

ОБЩИЕ ВОПРОСЫ АВТОМОБИЛЬНОГО ТРАНСПОРТА

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THE ETCHING OF THE COPPER ALLOYS USED IN AUTOMOTIVE INDUSTRY

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Abstract. The pattern of the electrochemical ionization and passivation of Cu 62 Zn brass in chloride solutions with different compositions is studied. It is shown that the electrochemical dissolution of Cu 62 alloy in concentrated chloride solutions is controlled by ionization of the copper component in the alloy. There was studied the selectiveness of Cu 62 Zn brass component dissolution and modification of the alloy surface at electrochemical dissolution in chloride solutions.

Key words: brass, ionization, dissolution medium, dissolution selectiveness.

ТРАВЛЕНИЕ МЕДНЫХ СПЛАВОВ, ИСПОЛЬЗУЕМЫХ
В АВТОМОБИЛЬНОЙ ПРОМЫШЛЕННОСТИ

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Аннотация. Изучен механизм электрохимической ионизации и пассивации латуни Л-62 в хлоридных растворах различного состава. Показано, что электрохимическое растворение сплава Л-62 в концентрированных хлоридных растворах контролируется ионизацией медной компоненты сплава. Установлено, что равномерное электрохимическое растворение α -латуни протекает в кислой среде в присутствии ионов хлора и окислителя – Fe^{3+} .

Ключевые слова: латунь, ионизация, травильный раствор, селективность растворения.

ТРАВЛЕННЯ МІДНИХ СПЛАВІВ, ЩО ВИКОРИСТОВУЮТЬСЯ
В АВТОМОБІЛЬНІЙ ПРОМИСЛОВОСТІ

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Анотація. Вивчено механізм електрохімічної іонізації і пасивації латуні Л-62 у хлоридних розчинах різного складу. Показано, що електрохімічне розчинення сплаву Л-62 в концентрованих хлоридних розчинах контролюється іонізацією мідної компоненти сплаву. Встановлено, що рівномірне електрохімічне розчинення α -латуні протікає в кислому середовищі за наявності іонів хлору й окисника – Fe^{3+} .

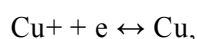
Ключові слова: латунь, іонізація, травильний розчин, селективність розчинення.

Introduction

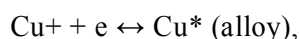
The progressive application of microelectronic components in electronic engineering expands the spectrum of printed circuits used. Among them are the standard printing boards for output components, plates for surface mounted assemblies, modem boards for personal computers, multichip modules, high frequency boards, plates with an optical interface, etc. [1–5]. The amount of electrical equipment has considerably increased in modern vehicles. When manufacturing the equipment in question, etching of printed circuit boards made of copper and its alloys is required.

In the technologies for their manufacture, anodic processes with application of a metal, namely, copper and its alloys, are of importance. It is necessary to study the mechanisms of the processes of chemical and electrochemical dissolution of copper and its alloys in order to control the kinetics, the selectivity of the etching processes, and increasing their efficiency.

The mechanism of anodic dissolution of α brass in chloride media was described in [4–6]. The authors described the initial dissolution selectivity of zinc, which created a surface layer enriched with copper with nonequilibrium vacancies. The anodic dissolution both of pure copper and that on the surface of brass was found to occur with the formation of strong 1–n from their dissociation, enter into a balanced reaction with copper



and determine its potential. In the case of brass, the potential determining reaction is different



where $\text{Cu}^* (\text{alloy})$ are hyperactive copper atoms in the brass surface layer, which were formed as a result of the dissolution selectivity of zinc. Owing to the increased activity of $\text{Cu}^* (\text{alloy})$, the stationary potential of brass is more negative than the stationary potential of copper in its own phase at the same ion concentration of the latter. In this case, Cu^* ions that were formed during the anode oxidation of brass are reduced to their own phase. During the reduction, the concentration of Cu^* ions decreases in the near electrode layer of the solution; there-

fore, the stationary potential of the brass must shift towards the negative side, which allows us to infer the presence of dezincing of brasses [7]. It is shown [8] that, at alternating current polarization of α brass in a chloride media, the first anodic half period of dissolution of the alloy is controlled by

+
the diffusion of CuCl_2 complexes from the electrode to the solution. Thus, the controlling stage of the anodic dissolution of α brass is the dissolution of the precious component.

Theoretical analysis

Each of the components of the alloys during the dissolution displays its electrochemical properties. The experimental studies of electrochemical ionization of brasses [9] created a foundation for the modern image of the anodic dissolution of intermetallic phases. A.V. Vედenskii showed [10, 11] that the state of the nonequilibrium layer that is formed during the dissolution selectivity of a homogeneous system determines the peculiarities of the ionization, the electrochemical properties of the alloy, and the change of the electrocatalytic activity of the alloys.

At present, despite the great variety of literary data, there has not yet been developed a unified theory on the chemical and electrochemical dissolution of metals. The study of the processes of electrochemical dissolution of copper and its alloys is very important for the creation of a unified theory to connect the processes that occur in the liquid phase and on the surface of the «metal–solution» for the development of the theory on passivation and for solving a number of application problems of size etching of metals and alloys.

Purpose and tasks. The aim of this work is to study the regularities of the electrochemical dissolution of Cu62Zn brass in chloride solutions and the topography of the surface of the alloy.

Experimental

The electrochemical polarization measurements were carried out using a PI 50 1.1 potentiostat with a PR 8 programmer. The cyclic voltammograms (CVA) were obtained during the dissolution of Cu 62 Zn alloy in solutions of NaCl, HCl, and FeCl₃ with various

concentrations in the potential range of $E = -0,2-2,0$ V with a potential sweep of $V = 2 \times 10^{-2}$ V/s. The reference electrode used was a silver chloride electrode, and a platinum plate served as the auxiliary electrode. The auxiliary *Pt* electrode was kept for ten minutes in concentrated nitric acid prior to the measurements, after which it was rinsed thoroughly. A standard initial treatment of the surface of the disk electrode was selected that included mechanical peeling and polishing, degreasing, and chemical polishing in an H_3PO_4 solution. All the E values in this work are presented with respect to the hydrogen electrode. The accuracy of the maintenance of the potential is $\pm 3 \times 10^{-3}$ V. The error of setting the polarizing current is ± 2 %. The error of a B7 21 voltmeter at the boundary of the measuring is $1 \text{ V} \pm 0,7$ %.

The measurements were performed at $25 \pm 0,1$ °C. Thermostating was carried out using a YT 15 Y 42 thermostat. The working cell was equipped with a casing through which distilled water from the thermostat was constantly pumped. The tests were conducted with the lid closed, which was equipped with holders for the electrodes.

The Luggin–Haber capillary was brought to the very surface of the working electrode. The area of the brass surface of the electrode was $6,4 \times 10^{-5}$ m². The concentrations of Cu(II) and Zn(II) ions in the etching solutions were determined by an atomic absorption method using a «Saturn» spectrophotometer with wavelengths of 213,9 nm for Zn and 324,8 nm for Cu. The morphologic peculiarities of the surface of the electrode were studied by the method of electron probe microanalysis (EPMA) on a JSM 6390 LV electron microscope with an INCA system of X ray microanalysis. An NT 206 scanning probe microscope equipped with a CSC 37 probe cantilever was used to examine the roughness of the electrodes and the difference in the nanosize peculiarities of the morphology of the electrode samples. The mineralogical composition of the sediments with low solubility compounds, which are formed in the waste etching solutions, was determined using X ray analysis on a Siemens D500 powder diffractometer in copper radiation with a graphite monochromator [12]. The initial search of the phases was performed using a PDF 1 card file [13] followed by the calculation of the X ray diffraction patterns veri-

fied using the Ritveld method according to the FullProf program [14].

The effect of the composition of the electrolyte on the electrochemical dissolution of the Cu 62 Zn alloy

The effect of chloride ions on the electrochemical dissolution of the Cu 62 Zn alloy was studied. Figure 1 shows the anodic polarization curves for the Cu 62 Zn alloy in NaCl solutions of various concentrations. With the shift of the potential towards the anodic area, the current density increases, and the slope of $dj/dE > 0$ (Fig. 1, curves 1–5). The active dissolution of brass in NaCl solutions of 0,5–2,0 mol/L (Fig. 1, curves 3–5) is observed in the range of potentials of 0–0,8 V.

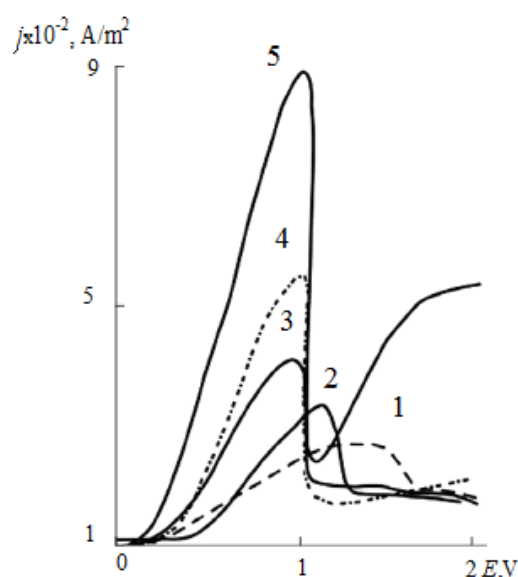


Fig. 1. Anodic polarization curves for the Cu 62 Zn alloy in NaCl solutions with the following concentrations, mol/L: (1) 0,1, (2) 0,25, (3) 0,5, (4) 1,0, and (5) 2,0 at $V = 2 \times 10^{-2}$ V/s and $\omega = 0$ rot/s

For the diluted solutions (Fig. 1, curves 1, 2), the Tafel fractions of the curves have a longer range of potentials. The medium of the NaCl solutions is neutral; therefore, there is an increase in the angle of the j slope; the E curves result only from the activating effect of the chlorine ions. A similar effect of anions on the electrochemical dissolution of metals is described in [15], namely, the increasing concentrations of Cl^- , Br^- , and I^- ions in the solution is accompanied by an increase in the rate of the process of dissolution of the metal phase. The observed maximum of the current density j is indicative of the onset of the pas-

sivation of the surface of the alloy. The maximum of j increases with an increase in C_{Cl^-} . Thus, the activating effect of chlorine ions manifests itself.

In the inactive region, the rate of dissolution of the alloy is almost independent of the potential (Fig. 1, curves 1–4), which is connected with an increase in the amount of the inactive compounds on its surface. The potential of the passivation E_p is in the range of 0.8–0.9 V (Fig. 1, curves 3–5), at which the transition of the metal from an active to a passive state starts. For curves 1 and 2, the passivation starts at higher values of the anodic potential. The occurrence of passivation at lower E_p with a growth in the concentration of the chlorine ions can be explained by the easier deposition of CuCl from the near electrode layer due to the parallel process of the chemical dissolution of copper. However, the range of passivation in the area of high C_{Cl^-} is short (Fig. 1, curve 5), and the inactive state of the metal or the alloy is disturbed either partially or entirely owing to the introduction of Cl^- , Br^- , and I^- anions into the solution [15]. A new increase in j with the growth of the potential is observed in a 2.0 M solution of sodium chloride. The process of the disturbance of the passivity near the potential of complete passivation E_{cp} is considered by the authors [16] as resulting from the appearance in unsound sites of an inactive layer with zones of rapid dissolution, which then turn into pittings. A crucial factor for the appearance of the pittings is the rivalry between the passive action of the water and the activating action of the chlorine anions.

The shape of the j and E curves is affected by a number of factors, one of which is the pH of the medium [16]. In the region of low pH, where the concentration of OH^- ions is low and the share of the surface occupied is insignificant, Cl^- anions can be adsorbed on a vacant surface. Under these conditions, the rate of dissolution increases with an increase in the overall concentration of anions [17]. In order to reveal the effect of the acidity of the solution on the electrochemical dissolution of the alloy, we obtained the anodic polarization curves for Cu 62 Zn in HCl solutions with various concentrations. For curves 1–5 (Fig. 2), a large angle of slope is observed for the fraction of the active dissolution of the alloy and an increase in the j maxima compared to the NaCl solutions, which can be associated not only with

the effect of the chlorine ions on the electrochemical dissolution of the alloy but also with the effect of the H^+ ions. In an acidic medium, the chemical dissolution of the Zn component of the alloy occurs more easily.

Two j extreme points were registered on curves 1–3 (Fig. 2). In [18], the appearance of two peaks on the Cu polarization curves was shown to be connected with the change in the structure of the passive layer of CuCl from spongy to dense packed as the anode potential grows.

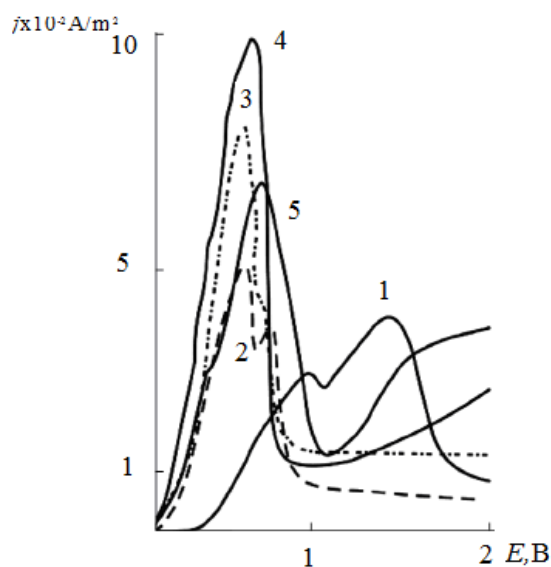


Fig. 2. Anodic polarization curves for the Cu 62 Zn alloy in HCl solutions with the following concentrations, mol/L: (1) 0,1, (2) 0,25, (3) 0,5, (4) 1,0, and (5) 2,0 at $V = 2 \times 10^{-2}$ V/s and $\omega = 0$ rot/s

At high concentrations of chlorine ions, the second peak of the anodic dissolution of copper disappeared owing to the formation of the spongy surface phase of CuCl. As the concentration of the HCl solutions grew, a second maximum of the current during the brass dissolution is produced to a lesser degree, and, at curve 3, it is in the shape of a bend of the curve. The reason for this is that both the passivation of the Cu 62 Zn alloy and the disturbance of the passivity by Cl^- ions can occur in the region of potentials of $E \geq E_p$. Note that, with an increase in the concentration of HCl in the solution, the second process predominates.

The passivation of brass can take place not only due to the anodic polarization but also during the introduction of an oxidizing component

into the solution. In [15], the intensity of the pitting corrosion of metals is found to increase in the presence of dissolved oxygen and Fe^{3+} ions. The introduction of iron(III) ions into the chloride solution caused a shift of the potential of the metal up to a critical value and to the formation of pittings [15]. The activity of the oxidizing agent is determined by the nature of the metal, the pH value, the nature and concentration of the corrosion active anion, and the temperature and rate of mixing of the solution.

To study the influence of ions of the oxidizing agent on the shape of j of the E curve, we obtained the anodic polarization curves using the Cu 62 Zn alloy in solutions of ferric (III) chloride with various concentrations (Fig. 3). For a 0,1 M $FeCl_3$ solution, the anodic polarization curve is characterized by a region of active dissolution of the alloy (Fig. 3, curve 1) and the preservation of the passivation of the brass electrode.

The extremum of j is observed at $E_p = +1,1$ V. As E increases, the passive region passes to the region of repassivation. With an increase in the $FeCl_3$ concentration, the slope of the activation branch grows (Fig. 3, curves 2, 3). On j of the E curves, a second j maximum is also observed, which disappears with an increase in the concentrations of the solutions (Fig. 3, curve 4).

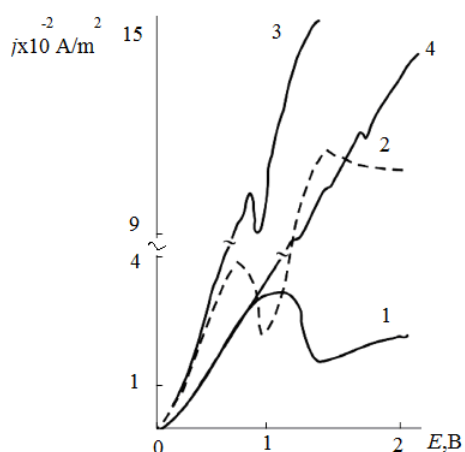


Fig. 3. Anodic polarization curves for Cu 62 Zn alloy in $FeCl_3$ solutions with the following concentrations, mol/L: (1) 0,1, (2) 0,25, (3) 0,5, and (4) 2,0 at $V = 2 \times 10^{-2}$ V/s and $\omega = 0$ rot/s

The anodic j of the E curves for the Cu 62 Zn alloy in the solutions of ferric(III) chloride are

similar to those for copper. It was shown in [18] that the formation of a $CuCl$ compound with low solubility on the surface of copper corresponds to the region of the minimum of the current, while, in the region of high anodic polarizations, CuO is found to form.

With a further increase of the potential, a new rise in the current is observed, which corresponds to the dissolution of the manufactured layer and the formation of Cu^{2+} and $CuCl^+$ ions and a $CuCl_2$ compound. The copper dissolution continues up to the beginning of a new passivation by copper (II) compounds.

Conclusions

Thus, the dependence of the pattern of the electrochemical dissolution of the Cu 62 Zn alloy on the composition of the electrolyte, the anion concentration, the acidity, and the presence of an oxidizing agent was justified. Chlorine ions in the region of high concentrations were shown to activate the process of the electrochemical dissolution of the Cu 62 Zn alloy and disturb the passivation of its surface.

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