



APPLICATION OF PULSE WELDING POWER SOURCES IN ELECTROCHEMICAL PROCESSES

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It was determined that area of application of pulse welding power sources for processes of metal flame treatment can be expanded. At that continuously rising in price natural gas is substituted by hydrogen-oxygen mixtures or hydrogen. Application of nickel instead of low-carbon steel as electrodes at water electrolysis allowed reducing process voltage to 2.1 V. Dependence of increase of percent content of finer powder fractions (1–50 μm and 1 μm , and less) at increase of frequency of current of anode dissolution was determined. Received results indicate perspectives of investigations in this direction for increase of efficiency of electrochemical processes of hydrogen production as well as micro- and nanopowders for manufacture of welding and brazing powder consumables. 12 Ref., 3 Figures.

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Pulse power sources for gas-shielded metal arc welding are widely used in such branches of industry as shipbuilding, chemical-machine building, rocket production, car industry, pipeline construction and many others [1, 2]. Frequency of transfer of electrode metal droplets is an important parameter among the different parameters for regulation of process of pulse-arc welding and it usually lies in 30–300 (500) Hz range. Smooth regulation of frequency of welding current pulses allows electrode metal transfer by principle «1 pulse-1 droplet». The E.O. Paton Electric Welding Institute works on development of equipment and technology of pulse-arc processes for a long time. Different types of welding equipment were developed including power sources for pulse-arc welding. They showed themselves good in welding of critical designation structures [3, 4]. The main peculiarities of such sources are possibility of smooth regulation of frequency of current pulses from 30 to 300 Hz, duration of pulses 0.5–5.0 ms and amplitude to 850 A.

Power sources are used in related technologies, for example, in production of hydrogen-oxygen mixtures for processes of welding, brazing, welding-brazing and operations of flame treatment of metals. Gas generators in indicated processes consist of direct current welding source and electrolytic cell. Possibility of dramatic reduction of consumption of continuously rising in price natural gas and decrease of environment pollution are the advantages of application of

hydrogen and hydrogen-oxygen mixtures in flame treatment processes.

Besides, one of the variants of significant reduction of costs for welding and brazing consumables are the possibility of in-situ production, for example, of braze pastes of necessary composition with guaranteed quality, by methods of electrochemical dispersion of ferrous, nonferrous and noble metals. Therefore, it is relevant to carry out experimental investigations on increase of efficiency of electrochemical processes due to regulation (increase) of current frequency.

The most repeatable in final result processes were selected for performance of experimental investigations of effect of current frequency on some electrochemical processes. First of all, these are the processes essential for power engineering of future, for example, production of hydrogen by water electrolysis. Secondly, the processes of micropowder production, including nanopowders, can be referred to them. The latter proved their perspectives in area of metallurgy as well as many other areas of technology and medicine.

Regardless apparent versatile of considered processes, they are combined by similar conditions for realizing electrochemical reactions taking place in aquatic environment on the surface of electrodes being connected to DC sources.

Among the significant differences of these processes are the parameters of their performance, for example, composition of aquatic environments, electrode materials, parameters of power sources (voltage, current and frequency), and final products, obtained as a result of these processes.

Currently, around 95 % of hydrogen in all countries of the world are produced with the help of catalytic conversion of water steam or methane reforming. However, hydrogen produced by



these methods, is not suitable for supplying fuel cells transforming chemical energy in electric one, for example, in vehicle motor drive. Fuel cells require hydrogen of high purity, for example, produced from water via electrolysis.

Electrolytic hydrogen is more expensive than catalytic one due to high expenses for providing explosive and electric safety at its production as well as significant specific expenses for electric energy.

Development of new type of electrolyzers allowed eliminating one of the main obstacles to wide application of hydrogen. They provide high level of explosive and electric safety in production of hydrogen as well as hydrogen-oxygen mixture [5, 6]. A problem of reduction of power consumption necessary for production of electrolytic hydrogen is still unsolved.

The most widespread methods of production of micro- and nanopowders of metals or their oxides are spark and electro-explosive dispersion [7], spraying of liquid metal by water and gas jet or condensing of metal vapors in its heating using electron beam, high-frequency plasma [8], or laser.

These processes are characterized by high power consumption related with necessity of metal heating well above than its melting temperature. In this connection application of micro- and nanopowders, produced by these methods, can be economically sound only in special cases, for example, in research projects and in medicine, where necessity in micro- and nanopowders is measured in grams, but not in widely used technological processes, for example, welding and brazing, requiring hundred of kilograms. Moreover, application of mentioned above processes for production of micro- and nanopowders is justified only under condition of efficient solution of the problem of their production in monodispersed form, that allowed eliminating laborious operation on dispersion of produced product by fractions.

Aim of the present work is an investigation of effect of frequency of electrolysis current on

efficiency of electrochemical processes mentioned above.

Existing equipment used for realizing electrolytic method of hydrogen production has a coefficient of transformation of electric current energy into chemical one at 70 % level. Currently, there is a possibility of improvement of this index to 80 % and more not only due to increase of pressure and application of low-wear anodes with coatings from metals of platinum group, but as a result of application of modern power sources for electrolysis processes. This allows reducing prime cost of electrolytic hydrogen.

Experimental verification of idea of electrolysis using increased frequencies was carried out with the help of power sources for pulse-arc welding developed at the PWI.

A research bench in addition to measurement and controlling equipment included pulse power supply providing electrolysis current up to 300 A and electrolyzer consisting of 10–12 series electrolytic cells.

Experiments on determination of effect of frequency of current pulses on process of water electrolysis carried at the PWI more than 10 years ago showed the possibility of efficiency increase due to reduction of electrolysis voltage from 2.4 to 2.16 V [9]. These results were received on electrolytic cell using low-carbon steel electrodes. Water electrolysis at increased frequency using more expensive metals, for example, nickel as the electrodes, allowed reducing electrolysis voltage to 2.1 V (Figure 1).

Based on diagram given, insignificant, from first point of view, reduction of electrolysis voltage can promote notable economy of electric energy in processes of receiving of electrolytic hydrogen, due to volumes of its production measured as million of tons per year.

In the case of application of direct current with pulsation, typical for power sources with simple rectification circuits (Larionov connection and bridge connection), process of anode dissolution of the most projecting electrode areas, i.e. some kind of polishing of electrode working surface, is observed, in addition to products of electrolysis appearing on the surface of electrodes. At that, its passivation takes place due to formation on it of oxide films, dissolved gases and chemical compounds increasing electric resistance of electrode surface. Compensation of gradual increase of electrolytic cell voltage requires periodic switching-off of electrolyzers and depolarizing of the electrodes by means of change of voltage polarity on cell.

Analysis of the processes taking place in our case on the surface of electrode at water electrolysis allowed noting inevitable appearance of electric current streamers (lines of the most probable break-

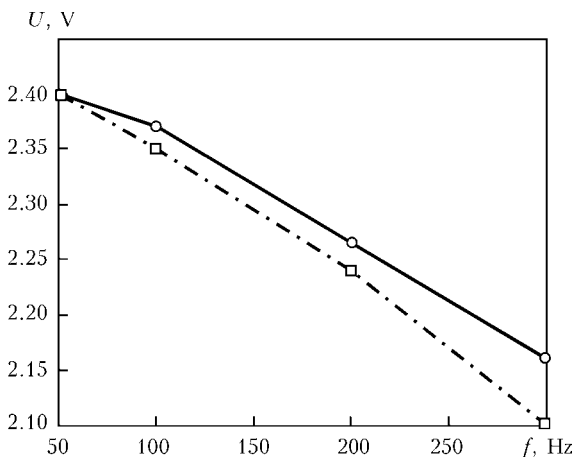


Figure 1. Electrolytic cell voltage versus frequency of current pulses for low-carbon steel (solid) and nickel (dashed line)

down of dielectric environment, to which water and aqueous solutions of salt are referred) in the zone of double electric layer (DEL) in addition to oxidation-reduction reactions taking place close to the surface of electrode.

Highly possible that experimentally determined advantages of application of HF currents in processes of electrolysis and anode dissolution of metals can be explained based on proposed model of electrolysis process (Figure 2).

Arrows in Figure indicate the lines of desirable movement of electric current directed to projections of electrode rough surface. Similar processes to be place on projections of cathode surface, where dissolution of hydrogen in metal and increase of thickness of layer of adsorbed hydrogen occur. The level of electric field of applied voltage is not always enough for breakdown of the latter. In this case DEL thickness is risen, where the main drop of voltage on electrolytic cell takes place. Further screening of deepened places of electrode surface by layer of adsorbed gases provokes the necessity of additional increase of electric field voltage.

Rapid increase of temperature in microzones of electrode, in which current density rises, is accompanied by local heating of the surface, that results in appearance of impact mechanical waves in electrolyte and intensive detachment of hydrogen molecules from cathode and revealing of its working surface as well as films of metal oxides forming on anode surface.

Pauses between the pulses of current in the case of electrolysis using pulses of current of increased frequency results in the fact that average value of voltage on electrolytic cell is lower in application of increased frequency (50–100 Hz) regardless the increased voltage of each separate pulse.

Investigations of processes of oxygen emission on anode surface always had more attention than processes of hydrogen emission due to preferred anode electrochemical dissolution. At that, known fact of more intensive heat emission on cathode than on anode was not taken into account, that indicates the necessity of more detailed consideration of processes taking place particularly on cathode.

Reference data [10, 11] show that value of hydrogen overpotential at electrolysis of water solutions mainly depends on cathode material and electrolysis current density. Increase of current density results in cathode covering by layer of adsorbed hydrogen for several tens of seconds in process of electrolysis. Its is accompanied by increase of electrolysis voltage due to rise of transition resistance on metal–electrolyte boundary. Parallel processes of increase of oxide film thickness take place on anode.

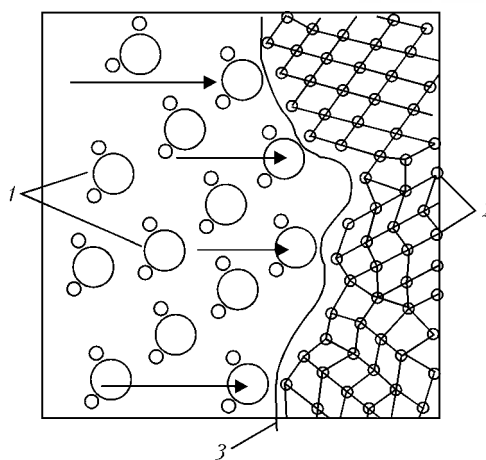


Figure 2. Scheme of processes taking place on surface of electrode in water electrolysis: 1 – water molecules; 2 – atoms of metal electrode; 3 – DEL boundary

Experiments showed that using pulse current with inverted pulses at zero-crossing provokes cathode potential jump. Probably, this is the fact resulting in formation of new adsorption centers and redistribution of adsorbed gas bubbles. At that the largest hydrogen bubbles, which are removed from electrolyte volume, are detached from the cathode surface. Emission of hydrogen at the next electrolysis current pulse will be the most intensive in the new zones on cathode surface, generated in process of depolarization, moreover at lower value of power source voltage.

Primary importance in this case is not in reduction of voltage, promoted by pulsation, typical for simple rectifiers with supply from alternating current main, but complete stop of electrolysis current achieved at voltage drop to zero. Obviously that presence of insignificant peak of negative voltage will also promote removal of gaseous sublayer on cathode surface that provides for reduction of overpotential level.

Technological experiments on brazing of samples from copper and brass [12] showed the perspectives of application of braze pastes based on micropowders for production of joints from metals of 40–1000 μm thickness range.

Results of further experiments indicate that braze pastes based on micropowders, in comparison with pastes based on powders with particles of 40 μm size and more produced by conventional methods, have series of advantages, namely, possibility of reduction of heating temperature in brazing for 50–70 degrees and decrease of brazing time, that is relevant for joining of materials critical by heating temperature; shortening of consumption of braze alloy and flux not less than by 20 %; expansion of range of thickness of materials being joined to 40 μm and less.

Advantages of application of increased frequency current were also found in processes of electrolytic dissolution of anode metal in aqueous

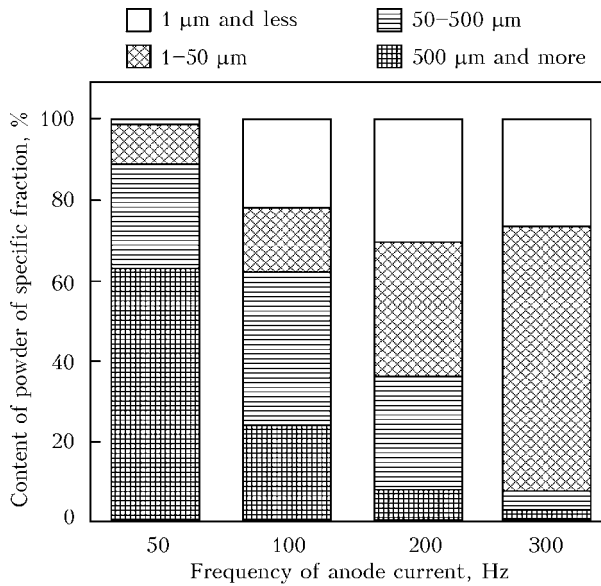


Figure 3. Effect of current frequency in dissolution of nickel anode on micropowder size

environment and alcohol solution. First of all, they include possibility of increase of level of powder monodispersity, secondly, it is the possibility of reduction of energy consumption of dispersion processes, in comparison with methods characterized by heating of metal above its melting point.

Copper M1, nickel NP2 and silver of 99.9 purity (precious metal) were used in dispersion. Moreover, each of dispersion variants were carried out in 50–300 Hz frequency range as well as 10 kHz frequency (at silver dispersion).

It was determined in course of experiments that electrolytic (anode) dissolution of metals result in formation of microparticles of different size, which are conditionally divided on following groups: *a* – 500 μm and larger; *b* – 500–50 μm; *c* – 1–50 μm; *d* – 1 μm and less.

Mass of powders of grain size up to 50 μm was determined using the method of sampling of powder with corresponding grain size on sieving machine having set of control grading screens. Procedure based on calculation of number of grains at visual measurement of their sizes by hair lines of microscope graticules at 1800 magnification (in immersion liquid), respectively, was used for finer fraction powders. This procedure is used at determination of grain size of diamond powders.

Results of carried experiments were used for plotting the histogram of different fractions of micropowders depending on current frequency at anode dissolution of metal (Figure 3).

Dependence of increase of percent content of powder finer fractions at increase of current frequency of anode dissolution can be seen from histogram given.

Carried experiments on silver anode dissolution showed possibility of production of micro-

powder suspension of its oxides of less 1 μm dispersion. However, one of significant disadvantages of process of silver dispersion in aqueous environment is susceptibility of received micropowder to coagulation with further growth of separate crystallites of up to 2 μm length and around 2–5 μm width.

To eliminate indicated disadvantage a storage time of micropowders should not exceed one-two tens of hours from the moment of receiving to production of braze paste and its application in brazing process.

Conclusions

1. Using current increased frequency promotes rise of efficiency in process of electrolytic production of hydrogen-oxygen mixtures and hydrogen as well as increase of output of finer fraction metal powders for production of braze pastes.

2. Production of micropowders directly before brazing allows using them in active condition in form of monocomponent as well as mixtures of different metals.

3. Set of equipment consisting of power source of welding current of increased frequency and generator of hydrogen-oxygen mixture allows expanding its application range in flame treatment of metals as well as for processes of electrolytic dispersion of metals.

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