THEIR ALLOYS

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Abstract

In this work has been developed an energy-efficient method that is based on conjoint plasma-electrochemical processes allowing to obtain different coatings with given properties on different surface parts of valve metals and their alloys. This method based on alternating current flow between two counter electrodes (sample or detail), with are leakproof separated from one another and in different electrolytes situated.

1. Introduction

Traditional, thick anodizing, plasma electrolytic oxidation (PEO), plasma thermochemical treatment (PTCT) in aqueous solutions are the most widely used and investigated methods to obtain coatings on valve metals and their alloys [1, 2] during their anodic polarization. Each of them inherents essential advantages and disadvantages. Electric energy consumption to obtain coatings on these metals and alloys as a rule

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decrease in the following order: PEO, thick anodizing, PTCT, and traditional anodizing. However, the physical and mechanical properties of corrosion-resistant coatings (such as hardness, durability, adhesion to metal matrix, fatigue resistance etc.) on certain thickness of coatings decrease, in inverse order [2-13], which depends essentially on used method to obtain them on valve metals and alloys.

For example, if it is required to obtain a coating with high physical and mechanical properties only on the small part of surface and a decorative corrosion resistant one on the remaining part (as a rule considerably larger one), it is doubtless that simultaneous realization of two methods (e.g., PEO and PTCT or PEO and traditional anodizing) on different parts of the sample reduces the required electric quantity.

In view of the above, the prime target of this work was to develop an energy-efficient method that is based on conjoint plasma-electrochemical processes allowing to obtain different coatings with given properties on different surface parts of valve metals and their alloys.

2. Experimental Procedure

Samples of alloys 4L33 and 2024 were coated by using a capacitive equipment with nominal capacitance of 38kW.

The equipment (principle diagram is shown in Figure 1) was created to realize plasma electrochemical method to obtain simultaneously different coatings with given properties on two or three different surface parts of bars.

Geometrical dimensions of the counter electrodes exceeded that of the working electrodes in order to reduce the energy use and their corrosion rate caused by external current.

Corrosion resistance of coatings was estimated by the analysis of sample surface after exposure in a salt spray chamber during 336 hours.

Micro-hardness of inside coating layer sections was measured with the help of micro-hardness tester 402 MVD (Wilson Instruments). The indentation size and micro-hardness of coating layer were determined automatically by OmniMet MHTFS Software with Windows XP operating system. The measurements were carried out according to GOST 9450-76: The static loading was 0.490N, the stressing time – 15sec, and the amplification – $\times 600$. At least 20 micro-hardness measurements were made for each sample, as a result, the average value and standard deviation from it were registered by the use of computer assisted module of micro-hardness tester.

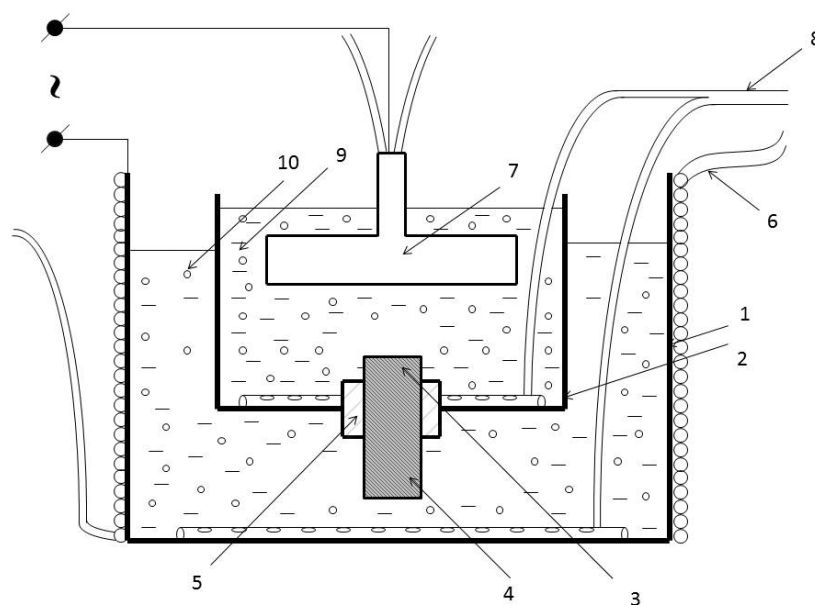


Figure 1. The principle diagram of equipment to obtain coatings with different properties on two or three parts of sample by noncontact method.

3. Results

Figure 2 shows examples of electrochemical noncontact method realization on samples of aluminium alloys 2024 (Figure 2 (a), (b), (d)) and 4L33 (Figure 2 (c)). As we can see the whole bar or its parts immersed into different electrolytes have unlike appearance and colours.



Figure 2. The appearance of coatings obtained on bars of aluminium based alloys with plasma electrochemical method: (a), (b), (d) – 2024; (c) – 4L33.

These coatings were obtained by the following regimens:

(A) Commuted current of 4A was applied, an aqueous solution that contains 2g/l NaOH, 3g/l TLG was used; the duration of PEO was 70 min; squares of left and right parts of bar – 2; 0.2dm^2 , respectively (Figure 2 (a)).

(B) Commuted current of 4A was applied, an aqueous solution that contains 110g/l TLG, 3g/l TLG, and 2g/l NaOH was used (Figure 1); the duration of PTCT and PEO was 70 min; squares of left and right parts of bar – 3; 0.2dm^2 , respectively (Figure 2 (b)).

(C) Commuted current of 1A was applied, an aqueous solution that consists of H_2SO_4 20% and 110g/l TLG was used (Figure 1); the duration of anodizing and PTCT was 20 min; squares of left and right parts of bar – 0.6; 0.2dm^2 , respectively (Figure 2(c)).

(D) Commuted current of 4.5A was applied, an aqueous solution that consists of 110g/l TLG, 1g/l NaOH, 3 TLG, and $2\text{V}_2\text{O}_5$ was used (Figure 1); the duration of PTCT and PEO + PTCT + electrophoresis was 60 min; squares of left and right parts of bar – 0.65; 0.3dm^2 , respectively (Figure 2(d)).

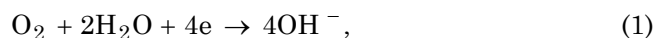
After exposure in salt spray chamber, there were no traces of corrosion confirmed by visual inspection on bars surface treated with A, B, D regimens (Figure 2 (a), (b), (d)), but on the anodized part of 4L33 bar (C regimen, Figure 2(c)) local corrosion attack was found. It is necessary to treat the anodic decorative surface of aluminium alloys with anodizing in sulphuric acid to improve its anticorrosive feature [3, 11]. Coatings with thickness more than 80µm obtained by PEO on the bar parts of 2024 alloy have medium and maximum micro-hardnesses – more than 1600 and 1800 HV, respectively (Table 1).

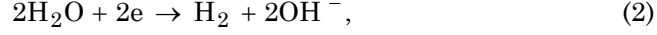
Table 1. The thickness of coatings obtained with different methods on various sample parts of aluminium based alloys and their medium and maximum micro-hardnesses

Alloy	Medium thickness of coatings on bar surface, µm		Medium and maximum micro-hardnesses of bar parts, HV		Method of obtaining coatings on the surface of bar parts	
	Left	Right	Left	Right	Left	Right
2024	47	89.4	650 830	1640 1870	PEO	PEO
2024	43.2	83.9	420 580	1650 1990	PTCT	PEO
4L33	14.1	31.3	–	–	Anodizing	PTCT
2024	72.1	99.4	490 610	690 810	PTCT	PEO + electrophoresis

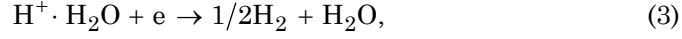
Discussion. The PTCT mechanism to treat light-weight structural alloys.

If the counter electrode 7 is a cathode (during one half-period of alternating current flow) and the obtaining of coatings on conducting materials by this method may cause further reaction behaviours (it depends on pH of electrolyte):

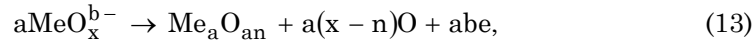
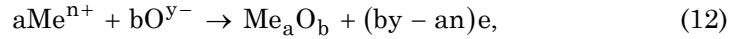
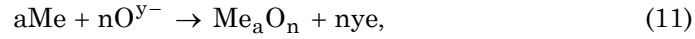
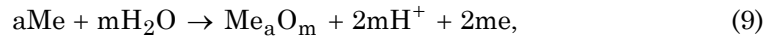
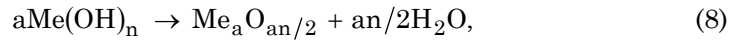
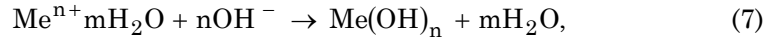
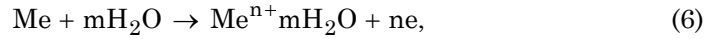
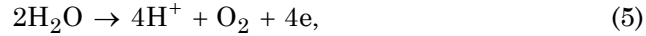
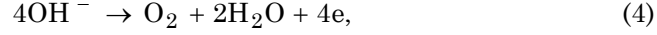




or



the working electrode 3 is an anode. The further reactions can flow on its surface (it depends on given electrical conditions, electrolyte and alloy compositions, metal properties):



where m, n, a, y, b, x, m – stoichiometric coefficients.

Anodizing includes reactions from (6) to (9), PEO mechanism is an exothermic oxidation of metallic bottom through pores, where microplasma discharges are realized (10)-(12). If microplasma discharges are on the surface of the working electrode, the oxide entering into coatings happens by PTCT (13).

In this half-period, the counter electrode is an anode and on its surface can flow, for example, anodic reactions from (4) to (9) and on the other (second) part of the working electrode surface—cathodic reactions (1), (2) or (3). It depends on material, pH of electrolyte, and electrode potential.

Therefore, the current flows through object and sample between the counter electrodes 1 and 7, which do not contact but immersed into different electrolytes (9 and 10, Figure 1). This happens because of conjoint reactions between the counter electrode 7 and the working electrode 3, the counter electrode 1 and the working electrode 4 (reactions like (1)-(6), (9), (11)-(13)).

In the next half period of the alternating current flow, the polarity inversion of electrodes takes place.

The working electrode 3 becomes a cathode and reactions from (1) to (2) flow on its surface and anodic reactions like (4)-(6), (9) flow on the surface of the counter electrode 7. In this half period, the coating grows up on the working electrodes 4 or 5. Here can take place reactions like (4)-(13).

So in interleaved half periods during the alternating current flowing between the counter electrodes 1 and 7, the surface modification of one and then of another working electrode parts (sample or object) occurs alternately.

If the given electric regimen is settled, the processes of coating grow on the surfaces of two working electrodes 3 and 4 flow practically simultaneously (the minimum difference in process realization time that cause the growing of coatings on the surfaces of two working electrodes is 10msec). The technological conditions, namely, electrolyte temperature and content, given current value, that provide anodizing process of both working electrodes 3 and 4 or one of them to the PEO or PTCT process transition, are settled. This depends on given surface properties particularly on the improvement of corrosion resistance, hardness, durability. After 10-40sec, the growing of coating may begin by PEO or/and PTCT on the surface of one or two electrodes.

Power consumption to obtain coatings by this method is lower as compared to that in obtaining hard coating (medium and maximum are more than 1600, 1800 HV) on the whole surface of a bar. For example, power consumption to obtain anticorrosive coatings with PEO with a thickness of $\approx 80\mu\text{m}$ and medium, maximum micro-hardnesses of 1640, 1970 HV, respectively, on the whole surface of this bar (its square is equal to 2.2dm^2) is bigger for 10.1 times than in obtaining identical coatings, but only on the given part of surface (its square is equal to 0.2dm^2) with developed method (Figures 1 and 2(b)).

4. Conclusion

Plasma electrochemical noncontact method to obtain coatings on valve metals and on their alloys was developed. It allows to apply coats with different given properties and thickness on various surface parts of sample or object. The usage of this method gives the ability to decrease power consumption in comparison to the obtaining of hardwear-resisting and/or anticorrosive coating on the whole surface of large sized product only by one method, for example, PEO of valve metal based alloy.

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