DEALLOYING OF PdNi5 ALLOY IN 1.0M NITRIC ACID

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Binary palladium alloys with nickel are known to have catalytic activity and are also used as catalyst-trap in the synthesis of nitric acid. High Pd alloys are corrosive resistant in many solutions, including highly alkaline and highly acidic. Although generally not prone to corrosion in low concentrations of mineral acids due to the high content of palladium in it, this alloy is still prone to the dealloying effect under specific conditions. The dealloying process was researched under anodic polarization in 1.0M nitric acid solution. Scanning electronic microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and electrochemical methods were used to study the susceptibility of PdNi5 alloy to dealloying.

Keywords: PdNi5 alloy, corrosion, dealloying, ICPMS, SEM-EDS

Introduction

PdNi5 alloy was chosen as a material for research because the properties and structure of this alloy still need to be studied and better covered in the scientific literature. However, the widespread application of palladium-based alloys in processes of catalysis, the electronics industry, the jewelry industry, and medical and dental equipment production has led researchers in many countries to make significant efforts to study alloys of this system [1-6]. This alloy PdNi5 is widely used to make Pd-catalyst traps used in the production process of nitric acid. The Pd-catalyst trap's role consists in reducing volatile platinum oxide from gas flow to the metal form and retaining platinum metal on the surface of the Pd catalyst-trap.

Very rigorous conditions in reactors for ammonia oxidation lead to the very rapid destruction of catalysts. The losses of precious metals occur from catalytic networks due to the formation of volatile metal oxides PtO_2, PdO, and RhO_2 that are dragged away by gas flow [7]. The amount of platinum and rhodium lost varies from plant to plant but is generally less in plants operating at atmospheric pressure than those operating at high pressures. Empirically, these losses range from 35 to 65 mg/t HNO_3 for reactors operating at atmospheric pressure, i.e., from 0.32 to 0.39 g/t HNO_3 for reactors operating at high pressure [7].

Dealloying is the process of the selective dissolution of metals from an alloy, usually less noble (with lower standard electrode potential) metal, as the metallurgy phase or in the solid solution. Historically, this process has been studied most intensively for binary noble-metal alloys such as Ag-Au, Cu-Au, and Zn-Cu [8]. Dealloying has begun a new technological process for different purposes in the last decade. The dealloying technique involving the selective dissolution of one or more constituents from precursor alloys has become one of the most efficient approaches to fabricating nanoporous metals [9]. Utilization of the dealloying effect of nanoparticles based on PdNi alloys in different solutions was investigated by some authors [10-13], although the topic was not investigated to a great extent. All of these papers were focused on the procedure for obtaining nanoporous PdNi alloys as electrocatalysts towards oxygen reduction reaction for synthesizing methanol in an alkaline medium. The use of sulfuric acid as a dealloying agent without electrochemical methods was a rare procedure [10] since the majority of studies operate with electrochemical methods. Thermal dealloying of PdNiBi alloy was also investigated [14]. This paper aims to examine the dealloying of PdNi5 alloy in 1M HNO_3 using potentiostatic conditions and its prone to the process.

Materials and methods

The melting process was carried out in a high-frequency induction furnace (Balzers) in a vacuum. In order to eliminate internal stresses, homogenized annealing at 900 °C for 90 minutes was performed in an electric resistance furnace with a chamber. The plastic processing was carried out by the rolling process at a total degree of deformation of 70%. Heat treatment after rolling consisted of recrystallization annealing the samples of PdNi5 alloy, in wire form, in the electric resistance furnace at the temperature of 900 °C during the time of 30 minutes.

Chemical characterization of the solutions was performed using the Agilent 7900 ICP-MS. For the electrochemical characterization of the alloy, the following methods were used: open circuit potential (OCP), linear polarization resistance (LPR), and Tafel extrapolation. Experiments were performed in the standard three electrodes electrochemical cell (working, reference, and counter). Measurements were done on Gamry Interface 1000 potentiostat/galvanostat (Gamry Instruments Inc.). The control of the electrochemical measurements and analysis of the results was carried out with Gamry Framework and Echem Analyst software, respectively. The area of working electrode was 0.25 cm^2. A platinum sheet with a surface of 1 cm^2 was used as a counter electrode. The potential of the working electrode was measured with respect to a saturated calomel reference electrode (SCE), with +241 mV vs. standard hydrogen electrode (SHE).

The research was carried out in a solution of p.a. nitric acid (Zorka Šabac, Serbia) with a concentration of 1.0 mol/dm^3. The calculated pH value (taking ions activity into account) of the solution was 0.126. The sample was ground with a series of SiC papers and was polished using the 2 μm diamond paste. The experiments were performed at room temperature, which was 22±2 °C. Open circuit potential (OCP) measured with a duration of 60 minutes. LPR potentials limits were ±20 mV related to OCP, at a potential change rate of 0.25 mV/s. Tafel polarization curves were measured at potentials of ±250 mV from OCP and at a potential change rate of 1 mV/s.

Results and discussion

The chemical composition of PdNi5 alloy, used in the study and obtained in the above described procedure, is given in Table 1.

Table 1 The chemical compositions of PdNi5 alloy

Main metals and main impurities					
(%)		(ppm)			
Pd	Ni	Pt	Rh	Au	Cu
95.03	4.95	47	12	2	4.8

Table 1 shows that the chemical composition of PdNi5 alloy was in accordance with the planned one, with tolerances in concentrations of ±0.1% for both main metals and less than 100 ppm for any of the impurities. The difference of 0.013% to 100% is due to components that are not analyzed and partly to the rounding and imprecision of the analysis. This alloy was used for electrochemical tests.

In Figure 1 polarization curve in the apparent Tafel region for PdNi5 alloy in nitric acid with a concentration of 1.0 mol/dm^3 has been shown. Figure 1 presents a typical appearance of Tafel's curve for the metal or one-phase alloy in an acid-corrosive environment. Parameters from the figure can be obtained with high accuracy and without any complications. The curve starts at about 10 mA/cm^2 and ends with the j of about 3 mA/cm^2. One of the characteristics is that in the anodic part, values for j start to decrease at about 250-300 mV (which is near the end of the measured interval).

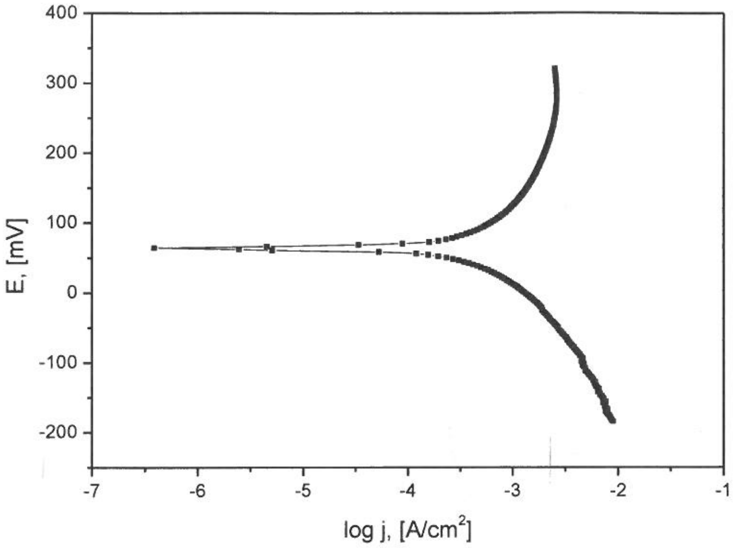

Figure 1 Polarization curve of PdNi5 alloy in 1M HNO_3 (pH 0.10-0.15) in the Tafel region

Figure 2 shows the measurement of polarization for the linear polarization resistance method. It is the slow rate polarization change in the region very near the OCP, starting from -20 mV to 20 mV (from cathodic to anodic area around OCP value).

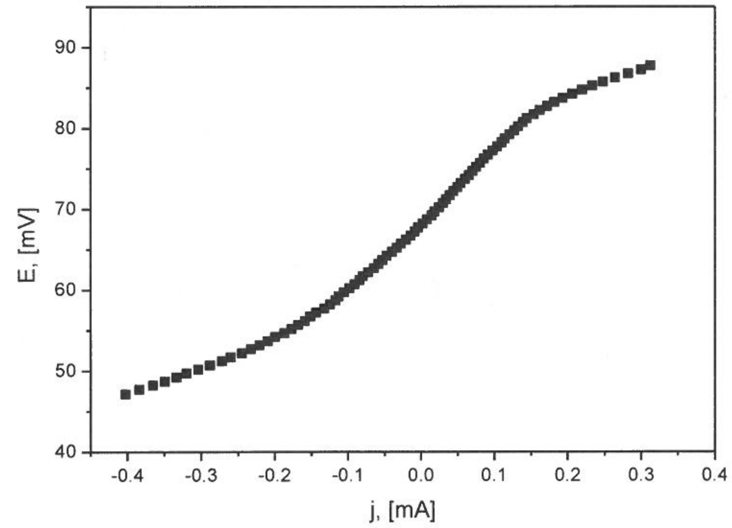

Figure 2 LPR method measurement for PdNi5 alloy in 1M HNO_3 (pH 0.10-0.15)

In Figure 2, we can see a typical curve shape for the LPR method. Although the entire interval of potential is in the proximity of the OCP and some systems (ideally any) have linearity through the whole ranges of the potential change, the most negative (cathodic) and positive (anodic) values of current density tend to exponential and not pure linear manner. It is a little more stressed here, with about 70% of the curve with perfect linearity. About the first seven mV of the cathodic part and the last five mV of the anodic did not have current density linear dependence from the potential. From Figure 2 order of magnitude is clearly visible since these ~30 mV shifts produce a few tenths of the mA difference in j, leading directly to tens of ohms (multiplied with cm^2), which is, obliviously, required (linear polarization) resistance.

The parameters obtained by measurement and analysis for OCP, Tafel, and LPR methods and used to determine the corrosion current are given in Table 2.

Table 2 OCP, Tafel parameters, and coefficient B of PdNi5 alloy in 1M HNO_3

Sample/Alloy	β_a, [mV/dec]	β_k, [mV/dec]	B*, [mV]	OCP vs. SCE, [mV]
PdNi5	52.55	−71.80	13.18	+67.23 mV

* proportionality constant defined in the Stern–Geary equation

From Table 2, it can be observed that the anodic Tafel slope is similar to the pure nickel in 1M nitric acid [15]. In contrast, the cathodic slope is much lower than for Ni. It is inside the interval of -60 mV/dec to -80 mV/dec, characteristically for the hydrogen evolution on Pd-based materials [16]. In Table 3, calculated corrosive parameters for the sample are given.

Table 3 Corrosive parameters of PdNi5 in 1M HNO_3 solution at 22 °C

Sample/Alloy	Linear polarization			Tafel	
	R_p, $\Omega\cdot cm^2$	$I_{corr.}$, mA/cm^2	$E_{corr.}$, mV vs. SCE	$I_{corr.}$, mA/cm^2	$E_{corr.}$, mV
PdNi5	80.67	**0.163**	+67.58	**0.196**	+66.53

The value of the corrosion current density obtained by Tafel extrapolation is about 20% higher than that derived from the LPR method (Table 3), which can be considered an as well agreement between these two methods. It is about 30% of the j_{corr} of the nickel in the same corrosion environment [17]. Although it was expected to be significantly lower for the PdNi5 alloy, the same order of magnitude is an exciting result. It could be a topic for new research since the influence of palladium on nickel corrosion (in Pd-Ni alloys) in nitric acid, and vice versa, was not investigated to any substantial extent. The dealloying was carried out in the same corrosion environment at a constant potential of 250 mV. The potential was chosen to be in the proximity of the OCP but high enough to cause nickel dissolution. Further, it has to be much lower than the standard electrode potential of palladium (+0.710 V vs. SCE [18]) to avoid Pd oxidation. The change of the current versus time for the PdNi5 electrode at +0.25 V is shown in Figure 3.

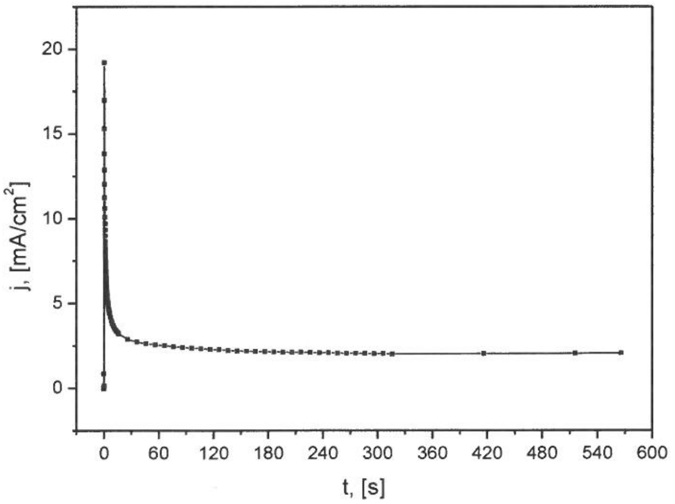

Figure 3 Chronoamperometric current-time curves for PdNi5 alloy in 1M HNO_3 (pH 0.10-0.15) at 0.25 V

Figure 3 shows a typical current transient with the j that reached very high values and a constant decrease in the value throughout the experiment. The maximum value of the j was obtained in 0.2 s, but after about 4 s, it dropped to about a quarter of it. The final value of the j is about 1-fold lower than the maximum at the start and is about 2 mA/cm^2. Dealloying starts rapidly but lasts for a short period. The stable value in much of the duration of polarization is more due to the resistances in the system. The concentrations in the solution prove this, as shown in Table 4.

Table 4 Concentrations of the Ni and Pd in the solution after 600 s of potentiostatic polarization

Metal	Ni	Pd
Concentration of dissolved ions, [ppb]	44.6	0.48

Concentrations of dissolved metals are extremely low, but a 2-fold lower concentration of Ni than Pd is obvious. The dealloying factor (Z) shows the extent of the selective dissolution:

$$Z=([Ni^{2+}]/\chi_{Ni})/([Pd^{2+}]/\chi Pd) \quad (1)$$

where $[Ni^{2+}]$ and $[Pd^{2+}]$ are molar concentrations in the electrolyte, χ_{Ni} and χ_{Pd} are mole fractions of metals in the alloy.

From equation (1), the calculated Z value equals 1765. Every Z>1 means selective dissolution, and Z=1765 proves a significant dealloying effect in the experimental conditions. Figure 4 illustrates dealloying, with the appearance of the voids at the surface of the alloy.

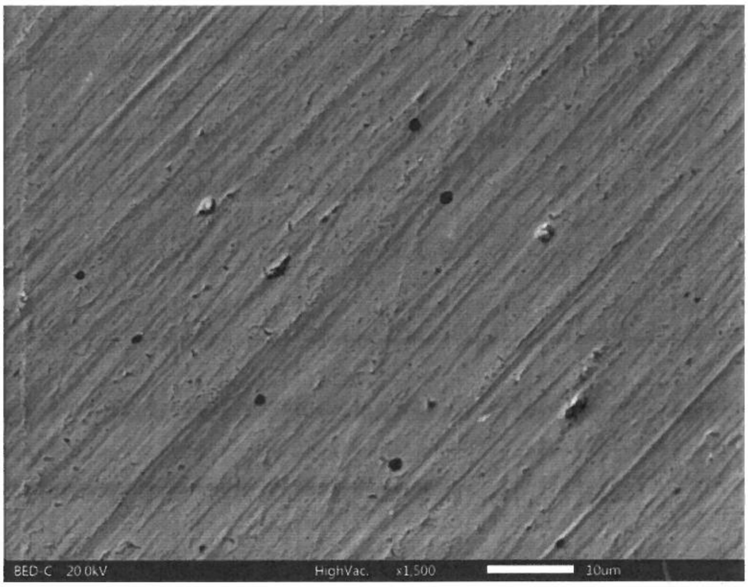

Figure 4 SEM micrograph of the alloy surface after potentiostatic polarization

EDS analysis additionally proves selective dissolution of Ni; lower nickel concentrations are near the voids at the surface than 5 wt.% (8.71 at.%) in the alloy.

Conclusion

The following conclusions can be drawn from the research:

1) Corrosion current density of PdNi5 alloy in 1M HNO_3 is 0.163 mA/cm^2. It is substantial alloy corrosion in the technical meaning since it is a corrosion rate of 1.76 mm/year (calculated on nickel as a less resistive component), meaning a low Pd protection of Ni even in free corrosion conditions.

2) The dealloying factor (Z) of 1765 determines the exceptionally high selective dissolution of nickel in the chronoamperometric experiment. The SEM image shows the surface with the voids originating from the nickel dissolution and additionally proves a high dealloying effect.

3) Generally, nitric acid is the environment in which both metals can be dissolved (nitrates of Pd and Ni are water soluble). Still, under specific conditions, a lower concentration and defined electrode potential may be suitable and even favorable for the selective dissolution of nickel.

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