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Features of the corrosion processes development at the magnesium alloys surface

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ABSTRACT

A greater corrosion stability of the MA8 (Mg – Mn – Ce) alloy as compared to that of VMD10 (Mg – Zn – Zr – Y) magnesium alloy in the chloride-containing solution has been demonstrated using the scanning vibrating probe method (SVP) as well as the methods of optical microscopy, gravimetry, and volumetry. It has been established that the crucial factor of the corrosion activity of the samples under study consists in the occurrence of microgalvanic couples at the sample surface. The corrosion rate of the samples with coatings formed by the plasma electrolytic oxidation (PEO) method and composite polymer-containing coatings at the surface of various magnesium alloys has been measured. The best anticorrosion properties have been manifested by composite polymer-containing coatings. The corrosion rate (P_H) values for both types of the magnesium alloys (MA8 and VMD10) were about 0 mm per year upon exposure of the samples to the 3% NaCl solution for 7 days.

1. Introduction

The detailed investigation of the electrochemical behavior of magnesium alloys in various corrosion-active solutions in view of the development of novel approaches to anticorrosion protection constitutes an important theoretical and practical problem focusing the attention of many research groups all over the world [1–24]. In the present paper, the results of studies of the corrosion activity of magnesium alloys with and without protection coatings in the chloride-containing media by several independent methods is reported.

The use of the conventional methods of study of the corrosion properties of the materials, such as gravimetry, volumetry, potentiodynamic polarization, and electrochemical impedance spectroscopy, is concerned with the proportional occurrence of the corrosion process over the whole surface of the examined sample. However, for the majority of corrosion processes this approach is not appropriate because of the difference in the phase and chemical compositions and the morphological structure of the corroded material. The formation of anodic and cathodic regions on the surface of the some materials in contact with a corrosion-active media is the main reason of the occurrence of local corrosion processes. The scanning vibrating probe method — SVP (another used abbreviation is SVET, Scanning Vibrating Electrode Technique) allows studying the changes in the microelectrochemical activity of the sample under study on the microscale level. The changes in the potential distribution depend on the local current in the electrolyte over the samples surface. These changes revealed by the SVP method provide detailed information on the intensity of the individual corrosion processes. For example, in [25] SVP was used for the investigation of pitting corrosion in FV448 gas turbine disc steel, in [26] SVP was applied to evaluate the corrosion protection performance of polymeric resins. The author of [27] proposed the idea of using fine tipped scanning probes to detect changes in micro-galvanic activity near the sample surface. In addition, other possible fields of this technique application comprise pitting initiation and development, detecting of electrochemically active pin-hole defects in coatings, ascertaining the effect of microstructure and finish on the electrochemical activity, evaluation of the passivation–repassivation characteristics, corrosion inhibitors performance, micro-corrosion and electrochemical effects, and materials behavior in aggressive environments [28]. Many scientific groups used this method for electrochemical and corrosion tests [14,15,29–34].

High corrosion activity of the magnesium alloys is generally known [35]. Moreover, there are publications devoted to studies of the mechanisms and the kinetics of the Mg corrosion [36]. However, just a few works were devoted to the application of local electrochemical methods for the above purposes. The objective of the SVP method application in the present work was to fill the above gap. Conventional techniques like gravimetry and volumetry analysis cannot provide an explanation of staging and mechanisms of the corrosion process. In addition, the scanning vibrating probe method enables one to study the electrochemical processes on the microscale level. The difference in the corrosion mechanisms for two types of Mg has been established in the present paper. The stages of the corrosion process of the MA8 and VMD10 magnesium alloys have been also revealed and described.

Application of the SVP method enables one to characterize in detail the corrosion destruction of the magnesium alloys in the corrosive media due to high corrosion activity of the magnesium alloys,

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the formation of the anodic and cathodic regions at the sample surface, and the morphological heterogeneity of the surface layers.

Unlike conventional methods (gravimetry, volumetry), the SVP corrosion tests enabled us to reveal the effect of the alloys composition and structure (presence of phases and inclusions with different potential values) on its corrosion behavior. The latter comprises one of the main problems related to the development of novel approaches and techniques of the corrosion protection. Conventional methods are not capable to provide the required information on the local character of the materials corrosion. They do not reveal the anodic or cathodic areas of the sample and the sample areas characterized by high values of the current density. The gravimetry and volumetry methods provide the average values of the corrosion rate, but only as a sum of the corrosion process occurring over the whole area of the surface under study. Application of the SVP method along with conventional approaches enabled us to obtain the full picture of the corrosion behavior on the microscale level (stages, kinetics, mechanisms, effect of the composition, and, finally, the corrosion rate). Just the determination of the combination of the above factors can result in the formation of the coating having the optimal properties (anticorrosion, antifriction, etc.).

The plasma electrolytic oxidation (PEO) method is used for fabrication of coatings that improve the surface properties of various metals and alloys [1,2,28,37–41]. The porous coatings are produced by high voltage AC, DC or bipolar polarization of the substrate in appropriate electrolyte solutions. The plasma discharges occur at the electrode surface during the PEO process and lead to the formation of coatings similar to ceramic ones. The frictional, corrosive, electrical, and thermal properties of these coatings have generated interest in view of their possible use in mechanical, aerospace, aircraft, and automobile industry, engineering equipment components, and biomedical devices. This method can be used for the Mg alloys corrosion protection [2]. An additional treatment of PEO-coatings by superdispersed polytetrafluoroethylene (SPTFE, Forum® trademark) followed by a special heat treatment enables one to create composite polymer-containing coatings having the highest anticorrosion and antifriction properties [28,42].

The main feature of the present work consists in the investigation of the kinetics and mechanisms of the corrosion process on the surface of magnesium alloys by the SVP method in comparison with conventional approaches (optical microscopy, gravimetry and volumetry analysis). In addition, the establishment of the chemical composition effect on the corrosion behavior of the Mg alloys of two types is another important problem to be solved by the SVP method, which is described in the present paper as well.

2. Theoretical basis of the SVP method

It has been observed experimentally that a flow of metal ions into a solution exists above a localized corrosion region invoking a respective distribution of the electronic current density within the metal (Fig. 1). The main principle of the SVP technique [43] consists in evaluation of the character of the potential distribution in the electrode/electrolyte system illustrated by equipotential lines. The potential gradient between the working and counter electrodes is directly proportional to the current density in the system under study. The scanning probe with a thin Pt tip coated by platinum black is used for determination of the potential gradient. The probe scans the surface of the sample in the electrolyte solution. The scanning probe is placed on a special vibrated platform, and the distance between the probe tip and the sample surface is about 100 μm. The use of a vibrating probe in conjunction with a lock-in amplifier makes it possible to eliminate the noise occurring at any frequency. The latter increases the electrical sensitivities and the system stability. The scanning probe vibrates with amplitudes from 1 up to 60 μm in the direction perpendicular to the sample surface (Fig. 1) [43].

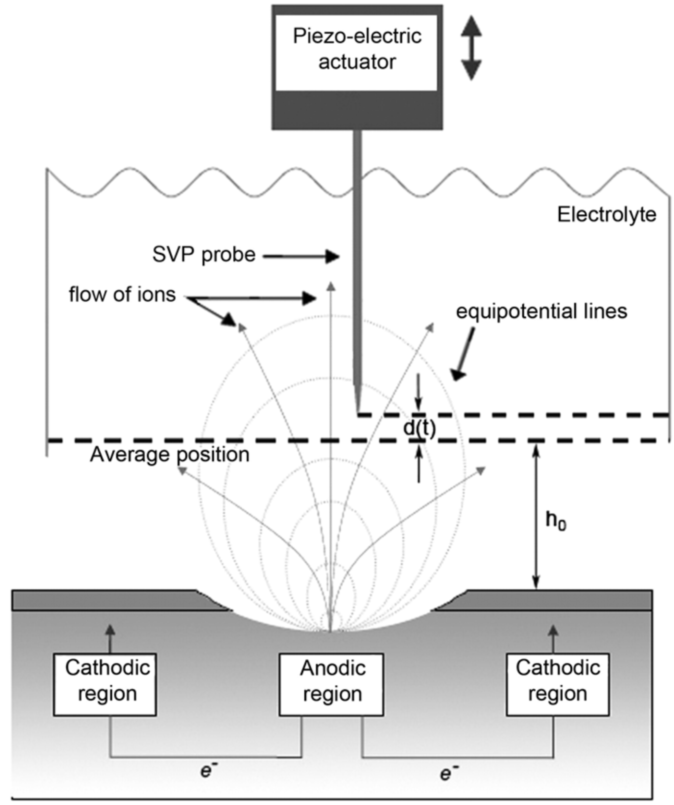

Fig. 1. Electrical field distribution in conjunction with regions of different electrochemical activity of the material in the electrolyte at Scanning Vibrating Probe (SVP) measuring.

The explanation of the working principles of this technique is based on the analysis reported in [43,44]. According to these studies, the microprobe vibrates at an angular frequency of Ω. The distance between the probe and the sample (working electrode) varies over time as follows:

$$h(t) = h_0 + d\sin(\Omega t), \tag{1}$$

where d — the amplitude of the probe vibration, and h_0 — the average distance between the probe and the sample (see. Fig. 1).

Under the galvanostatic control and in the AC mode, the local current density, j, just above the electrode surface, can be expressed as:

$$j_{loc}(t) = j_{loc}(t)_{,0} + \Delta j_{loc}\sin(\omega t), \tag{2}$$

where $j_{loc}(t)_{,0}$ — the local current density at the initial time (under $t = 0$), and Δ — the small AC perturbing component with an angular frequency, ω. The local potential of the interface $E_{loc}(t)$, is given by the equation:

$$E_{loc}(t) = E_{loc,0} + |\Delta E_{loc}(\omega)|\sin(\omega t + \varphi), \tag{3}$$

where $|\Delta E_{loc}(\omega)|$ — the amplitude of the local potential response at an angular frequency ω; φ — the phase shift with respect to j_{loc}. Then the local complex impedance Z_{loc} can be defined as:

$$Z_{loc}(\omega) = |\Delta E_{loc}(\omega)|e^{j\varphi}/\Delta j_{loc}. \tag{4}$$