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Plasma electrolytic processing of bimetals at the anodic process

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Bimetals have a unique combination of functional characteristics, which are not inherent to components. Usually, the joining is the final procedure of the bimetals manufacturing because the conditions of heat or thermochemical treatment of the bimetal components are very different. Plasma electrolytic processing is a highly effective and environmentally friendly method to process surfaces of metals and alloys. This technology can be used for heat or thermochemical treatment as well as to clean or polish metal surfaces. Due to the voltage ranges of different modes of the anodic process of plasma electrolytic processing for various metals in the same electrolyte partially overlaps, the components of bimetals can be treated identically or differently. It is demonstrated that there exists an option of separate or simultaneous heat or thermochemical treatment, as well as polishing of one or both components of bimetals. For example, in Ti/Stainless Steel (SS) bimetal, the steel was heated up to 620°C, in Mo/SS one — up to 630°C, in Al/SS one — up to 720 ÷ 850°C without heating of the second component higher than 140°C. Also, an ability of simultaneous polishing of both components of Al/SS bimetal was shown. During 8 min polishing, the reflection coefficients of both surfaces increase from $0.5 \div 2\%$ to >40%.

Keywords: electrolyte plasma, bimetal, heat treatment, polishing.

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Плазменно-электролитическая обработка биметаллов в анодном процессе

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Биметаллы обладают уникальным сочетанием функциональных характеристик, не присущих компонентам. Обычно соединение является завершающей процедурой изготовления биметаллов, поскольку условия термической или термохимической обработки биметаллических компонентов сильно различаются. Плазменно-электролитическая обработка — это высокоэффективный и экологически чистый метод обработки поверхностей металлов и сплавов. Эта технология может использоваться для термической или химико-термической обработки, а также для очистки или полировки металлических поверхностей. Из-за того, что диапазоны напряжений разных режимов анодного процесса плазменно-электролитической обработки для разных металлов в одном и том же электролите частично перекрываются, компоненты биметаллов можно обрабатывать одинаково или по-разному. Показано, что существует возможность раздельной или одновременной термической или химико-термической обработки, а также полировки одного или обоих компонентов биметаллов. Например, в биметалле Ti/Hержавеющая сталь (SS) сталь нагревали до 620°С, в Mo/SS — до 630°С, в Al/SS — до 720 ÷ 850°С без нагрева. второй компонент выше 140°С. Также была показана возможность одновременной полировки обоих компонентов биметалла Al/SS. В течение 8 минут полировки коэффициенты отражения обеих поверхностей увеличиваются с 0.5 ÷ 2% до >40%.

Ключевые слова: электролитная плазма, биметалл, термообработка, полировка.

1. Introduction

Composite materials, which include two or more metallic layers jointed by adhesion or chemical bonding, are named bimetals. Bimetals have a unique combination of functional characteristics, which are not inherent to components. For example, bimetals can simultaneously have high corrosion resistance combined with high strength and workability or high wear resistance combined with high electrical and heat conductivity.

There are many methods to produce bimetals, such as surfacing [1,2], spraying [3], powder metallurgy [4], brazing [5], electrodeposition [6], deformation welding (cladding [7] or joint extrusion [8]), friction welding [9], explosion welding [10], welding by high-energy flows [11], etc. Usually, the joining is the final procedure of the bimetals manufacturing. However, there are cases in which it is necessary to produce heat or thermochemical treatment of one component without changing of properties of another. It is also often necessary to clean, descale or polish both surfaces of the bimetal.

Many methods for heat or thermochemical treatment of metals, in which the entire material is subject to heating, are developed. In these cases, localization of the thermochemical action is carried out by protecting the non-machined areas of the part surface by galvanic tinning, coppering, nickeling or by applying various pastes and coatings [12]. However, these methods are not usually applicable for bimetals due to undesirable changes of mechanical or other functional properties of the second component (for example, the temperature of most types of heat treatment of steel exceeds the melting point of aluminum), which are resulted from the heating due to the heat conductivity.

There are various technologies to heat local areas of the material, such as induction [13], laser [14], electron beam [15] heating, etc. However, this heating usually can be short-time (not more than a few seconds, but usually a split second), because an increase in heating time leads to overheating of zones where this is unacceptable. Unfortunately, the short time of heating usually cannot provide the necessary depth of thermochemically treated zone.

Other problems arise during polishing of the surface of bimetallic products since there are differences in the physical, chemical, and mechanical properties of each of the bimetal surfaces. The most popular methods of metal polishing are [16] mechanical or abrasive polishing, chemical polishing, electrochemical or galvanic polishing. Unfortunately, these methods have several drawbacks that do not allow (or significantly complicate) polishing of the surface of bimetal.

Mechanical properties of the bimetal components are usually strongly different and thus their simultaneous abrasive polishing is impossible. For example, polishing of non-ferrous metals is usually a much simpler (and thus quicker) operation than polishing of stainless steels. Chemical and electrochemical polishing differs by the reagent or electrolyte compositions for various metals and alloys. For example, for polishing of Al, the electrolyte usually includes H_3PO_4 and H_2SO_4 , for Cu and carbon steel — H_3PO_4 and CrO_3 ; for stainless steel — H_3PO_4 with a little addition of H_2SO_4 . Besides that, electrolytes may include other additions. Commonly used reagents are ecologically hazardous and difficult for recycling.

The plasma electrolytic processing (PeP) of bimetals at the anodic process (AP) [17,18] can solve these problems.

Processes in the electrolytic cell at the active anode can be divided onto five modes depending on electric parameters [19,20]. These modes are low voltage electrolysis (classical electrochemistry) (LVE) — $0...(15 \div 25)$ V; switch mode (Wehnelt's breaker) (SM) — $(15 \div 25)...(70 \div 100)$ V; heating mode (HM) — $(70 \div 100)...(180 \div 320)$ V; electro-hydrodynamic mode (EHDM) — $(180 \div 320)...(300 \div 400)$ V; contact electric discharges mode (CEDM) — over $(300 \div 400)$ V. Real values of voltage boundaries of the modes depend on the composition and temperature of the electrolyte and the treated metal.

Each of these modes can be used to treat surfaces of metals. The LVE results in anodic dissolution of the metal surface according to Faraday's law. A current output during this mode is depending on the metal type and varies from $15 \div 20\%$ for W to $95 \div 98\%$ for Cu [21]. This mode is applied in various industries also for polishing, deburring, etc.

An increase in the voltage activates the water dissociation. Gas-vapor bubbles become larger. The flow of current through the gas (gas discharges) causes its partial ionization, that is, the formation of plasma. The process transits into the SM. The SM stimulates rapid dissolution of the active electrode both by pulse discharges and by intensive chemical reactions in a gas-vapor shell [22]. This mode can be used to produce needle-like tips from hard-to-process materials such as W, Mo, Ir, etc., or chemical compounds.

The specific erosion of the anode during the HM or EHDM of the AP can be significant [17]. In these modes, there are narrow ranges of the voltages with the maximal dissolution rate. The current output is much higher than that during the LVE. Besides that, classical electrochemistry distinguishes insoluble (inert) electrodes (Pt, Ir, graphite) and soluble ones, but after the plasma shell formation this difference is not actual. Particularities of the electrolyte plasma influence on the active electrode surface provide the ability to treat metals in such electrolytes where they don't dissolve during LVE or where the current output is very little. These processes are used to polish metals in the electrolyte plasma [17,18,23].

During CEDM, the gas-vapor shell becomes too thick and partially strips off the surface of the active electrode. As a result, the local contact between the electrolyte and the active electrode surface is restored, and the process becomes similar to bubble boiling (analogously to SM).

Water solutions of salts are usually used to polish metals by PeP. For example, to treat Al or Ag can be used the water solutions of fluoride and citrate of ammonium at the electrolyte temperature of $60 \div 90^{\circ}$ C [24].

2. Experiments

PeP of bimetals were carried out at AP using experimental equipment (Fig. 1) described in [25]. The water-cooling bath was 2 l in volume. The second electrode (cathode) was made from lead or stainless steel. Cell voltage and current varied in the ranges of $0 \div 450$ V and $0 \div 50$ A, correspondingly. We used aqueous solutions with specific conductivity higher than 5 Ohm⁻¹· m⁻¹. The processing duration varied from tens of seconds to 10 minutes. The electrolyte temperature varied

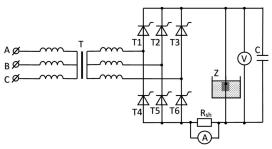


Fig. 1. Three-phase power supply for plasma electrolytic processing of metals during anodic process.

from 15 to 30°C for heat and thermochemical treatment and from 60 to 90°C for polishing. The rate of immersion of the anode into the electrolyte in all cases did not exceed 10 mm/s. After the processing, the samples were washed by distilled water. The current density at the active electrode at the HM was 6÷10 kA/m² and at the EHDM 2÷5 kA/m², the temperature of the active electrode at EHDM was 90–100°C. The temperature of electrolyte was measured by a Hg thermometer. The temperature of the active electrode at the heating mode was measured by a testo 845 optical pyrometer. Morphologies of the surface was studied by a Zeiss AxioScope A1 optical microscope. A reflection coefficient was measured through the relative intensity of the directed and the reflected beams of red laser light by PhyWe laboratory photometer.

We have studied plate bimetal samples produced by joint rolling.

3. Results and discussion

3.1. Influence of technological parameters of plasma electrolytic treatment on the heat treatment of bimetals at the heating mode of the anodic process

The HM of the AP is established when the gas-vapor shell completely covers the active electrode and the current density decreases to $100~\text{A/m}^2$. This mode is used to heat the metal up to $400...1000^{\circ}\text{C}$ [17]. EHDM is characterized by an increase of the gas-vapor shell thickness, intensive corona discharge, decreasing of the current density lower than $5~\text{kA/m}^2$, and absence of high-temperature heating (the active electrode temperature is not higher than 100°C).

It is possible to choose the parameters for the AP to provide the HM on the surface of one component of the bimetal (its temperature can be higher than 800°C) and the EHDM on the surface of the second component (its temperature does not exceed 100°C). Thus, the heating of

the bimetal will be selective. It is important that significant erosion will not appear on both surfaces.

One example of such processing is given by the following. We have studied the processing of bimetal plate $(1.5 \times 2 \text{ cm}^2)$ of steel AISI 321 (3 mm in thick) and Al-based alloy 6063 (2 mm in thick). Direct voltage electrolytic cell included bimetallic anode and lead cathode. The electrolyte was ammonium chloride water solution with specific electric conductivity of 34 Ohm⁻¹⋅ m⁻¹ and the surface tension coefficient of 76 mN/m at temperature of 22°C. When the working voltage of 180 V was reached, the bimetallic electrode was vertically immersed into the electrolyte. On the steel part of the anode, the HM was realized, and its temperature was equal to 720°C. On the aluminum part of the anode, the EHDM was realized, and its temperature was equal to 90°C. Cooling of the bimetal after the processing was carried out by turning off the current. The addition of corresponding reagents to the electrolyte [17] can provide nitration, carburization, or carbonitration of the steel part of the bimetal.

Treatments of other bimetals were similar (Table 1).

The use of this method to treat bimetals in electrolyte plasma allows the heat or thermochemical treatment of one metal to be carried out without heating the outer/inner surface of the second metal over 100°C/250°C, correspondingly. Thus, this method increases the quality of the processed bimetals and improves the manufacturability of the technological processes (the workpiece can have any configuration).

3.2. Influence of technological parameters of plasma electrolytic processing on the polishing of bimetals at the electro-hydro-dynamic mode of the anodic process

PeP is the method of finishing conductive materials. This processing allows removing the oxide scales, preparing the surface before covering by thin films and coatings [17,18], polishing difficult profile surfaces of critical parts, removing burrs and blunting sharp edges, and producing decorative polishing of metal products. The PeP is largely devoid of the drawbacks inherent in mechanical and electrochemical polishing. In comparison with other methods of polishing its advantages are high productivity and efficiency, environmental cleanliness, high quality and rate of performed operations, as well as low cost.

To polish simultaneously the surface of the entire bimetal product, the EHDM has to be realized on all surfaces. The voltage for EHDM depends on the processed metal type and such molecular properties of the electrolyte as the surface

Table 1. Parameters of the PeP of bimetals.

Bimetal	Heated metal	Temperature in area of	Temperature in area of	Evaluated temperature on the bond of	Valtage between	Composition of the water-based electrolyte,
		HM, °C	EHDM, °C	components, °C		mass.%
Titanium / steel	Steel	620	80	120	300	10% NH ₄ Cl
Molibdenum / steel	Steel	630	90	120	300	15% NH ₄ Cl
Aluminum / steel	Steel	720	90	130	180	15% NH ₄ Cl
Aluminum / steel	Steel	850	90	140	220	15% NH ₄ Cl
Aluminum / brass	Brass	850	90	250	210	10% Na ₂ WO ₄ ·2H ₂ O

tension coefficient and the kinematic viscosity: the larger these parameters, the lower the voltage, when this mode is set [17].

The main characteristics of the polishing quality are roughness and reflectability. They depend on the chemical composition of processed material, voltage, and duration of the PeP. The composition of processed material also determines the composition and concentration of the electrolyte. Beside that, in some cases the addition of such matters as glycerin, acetone, triethanolamine, trilon-B, etc., which significantly influence on both coefficient of surface tension and kinematic viscosity, can be used. These additions change conditions of gas-vapor shell formation and shift voltampere range of the EHDM [17].

The most important parameter which determines the polishing quality is working voltage. It was experimentally shown that when the voltage value decreases below a certain limit, the polishing quality significantly decreases. These minimal limits are: 220 V for stainless steels, 260 V for copper and copper-based alloys, 270...290 V for aluminum and its alloys, 280...290 V for argentum [18, 26]. However, an increase of the voltage over critical value (300...400 V depending from conditions of processing) is unacceptable not only through economic reasons but through technological ones. This increase can result in transition to CEDM of AP when the gas-vapor shell breaks down and the quality of the polished surface deteriorates [19].

The electrolyte temperature is one of the most important factors of polishing quality. High quality of the polished surface can be achieved only if the electrolyte temperature is in 50...90°C range. When the latter is outside this interval, the surface quality is lower. Beside that, it should be borne in mind that electrolytes included ammonium salts, hydrochloric acid, some other components which can dissociate higher 85°C with formation of volatiles, and thus frequent adjustment of the solution composition will be necessary.

Plasma electrolytic polishing is usually carried out using water solutions of salts. For example, to polish Al or Al-based alloys, the water solution either of ammonium chloride or sodium chloride [18], or of potassium chloride, oxalic acid, and glycerin [27] can be used, but, in order to polish stainless steels, the water solution of ammonium sulfate [28] can be used. Therefore, processing schedules and electrolyte should be determined experimentally for each metal, alloy, and especially bimetal or composite.

Two types of bimetals of stainless steel/aluminum-based alloy were studied. The first type consisted of austenitic stainless steel AISI 321 and aluminum-based alloy 6063, the second type included austenitic stainless steel AISI 304 and aluminum-based alloy A92017.

To polish these bimetals, we used water solution including 2...6 mass.% of potassium chloride, 1...4 mass.% of oxalic acid, and 1...2 mass.% of glycerin. The voltage on the electrolytic cell was 320 V. Both surfaces were mat (Fig. 2) and the reflection coefficient was very small (0.5...2%) (Fig. 3) in initial rolled state. The polishing during 2 min results in a significant decrease of roughness (see Fig. 2) and in an increase of the reflection coefficient up to 28% for stainless steel and up to 21% for aluminum alloy (see Fig. 3). The rapid decrease of the roughness highly likely is caused by an active

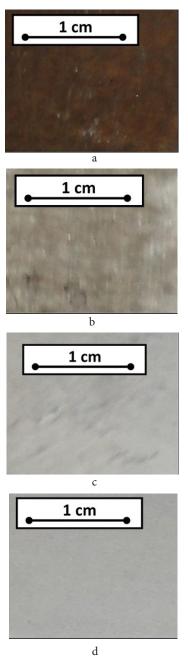


Fig. 2. (Color online) The surfaces of bimetal stainless steel AISI 321 (a, c), aluminum-based alloy 6063 (b, d) before (a, b) and after (c, d) the plasma electrolytic polishing, respectively.

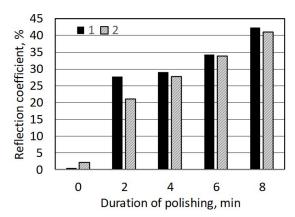


Fig. 3. An influence of duration of the polishing on the reflection coefficient for bimetal stainless steel AISI 304 (1)/aluminum-based alloy A92017 (2).

local smoothing of the micro-relief in the places of the largest protrusions. A subsequent increase of the polishing duration results in a slower decrease in the roughness and an increase in the reflection coefficient up to 41...42% (see Fig. 3).

4. Conclusions

- 1. It is possible to carry out heat or thermochemical treatment of one component of a bimetal without heating of the second component over 100...250°C using plasma electrolytic processing.
- 2. Simultaneous plasma electrolytic polishing of both components of the bimetals is possible. In particular, polishing of bimetal of stainless steel and aluminum-based alloy with 2 min duration significantly decreases the roughness and increases the reflection coefficient from less 2% to more 20% for both components. A subsequent increase in the polishing duration results in a slower decrease in the roughness and an increase in the reflection coefficient by over 40%.

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