



Application of plasma spray deposited coatings for seawater activated batteries

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Received 28 July 1997; revised 15 November 1997

Abstract

Seawater activated batteries based on Mg and Ni/Al electrodes were constructed and investigated at different electrolyte temperatures. The Ni/Al coatings which were applied as the cathodes for seawater activated batteries were produced by plasma spray deposition. Voltage–time ($U = E - IR(t)$) dependence was measured for the galvanic pair Mg–Ni/Al, where I was constant current, E the electromotive force of the galvanic pair and $R(t)$ the variable resistance. It was found that $U(t)$ inclination depends on the anode corrosion rate, and the mass of the anode is the only parameter that restricts the life time of the seawater activated cell. The current density of this cell was found to be a linear function of the temperature of the seawater. Output power density dependence on the spacing between electrodes and number of cells was investigated for cells with different electrode area. A maximum output power density of 3×10^4 W/m³ was obtained for these cells. © 1998 Elsevier Science S.A. All rights reserved.

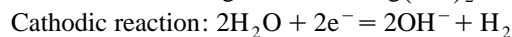
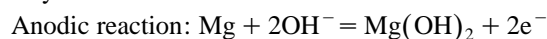
Keywords: Seawater batteries; Plasma spray; Ni/Al coatings

1. Introduction

Batteries which use seawater as the electrolyte are attractive power sources as they have moderate cost, excellent safety characteristics, infinite shelf life under dry conditions, and they are environmentally friendly [1]. Seawater activated batteries can power remote sea buoys and emergency signals, or underwater sensors and navigation aids.

This type of galvanic cell consists of an anode (negative terminal) and an inert cathode where hydrogen evolves [2]. Seawater batteries have an advantage over alkaline batteries because they do not need to be contained in water- and pressure-resistant vessels when they are used for subsea applications. Such cells need a continuous supply of seawater to remove the products of the cell reaction. The cathode functions as a hydrogen electrode. The magnesium anode dissolves in the seawater to form magnesium hydroxide that diffuses away. The electrochemical reactions

taking place in the cell can be described in the following way:



The corrosion rate of the magnesium alloy anode is usually proportional to the operating current density (current per unit area of electrode) [3]. Therefore, for a given power output the life is determined by the mass of the anode. The output voltage depends on the difference between the electrochemical potentials of the materials used to produce the anode and the cathode. This potential can be slightly influenced by the alloying of the anode material. The maximum current output that is available for the cell depends on the electronic structure and surface area of the cathode. A large area of a cathode is required to avoid polarization of the cell.

In this work, we present preliminary experimental results concerning Ni/Al coatings applied as a cathode for seawater activated batteries. These coatings were produced by a plasma spray technique which permits application of sufficiently thick, well bounded coatings of virtually any material that melts without decomposing (including most metals, ceramics and some polymers). The properties of the coating are highly dependent on the temperature of the

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powder on impact, as well as on its velocity. These parameters are also greatly influenced by the output level of the plasma gun [4].

The production of an active and nanoporous nickel surface by preparing of precursor alloys composed of nickel and a nonnoble metal with mole fraction of nickel lower than 0.5 (NiAl_3 , Ni_2Al_3 , NiSi , NiSi_2 , $\text{Ni}_5\text{Zn}_{21}$) and subsequent leaching has been well known for long time. Raney nickel is prepared in this way, which is widely used as an efficient cathodic electrocatalyst [5].

2. Experimental

The plasma gun used in our experiments was the SG-100 from Miller Thermal. This plasma gun operates at power levels of 100 kW maximum. An output power level (that defines the plasma temperature) of $P = 17.7$ kW was used. The powders were fed to the plasma torch by a Miller Thermal Model 1270 Computerized Powder Hopper. The powder manufactured at Miller Thermal. (Al(AI-1020) and Ni (AI-1023)), was applied for Ni–Al coatings. The diameter of particles was ~ 40 μm . Ni (98%) and Al (2%) powders were mechanically mixed. The coatings were deposited at low-vacuum (~ 1 Pa) to avoid incorporation of air into the flame and oxidation of the powder [6,7], which can sufficiently change the electrochemical properties of the coatings. Mixture of the plasma gases Ar + N_2 , and corresponding power output were used to achieve complete melting of the powder (in our experiment the flux of argon gas was 24×10^{-3} m^3/s , and nitrogen 2.5×10^{-3} m^3/s). More details of the deposition of the

Ni/Al coatings can be found elsewhere [6]. The morphology of the plasma spray coatings was investigated by Scanning Electron Microscope (SEM). The electrochemical properties of the coatings were examined using a galvanic couple magnesium-deposited coating. Electromotive force and short circuit current were measured using NaCl solution (3.0%) as electrolyte (synthetic seawater) in a 200-l vessel where the electrolyte was mechanically mixed to achieve a circulation which was kept constant through all the experiments. Cathode deterioration by calcium carbonate, that takes place in the real seawater, was avoided in the case of NaCl solution. The coatings were chemically treated (etched in the KOH) to enlarge their porosity—to produce extended surface.

The seawater activated test cell consisted of an anode made from a magnesium alloy produced at Marc Metals (Mg doped with Al < 9%, Zn < 6%, Zr < 1%). The thickness of the anode was 1 mm. The thickness of the cathode was 40 μm , (Fig. 1).

Typical electrochemical testing including the output power dependence on operating time, power density dependence on the space between electrodes, and number of cells, dependence of the current density on temperature of electrolyte were evaluated.

3. Results and discussion

Fig. 2 shows SEM photographs of the Ni/Al coatings produced. It is seen that the coatings consist of many droplets that have been torn off the solidified particles and have solidified on the surface (Fig. 2a). The developed

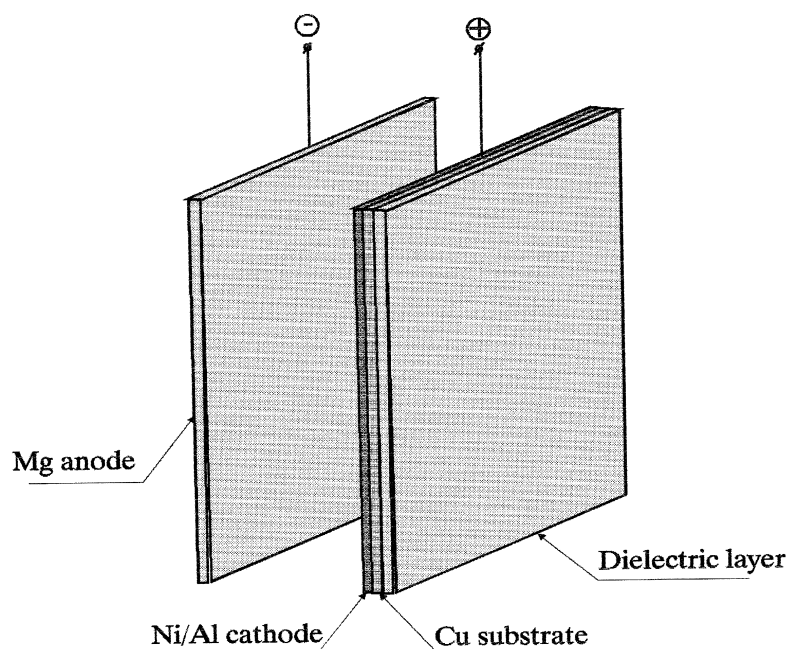


Fig. 1. Construction of the seawater activated battery.

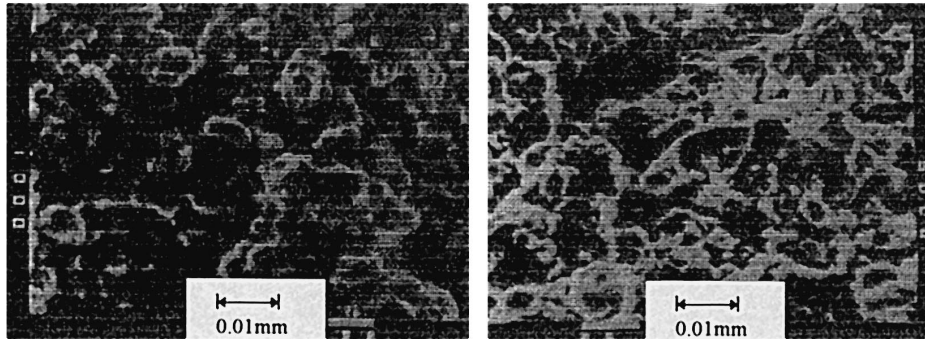


Fig. 2. The SEM photographs of plasma spray deposited coatings: (a) before chemical treatment in KOH solution; (b) after chemical treatment in KOH solution.

surface and large porosity can be seen. The porosity is mainly due to solidification shrinkage.

The electrochemical properties of the coatings were measured using a galvanic couple which consisted of a magnesium anode and the produced Ni/Al coating. Short circuit current density of the galvanic pair was $j = 13.5 \text{ mA/cm}^2$.

After that coatings were chemically treated in KOH. As one can see in Fig. 2b, the Ni/Al coating is smoother and its porosity is larger than it was before chemical treatment. The short circuit current density of the galvanic couple which consisted of chemically treated Ni/Al coating as a cathode was $j = 45.7 \text{ mA/cm}^2$.

One of the possible reasons for the increase of short circuit current density could be the enlargement of the

surface area of the cathode due to enlargement of porosity by the chemical treatment. During this process Al reacts with KOH.

The composition of the coatings was investigated by Auger Electron Spectroscopy (Fig. 3). Only the Al peak was detected during the investigation of the surface of the Ni/Al coating (Fig. 3a). From the position of the peaks with energies lower than the energies of pure Al, it can be concluded that Al and nonstoichiometric Al oxides dominate the surface of the coating. The Ni peak could be detected after etching by an ion beam (Ar^+ , 3 keV, $5 \times 10^{16} \text{ cm}^2$) (Fig. 3b). It is seen that energies of the Ni peaks are lower than for pure Ni which indicates the existence of a mixture of Ni and its compounds with Al and O. So it is evident that during plasma spray deposition,

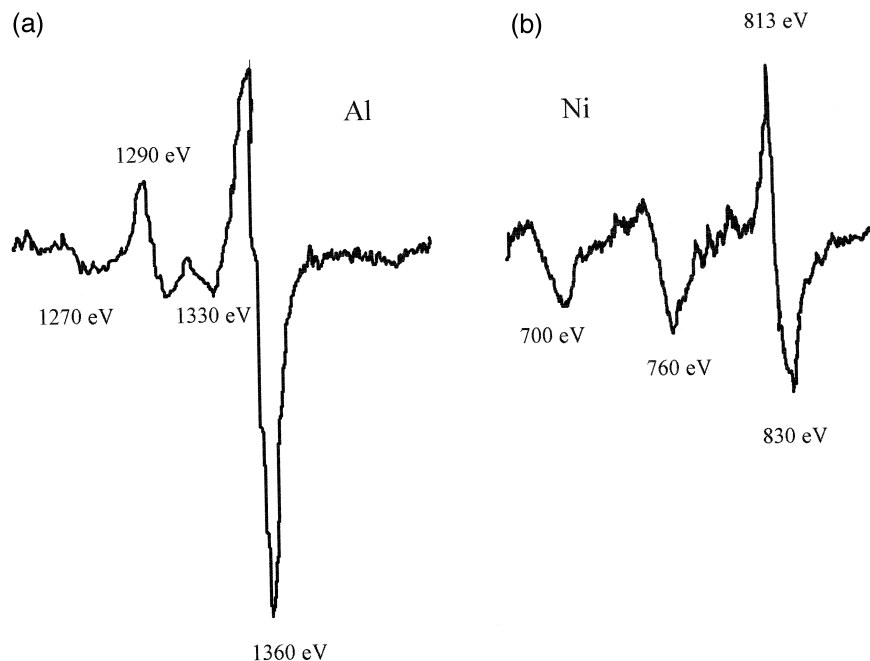


Fig. 3. The Auger spectra (typical energies and peak-to-peak intensities) of the plasma spray deposited coatings: (a) Al peaks of the plasma spray deposited coatings before etching by ion beam (as deposited); (b) Ni peaks of the plasma spray deposited coatings after etching by ion beam (Ar^+ , 3 keV, $5 \times 10^{16} \text{ cm}^{-2}$).

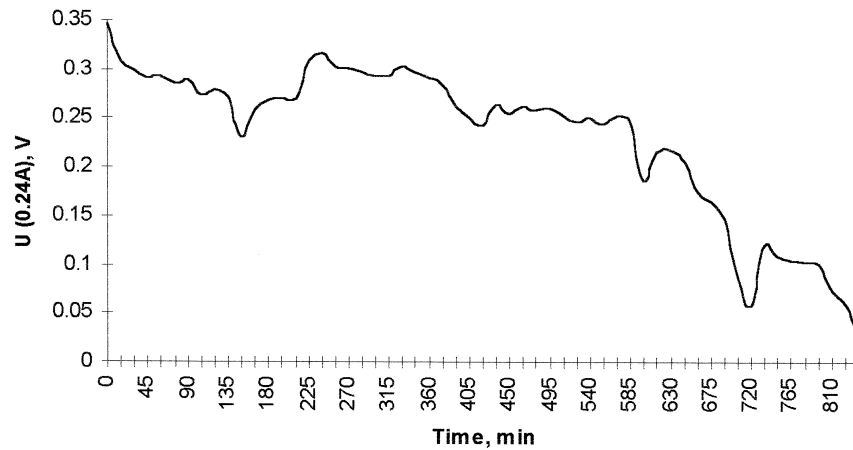


Fig. 4. The voltage–time dependence of galvanic pair Mg–Ni/Al, measured for the constant current $I = 0.24$ A.

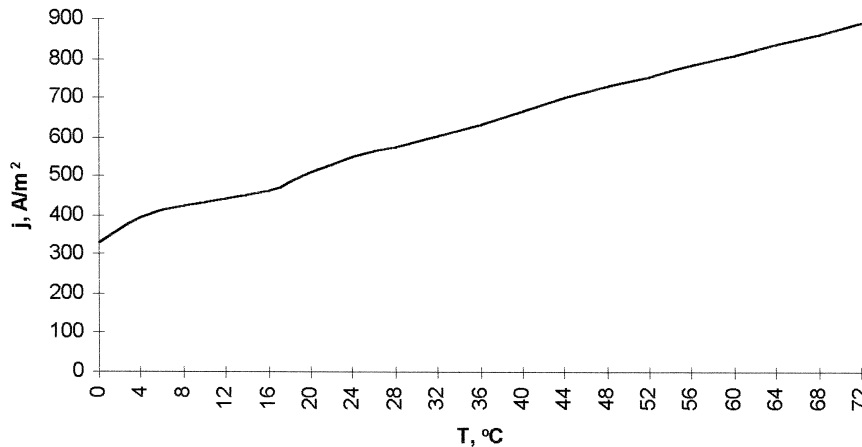


Fig. 5. The dependence of the short connection current density of the seawater battery on temperature of electrolyte.

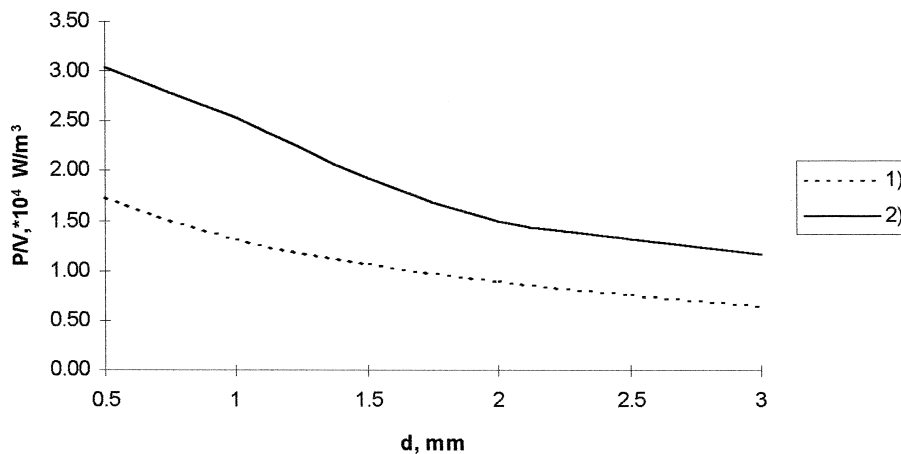


Fig. 6. The dependence of the power density of the seawater activated cells on the space between the electrodes for cells with different area of the electrodes: (1) area of the electrodes, 4.20×10^{-3} m²; (2) area of the electrodes, 1.75×10^{-3} m².

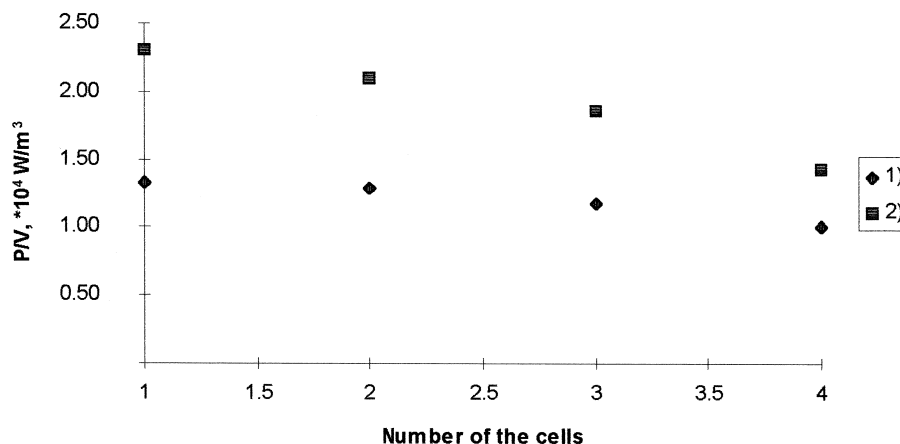


Fig. 7. The dependence of the power density of the seawater activated batteries on the number of cells for batteries with different area of the electrodes: (1) area of the electrodes, $420 \times 10^{-3} \text{ m}^2$; (2) area of the electrodes, $1.75 \times 10^{-3} \text{ m}^2$.

the diffusion of Al to the surface of the coating occurs. The mechanism of this diffusion has yet to be understood completely and needs to be investigated more deeply.

For further examination of the electrochemical properties of the seawater cell, chemically treated Ni/Al coatings were applied as a cathode. Fig. 4 shows the voltage–time ($U_{(t)} = E - Ir(t)$) dependence for the Mg–Ni/Al pair measured for the constant current I , where E is the electromotive force of the galvanic couple (equal to 0.7 V), $r(t)$ is the variable resistance, which was varied electronically to keep the value of I constant. Since the NaCl solution was used as an electrolyte, the deterioration of the cathode by calcium carbonate, which takes place in real seawater [1], was avoided. Masking of the electrodes by magnesium hydroxide, which is formed during the discharge, had no great effect because of its high porosity and poor adhesion to the electrode surface. Probably the $U(t)$ slope mainly depends on the anode erosion rate and it can be changed by applying different surface areas of the cells, i.e., in our experiments the mass of the anode is the only factor that restricts the life time of the seawater cell.

Short circuit current density of this cell was found to be a linear function of the temperature of seawater (Fig. 5).

The power density dependence on the space between electrodes and number of cells was investigated for the cells with different area of the electrodes, (Figs. 6 and 7, respectively). Fig. 6 illustrates that current density or output power for the Mg–Ni/Al pair is limited by the resistance of the electrolyte, i.e., salinity. Temperature will be the parameter that influences available output for the fixed surface area of electrodes. As seen from Fig. 6, for the cell which has the smaller area, power density de-

creases faster. To increase the output voltage of the galvanic cell connection of many cells in series can be used [6]. With the increased number of cells, the power density decreases because of leakage currents, and this decrease can be 20% or more. In our case, we have found that this connection is efficient enough for smaller areas of electrodes and for a small number of cells. Connection in series of three and even four cells can be used.

In summary, we have demonstrated that plasma spray technology can be used effectively to produce (Ni/Al) cathodes for seawater activated cells. Plasma gun output power is found to be a key technological parameter that defines electrochemical properties (short circuit current, available power density) of the Mg–Ni/Al cell. It is shown that output power for this type of batteries is defined by the erosion rate of the anode and the maximum output power density of $3 \times 10^4 \text{ W/m}^3$ was obtained for these cells.

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