

# DEALLOYING PDNi5 LEGURE U 0.5M SULFATNOJ KISELINI

## DEALLOYING OF PDNi5 ALLOY IN 0.5M SULFURIC ACID

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### Sažetak

*Legure paladijuma sa niskim sadržajem nikla se obično koriste kao havatači katalizatora za platinu ili platina-rodijum katalizatore u procesu proizvodnje azotne kiseline. Čisti paladijum i posledično legure sa visokom koncentracijom Pd su visoko otporni u mnogim korozionim sredinama u punom pH opsegu, od 0 do 14 i više, u prisustvu različitih anjona. Mineralne kiseline ne utiču na paladijum, posebno na nižim koncentracijama; može se rastvoriti samo u njihovoj mešavini.*

*Međutim, nikl u leguri može se selektivno rastvoriti u jednoj mineralnoj kiselini uz upotrebu oksidacionog agensa ili anodne polarizacije, što je proces koji se može više kontrolisati. Cilj rada je istraživanje dealloying-a PdNi5 u 0,5M sumpornoj kiselini u uslovima anodne polarizacije. Ova studija je koristila potencijal otvorenog kola, otpor linearne polarizacije i hronoamperometriju kao elektrohemijske metode. Skenirajuća elektronska mikroskopija sa energetski disperzivnom rendgenskom spektroskopijom (SEM-EDS) i masena spektrometrija induktivno spregnute plazme (ICP-MS) korišćene su kao strukturne i analitičke tehnike za proučavanje dealloying-a legure PdNi5 u 0,5M sumpornoj kiselini na tri različita anodna potencijala.*

**Ključne reči:** dealloying; korozija; SEM-EDS; Pd-Ni legura; ICP-MS

### Abstract

*Palladium alloys with low nickel content are commonly used as catalyst-trap for platinum or platinum-rhodium catalysts in the process of production of nitric acid. Pure palladium and, consequently, alloys with a high concentration of Pd are highly resistant in many corrosion environments across the full pH range, from 0 to 14 and beyond, in the presence of different anions.*

*Mineral acids do not affect palladium, especially at lower concentrations; they can be dissolved just in the mix of them. However, nickel in the alloy can be selectively dissolved in single mineral acid with the use of an oxidation agent or anodic polarization, which is the more controllable process. The aim of the work is the research of dealloying of PdNi5 in 0.5M sulfuric acid under anodic polarization conditions. This study used open circuit potential, linear polarization resistance, and chronoamperometry as electrochemical methods. Scanning electronic microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) and inductively coupled plasma mass spectrometry (ICP-MS) were used as structural and analytical techniques for the study of PdNi5 alloy dealloying in 0.5M sulfuric acid at three different anodic potentials.*

**Key words:** dealloying; corrosion; SEM-EDS; Pd-Ni alloy; ICP-MS

## 1 Introduction

Nickel and its alloys have high corrosion resistance and good mechanical characteristics and are important materials for machine engineering, chemical industry, electrochemical technologies and energy conversion devices [1-3]. It is well known as a main component of superalloys [4] and catalysts in the chemical industry [5]. It recently got attention as a material suitable for different types of additive manufacturing technologies [6]. Palladium is well known for its ability to absorb

hydrogen, which is ahead of all other metals and forms the basis of its application in industry. Pd and its alloys have its application for electrochemical power sources, primarily fuel cells [7,8]. Another important use of these materials is as catalysts in organic synthesis [9,10]. Pd's best-known and widely used application is as the primary component exhaust catalyst for diesel engines [11]. The focus of recent research for Pd-based materials is the use, mainly as membranes, in renewable energy sources, more precisely in hydrogen production, storage and separation [12-15]. Finally, the use of Pd-containing nanomaterials for renewable energy generation and conversion [16] and even more proactive use for the reduction of CO<sub>2</sub> [17] present the future of intensively studied fields.

Binary Pd-Ni alloys were mainly used as catalysator trap [18], in the electronic industry (as a gold substitute for contacts) [19], and in the chemical industry (e.g. nozzle plates [20]). Recently, palladium-nickel alloy has been used in composite with graphene oxide in fuel cells [21]. Corrosion characteristics of Pd binary alloys in H<sub>2</sub>SO<sub>4</sub> were detailed studied [22]; however, Ni was not included in the research, and the Pd-Ni electrochemical behaviour still needs to be included in the literature. In the last decade, nonporous metals have attracted intense interest from researchers due to their possible applications in many high-tech areas, like actuators or energy storage. Among numerous studied metals, Pd and Ni have received significant attention, and various alloys of these metals have shown great potential for nonporous (np) structures [23,24]. It was confirmed in a very recently published study of potentiostatic dealloying of Pd-Ni alloy [25]. In the paper, Ni<sub>80</sub>Pd<sub>20</sub> (at.%) alloy was used, potentiostatic potential was 0.5 V, 0.5M sulfuric acid as corrosion environment and prolonged duration, over 100k s, of two-step potentiostatic control; a dense, nonporous structure of Pd was produced.

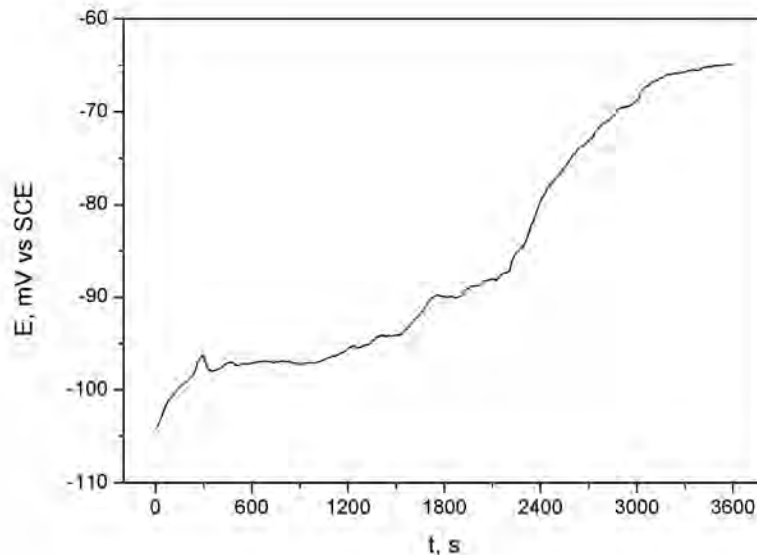
This paper aims to investigate the possibility of dealloying of Pd-Ni alloy with high Pd content (91.29 at.% or 95 wt.%) in 0.5M sulfuric acid with a relatively short (10 minutes) potentiostatic polarisation at low potential (0.25 V vs SCE) and to determine dealloying factor. An additional goal was the determination of the corrosion parameters of the PdNi<sub>5</sub> alloy in the test solution.

## 2 Materials and Methods

The alloy sample was obtained by ingot metallurgy route with later deformation of 70% caused by the rolling process, followed by recrystallisation annealing. The detailed process of the specimen obtaining and treatment, together with a detailed chemical analysis of the alloy, were given in our previous paper [26]. The main sample composition includes 95.0% of palladium and 4.95% of nickel (given as mass percentages). The study was performed in a 0.50 mol/dm<sup>3</sup> solution of p.a. sulfuric acid (Zorka Šabac, Serbia). The solution's calculated pH value (considering ions activity) was 0.808, and the measured one was 0.763. Distilled water with a conductivity of 2.8  $\mu$ S/cm was used for the preparation of the working solutions. The sample was ground with a series of grinding papers and was polished using the 3  $\mu$ m and 1  $\mu$ m diamond paste. The experiments were performed at an ambient temperature of 27 $\pm$ 1 °C. The Agilent 7900 ICP-MS was used for the chemical analysis from corrosive media (0.5M sulfuric acid solution). The phase analysis, composition and element mapping were studied using the JEOL model JSM IT 300LV scanning electron microscope with Oxford Instruments model X-max EDS detector. Open circuit potential (OCP), Tafel extrapolation and linear polarisation resistance (LPR) were used for the electrochemical analysis. The standard three-electrode electrochemical cell setting was used for these experiments. Gamry Interface 1000 (Gamry Instruments Inc.) was used as a potentiostat/galvanostat, and the electrochemical measurements were analysed using Gamry Framework and Echem Analyst software. The active area of the working electrode was 25 mm<sup>2</sup>. A platinum sheet with a surface of 2 cm<sup>2</sup> was used as a counter electrode. The working electrode's potential was measured with respect to a saturated calomel reference electrode (SCE), and they are mentioned afterwards as such in the paper. LPR potential limits were  $\pm$ 20 mV from OCP at a 10 mV/min potential change rate. Tafel polarization parameters were determined at potentials of  $\pm$ 100 mV from OCP in dynamic polarisation measurement at a potential change rate of 30 mV/min and in the range of -200 mV to +400 mV from OCP. The chronoamperometry experiment was performed at +250 mV and for 10 minutes.

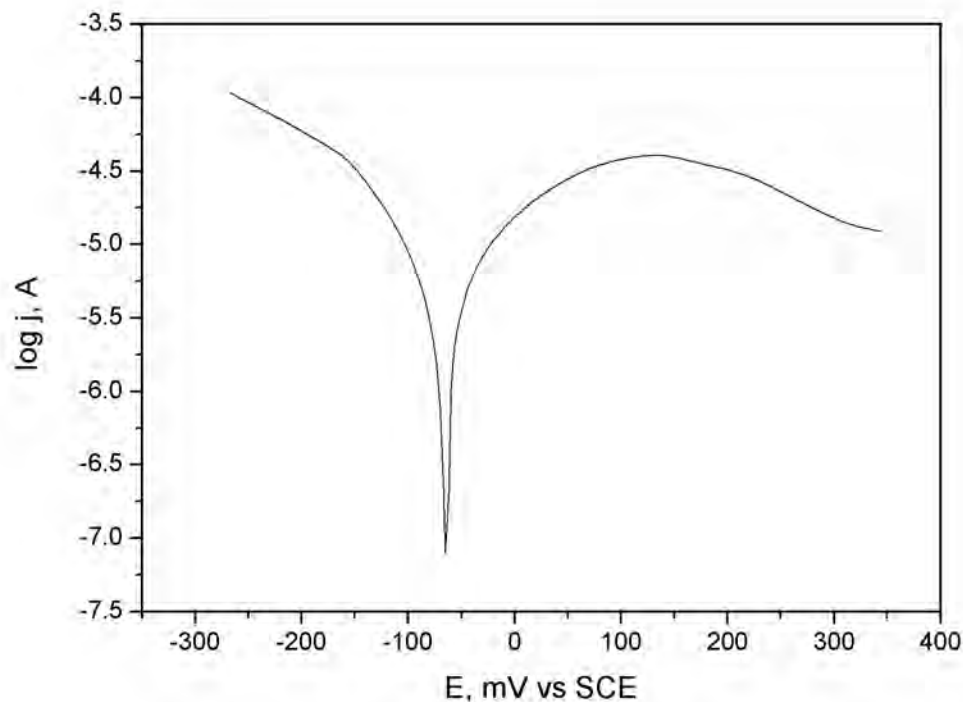
### 3 Results and Discussion

Electrochemical tests were started with the measurement of the OCP. Figure 1 presents the very common shape of the OCP curve for the alloy in a strongly corrosive environment. It starts from more negative potentials and monotonously rises until it stabilises at a somewhat more positive potential near the end of the standard time interval for the method. It indicates a faster corrosion process at the start of the test, which slows during the measurement due to the passivation or (more probably, in this case) depletion of the less noble component in the surface area. Value of the OCP at the end of the experiment was  $-64.9$  mV.



*Figure 1. OCP curve for PdNi5 alloy in 0.5M sulfuric acid*

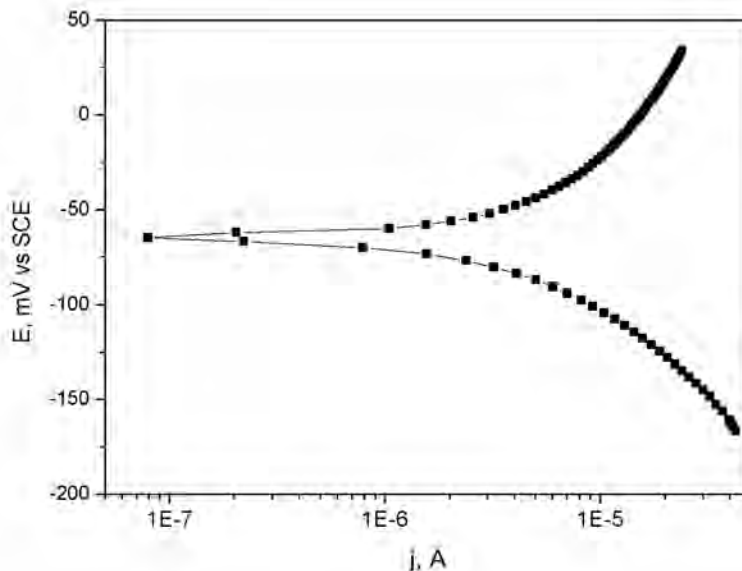
The polarisation curve is shown in Figure 2. The appearance of a peak in the vicinity of the OCP (at about  $+180$  mV above it) at the curve caused Tafel extrapolation to be performed  $\pm 100$  mV from OCP, which is a narrower area than usual.



*Figure 2. Polarisation curve for PdNi5 alloy in 0.5M sulfuric acid*

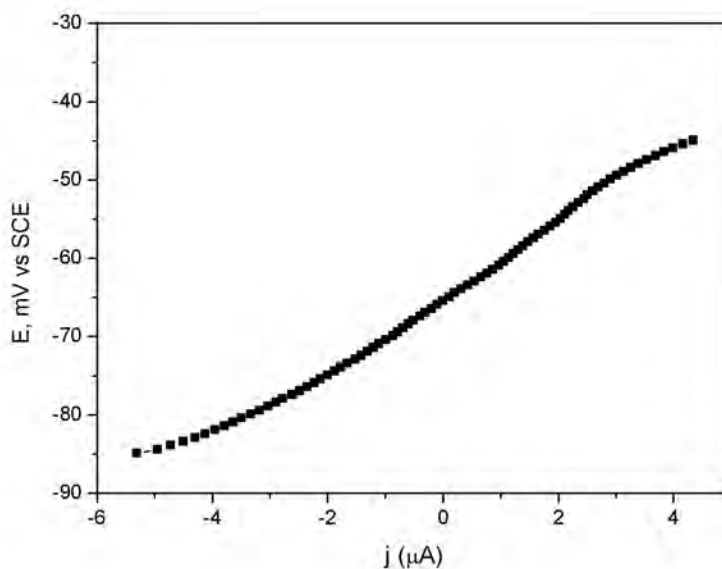
From Figure 2, it can be seen that anodic potential rises very sharply from approx. 80 mV above OCP; after reaching the maximum at nearly +150 mV, potential slowly decreases until the near stationary state at the end of the measured interval. The anodic current density in that area is about ten microamperes per cm<sup>2</sup> and can be considered a passivation state.

Figure 3 shows the region of performed Tafel analysis for the examined system.



**Figure 3.** The area of the apparent Tafel region for the system

The LPR method is used to obtain the main corrosion parameters and to confirm corrosion current density obtained by Tafel extrapolation. Figure 4 illustrates the current response to a very slow dynamic potential change very close to the OCP.



**Figure 4.** Results of the LPR measurements for PdNi5 in 0.5M sulfuric acid

The ideal LPR curve should be a straight line, and the studied system shows a high linearity of the curve. Deviation from linearity was small and visible only at the maximum difference from the OCP; it was larger in the cathode area. Summarized corrosion parameters are given in Table 1.

Table 1 Parameters from Tafel extrapolation and LPR methods for PdNi5 in 0.5M sulfuric acid

Sample (Alloy)	Linear polarisation				Tafel extrapolation			
	$R$ [ $k\Omega \cdot cm^2$ ]	$I_{corr.}$ [ $\mu A/cm^2$ ]	$E_{corr.}$ [ $mV$ vs SCE]	$B$ [ $mV$ ]	$I_{corr.}$ [ $\mu A/cm^2$ ]	$E_{corr.}$ [ $mV$ vs SCE]	$\beta_a$ [ $mV/dec$ ]	$\beta_k$ [ $mV/dec$ ]
PdNi5	5.664	2.873	-65.3	16.27	3.12	-65.5	90.47	-63.98

The corrosion current density in the system was low, showing the slow corrosion processes. Considering the linear corrosion of the nickel corrosion rate was 37.4  $\mu m$  per year. However, in reality, it is probably much lower since the dealloying effect leads to the higher corrosion resistance of the alloy, probably near the pure palladium in long time intervals. A comparison of the results from LPR and Tafel shows excellent agreement between the two methods. The obtained value of the corrosion current density for the Pd-Ni alloy is precisely (by 1-fold higher and lower, consecutively) between the values for pure palladium and nickel in the same or similar corrosion environment presented in other studies [22,27,28].

The dealloying behaviour of the alloy was studied applied constant potential of 250 mV. The potentiostatic curve of the PdNi5 alloy at +250 mV is shown in Figure 5.

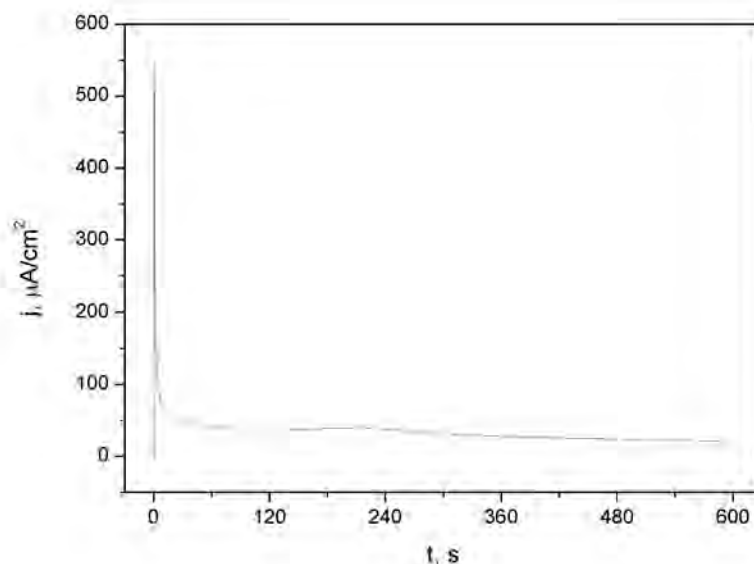


Figure 5. The results of chronoamperometric measurements for PdNi5 alloy in 0.5M  $H_2SO_4$

A usual current transient curve can be seen in Figure 5. This is a common shape of chronoamperometric curve generally and especially for the alloy in a moderately strong corrosion environment. The current increases sharply reaches a pronounced peak in a few tenths of a second, and similarly rapidly decreases until the values are about 1-fold higher than at the end of the experiment. Then in the next few seconds, the value has an exponential decrease. The decrease fastly deaccelerates, and the deflection point was reached about 15 s after the start of the experiment. The final value of the  $j$  was about 20  $\mu A/cm^2$ . The curve had a small and slow rise between the first and the second minute and then a continual and slow decrease till the end.

Although all electrochemical tests indicate dealloying, this process can be confirmed only by chemical analysis of the solution. The concentrations of ions of two metals, in the solution, from the alloy are shown in Table 2.

**Table 2** Concentrations of Pd and Ni ions in test solution after potentiostatic polarisation at 0.25 V for 600 s

Metal	Pd*	Ni
Concentration [ $\square$ g/dm <sup>3</sup> ]	0.1	5.2

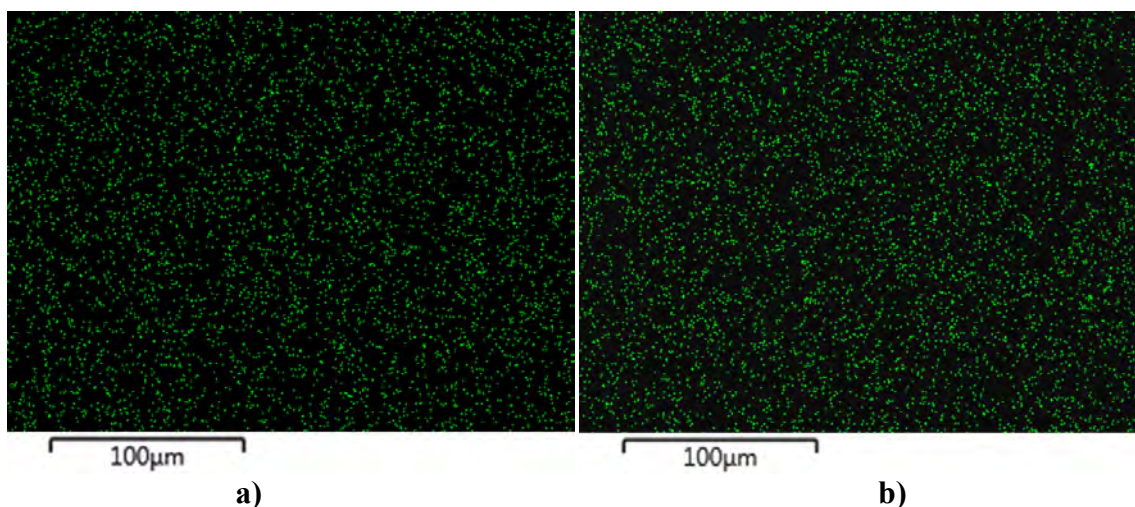
\*less or equal to

Concentrations of dissolved metals are extremely small, and in the case of Pd on the edge of the limits even for such method as ICP-MS. The about 50 times higher concentration of nickel than palladium in the mass per volume unit was found. This difference is even twice higher when consider molarity. The measure of selectivity of the dissolution from the alloy is dealloying factor (Z), and for this case was:

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

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

Equation (1) took the mole ratio in the alloy, which further increased the value of Z. The calculated value for the dealloying factor was 988. Every  $Z > 1$  means selective dissolution, and the high value, such as obtained in the research, means a significant dealloying of the alloy in the solution under the testing conditions. By this, dealloying in the system is strongly proven. Nevertheless, SEM/EDS method could not provide additional evidence for dealloying. This is due to the homogenous distribution of nickel in the palladium solid solution. This is illustrated in Figure 6.



**Figure 6.** Element mappings of PdNi5 alloy before and after potentiostatic polarization in 0.5M sulfuric acid; figure a) was before and b) after the chronoamperometric test

According to element mapping analysis of the alloy surface, only a homogenous distribution of nickel in both figures and tiny differences in content can be observed (for nickel, 4.85% before and 4.77% f after the test, which is inside of  $\pm 0.04\%$  difference). It is not sufficient proof of any change, including dealloying. The SEM magnification was insufficient to show the voids where nickel was dissolved. The EDS also needed to be more precise to detect tiny variations in the alloy composition before and after chronoamperometry which was no surprise since extremely low concentrations of both metals, even nickel, in the solution.

## 4 Conclusion

Several electrochemistry techniques have been used to characterise the corrosion rate and general corrosion behaviour of PdNi5 alloy in 0.5M H<sub>2</sub>SO<sub>4</sub>. Potentiostatic polarization (10 minutes at 0.25 V) has been used to cause dealloying in the system. The results of the presented study have shown the following:

- OCP value has been stabilised in the standardized (ASTM) duration of the experiment for the metals and alloys. However, since stabilization occurred in the last few minutes of the test, studies with a prolonged period (6, 12 or 24 h) could be beneficial in the aim of more detailed corrosion studies.
- The alloy has relatively high corrosion resistance in the tested corrosive media with  $j_{\text{corr}}$  of about 3  $\mu\text{A}/\text{cm}^2$ .
- Tafel extrapolation and LPR had similar results, confirming the previous claim.
- The polarisation curve showed a broad peak, which indicates quasi-passivation behaviour, probably due to nickel dissolution and surface enrichment in palladium.
- In the chronoamperometry test, tiny quantities of metals were dissolved, but enough to demonstrate a strong dealloying effect, and chemical analysis proved it. The dealloying factor was nearly a thousand, which is a high value and shows the tendency of dealloying for the researched system.

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