Abstract: The aim of this study was to develop a new material which has high hydrogen storage capacity and hydrogen absorption/desorption rate. This material, which is based on cobalt powder onto which palladium was chemically deposited can be used in environmentally friendly energy generation processes, thus ensuring preventive protection of human health. Hydrogen absorption was investigated using differential scanning calorimetry (DSC) and by measuring hydrogen pressure under isothermal and non-isothermal conditions in a chamber containing either pure cobalt powder either cobalt powder onto which palladium was chemically deposited (Co-0.003 Pd). The mechanism of hydrogen absorption has been described. It was noticed that palladium catalyses hydrogen absorption by dissociating the adsorbed H$_2$ molecules into H atoms more rapidly on its own atoms than on cobalt ones. The catalysis of dissociation of H$_2$ molecules enabled hydrogen absorption into Co-0.003 Pd powder to occur at lower temperatures. The results of this study enable integration of technological and public health investigation in order to ensure preventive protection of human health through environmental protection.

Keywords: Cobalt, Palladium, Hydrogen absorption/desorption, Environmental-friendly energy generation processes

1. Introduction

In the last several decades the awareness of environmental pollution has increased significantly. Taking into account that one of the largest long-term threats to human health is exposure to chemical products which affect Earths atmosphere, numerous investigations have been performed in order to eliminate existing and prevent potential environmental pollutants, particularly in the processes of energy generation. It has been found that metals or alloys which form hydrides in a reaction with hydrogen, can be used in a variety of applications, such as heat pumps, thermal storage systems, as catalysts, fuel cells, nickel-metal hydride rechargeable batteries, thus significantly reducing environmental pollution. In order to successfully store hydrogen, these materials have to show high hydrogen storage capacity and high hydrogen absorption/desorption rate [1-5]. For these reasons, experimental and
numerical studies have been conducted in an attempt to clarify and model the mechanisms of the hydrogen absorption and desorption kinetics [2-11]. In order to enhance the rate of hydrogenation and dehydrogenation, the effects of addition agents, preparation methods, and element substitution on the hydrating kinetics mechanisms have been systematically analysed as well [12-22].

The electrochemical properties of negative electrodes (hydrogen storage alloys) used in secondary nickel-metal hydride batteries are determined by preparation method, chemical composition and microstructure [23-25]. It was found that hydrogen content governs the mechanical properties and corrosion rates of a number of metals and alloys which are widely used under aggressive corrosion conditions (e.g. titanium and its alloys) [26-29]. The investigations also showed that an increase in hydrogen content can increase corrosion and degradation rates of mechanical properties, including strength and toughness [30-37]. Studies on the hydrogen absorption/desorption kinetics of these alloys yielded diverse experimental data and interpretations of these processes [30-37].

The kinetics of hydrogen absorption/desorption into cobalt and its alloys was also monitored [38-39]. Dependence between the amount of absorbed hydrogen in pressed cobalt powder and its electrical resistivity was investigated also [38]. Based on these investigations, in this article, a small amount of palladium was deposited onto the cobalt powder and the effect of deposited palladium on hydrogen absorption kinetics has been studied. As a result, development of a new material which can be used in environmentally friendly energy generation processes has been enabled.

2. Experimental

In this study, pure cobalt (5-200 µm) powder and cobalt powder onto which 0.003 wt.% Pd was chemically deposited (Co-0.003 Pd) were used. Palladium was deposited by soaking cobalt powder into an acid aqueous solution of PdCl₂ (1.0 mol dm⁻³ HCl + 0.0005 mol dm⁻³ PdCl₂) for two hours at t = 20°C. The solution was prepared from p.a. chemicals (Merck) and triple distilled water. The composition of the solution was evaluated before and after powder soaking in order to determine the amount of deposited palladium. The solution composition was determined using a PEKTAR-AA-200-VARIAN atomic absorber. Hydrogen absorption into the powders was investigated through differential scanning calorimetry (DSC). Thermograms were obtained using a Dupon 1090 thermal analyser at a heating rate of 20°C min⁻¹ under a flow of pure hydrogen.

The powder of Co-0.003 Pd was placed into the chamber filled with hydrogen. Thereafter, hydrogen pressure was measured as a function of absorption time. Hydrogen absorption into cobalt powders was also determined by measuring hydrogen pressure in the chamber of volume, V=0.5 dm³, as a function of temperature. The chamber heating rate was 20°C min⁻¹. The kinetics of hydrogen absorption into Co and Co-0.003 Pd powders was also studied under isothermal conditions at 183°C, 218°C and 230°C.

3. Results and discussion

Hydrogen absorption into cobalt is a complex process which involves the following successive elementary steps: a) adsorption of molecular hydrogen on the surface of cobalt powder; b) dissociation of molecular hydrogen into atomic hydrogen; c) penetration of atomic hydrogen into the crystal lattice of cobalt, and simultaneous trapping of electrons from the conduction band and H⁻ ion formation, and d) diffusion of H⁻ ions within the crystal lattice of cobalt [38].
According to DSC analysis of the hydrogenation of the polycrystalline cobalt powder (Fig.1), two partially overlapping peaks can be observed in the thermogram within the temperature interval of 150°C to 270°C. This indicates that absorption involves two exothermic steps with the overall hydrogenation enthalpy of -85.9 Jg⁻¹. The occurrence of the first exothermic peak in the thermogram is probably induced by the adsorption of molecular hydrogen i. e. CoH₂ad formation. The existence of the second exothermic peak is most likely associated with the endothermic dissociation of molecular hydrogen as well as with the exothermic process wherein hydrogen atoms are distributed among the interstitial sites in the crystal lattice of cobalt and the process of H⁻ ion formation.

Fig. 1. DSC thermogram of the hydrogenation of pure cobalt powder

According to DSC thermogram of the hydrogenation of Co-0.003 Pd powder, the onset temperature for hydrogen absorption into Co-0.003 Pd powder is about 70°C lower than that for the absorption into the pure cobalt powder. Moreover, the enthalpy of hydrogen absorption into this powder (-3.46 kJg⁻¹) is considerably higher than that of hydrogen absorption into the pure cobalt powder. Since the palladium atoms, which are located on the surface of the cobalt powder, catalyse the slow dissociation of adsorbed H₂ molecules, the lower activation energy for the H₂ molecules dissociation on Pd atoms than on Co, enables hydrogen absorption into Co-0.003 Pd powder to take place at a lower temperature than in pure cobalt powder. Furthermore, fast dissociation causes simultaneous penetration of hydrogen atoms into the crystal lattice of cobalt and formation of H ions at lower temperatures. Therefore the first and second peaks overlap and merge into a single asymmetric peak in the thermogram for Co-0.003 Pd powder.

Fig. 2. DSC thermogram of the hydrogenation of Co-0.003 Pd powder
Hydrogen absorption into cobalt powder was also monitored by measuring hydrogen pressure, within the constant-volume chamber as a function of temperature: a) in the absence of the powders, b) in the presence of pure Co-powder, and c) in the presence of Co-0.003 Pd powder.

![Graph showing hydrogen pressure, P, within the chamber as a function of temperature, t: a) in the absence of powders, b) in the presence of pure Co powder, and c) in the presence of Co-0.003 Pd powder.](image)

Fig. 3. Hydrogen pressure, P, within the chamber as a function of temperature, t: a) in the absence of powders, b) in the presence of pure Co powder, and c) in the presence of Co-0.003 Pd powder

The diagrams given in Fig. 3 show that the onset of hydrogen absorption into Co-0.003 Pd powder occurs at a 40°C lower temperature than into pure Co powder, and that the rate of hydrogen absorption into Co-0.003 Pd powder is considerably higher as compared to that for pure Co powder. The measured results are correlated with those of DSC analysis (Figs. 1 and 2). However, since the pressure of gaseous hydrogen is higher in the chamber, than in the DSC analyser, hydrogen absorption onto both types of powder starts at lower temperature in the chamber, than in the DSC analyser. The amount of absorbed hydrogen at temperature T after a certain period of time, was determined using the following equation:

\[ \Delta n = \frac{V (p_1 - p_2)}{RT}, \]  

Where \( \Delta n \) – denotes number of absorbed hydrogen moles, \( V \) – denotes chamber volume, \( T \) – denotes absolute temperature within the chamber, \( p_1 \) – denotes hydrogen pressure within the chamber in the absence of powder at temperature \( T \), \( p_2 \) – denotes hydrogen pressure within the chamber in the presence of powder at temperature \( T \) and \( R \) – denotes universal gas constant.

The number of hydrogen atoms absorbed per gram of Co powder at \( t = 160^\circ C \) and pressure \( p = 273.3 \) kPa is \( 46.2 \times 10^{20} \) and that per gram of Co-0.003 Pd at \( t=160^\circ C \) and \( p = 244.4 \) kPa is \( 178.0 \times 10^{20} \). In other words, since one mole of Co absorbs 1.4 and Co-0.003 Pd absorbs 5.38 H moles, during the same absorption time, Co-0.003 Pd powder absorbs 3.84 times more hydrogen than Co powder.

Moreover, according to DSC results, the absolute value of the enthalpy of hydrogen absorption into Co-0.003 Pd powder is 40.3 times higher than the enthalpy of absorption into the Co powder. Also, hydrogen absorption into Co-0.003 Pd powder occurs at a temperature lower than that of hydrogen absorption into Co powder. It should be noticed that at lower temperatures, the absolute value of the absorption enthalpy is substantially higher, since a decrease in temperature causes a more rapid decrease in the enthalpy of H\(^+\) ions in the crystal lattice of cobalt powder compared to the enthalpy of H\(_2\) molecules in the gas phase [38].
The kinetics of hydrogen absorption into Co and Co-0.003 Pd powders was studied at different temperatures (183°C, 218°C and 230°C), under isothermal conditions as well. The hydrogen pressure within the chamber containing the test powder was measured as a function of time.

![Graph showing hydrogen pressure, p, as a function of absorption time, τ, at 183°C.](image)

**Fig. 4** Hydrogen pressure, p, within the chamber containing Co-0.003 Pd powder at 183°C as a function of absorption time, τ

The shape of the $p = f(τ)$ curve presented in Fig. 4, indicates that the process of hydrogen absorption into Co-0.003 Pd powder occurs via a complex mechanism. The temporal analysis of the dependence of the change in hydrogen pressure within the chamber during absorption revealed both a linear dependence of ln $p$ versus time, $τ$, during the first time interval of 150 s (Fig. 5) and a linear dependence of pressure, $p$, versus $τ$ during the second interval of 150 s - 670 s (Fig. 6).

![Graph showing ln p as a function of time, τ, at 183°C.](image)

**Fig. 5** ln $p$ as a function of time, $τ$, in the presence of Co-0.003 Pd powder at 183°C
During the initial stage of absorption, linear dependence of $\ln p$ versus $\tau$ was obtained. Therefore, during initial interval, the dissociation of adsorbed $H_2$ molecules on Pd atoms was observed to be the slow step process [38]:

$$H_{2\text{ad}} \rightarrow 2 \ H_{\text{ad}}. \quad (2)$$

The slope of the $\ln p = f(\tau)$ line was used to determine the $H_2$ dissociation rate constant:

$$k_1 = \frac{\Delta \ln p}{\Delta \tau} = 0.6 \cdot 10^{-4} \ \text{s}^{-1}. \quad (3)$$

The linear dependence of $p = f(\tau)$ during the second interval of time indicates slow diffusion of $H^-$ ions in the crystal lattice of cobalt [38]. The slope of the $p^{-1}$ line was used to determine the apparent diffusion rate constant:

$$k_D = \frac{\Delta p}{\Delta \tau^{1/2}} = 0.164 \ \text{kPa s}^{-1/2}. \quad (4)$$

According to experimental results the increase in absorption temperature ($t_2 = 218^\circ\text{C}$, $t_3 = 230^\circ\text{C}$) leads to the reduction in the first interval of the linear dependence of $\ln p$ versus $\tau$. This can be explained by the fact that at elevated temperature, the increase in the rate of the reaction (2) is higher than that of $H^-$ ion diffusion in the crystal lattice of cobalt. All this indicate that palladium catalyses hydrogen absorption into cobalt by enhancing the dissociation of adsorbed hydrogen molecules.
4. Conclusion

Hydrogen absorption into cobalt powder was catalysed by chemically deposited palladium. Palladium content was 0.003 wt. % (Co-0.003 Pd). The absorption of H$_2$ into pure Co and Co-0.003 Pd powders occurs via a complex mechanism. During the initial stage of absorption, the slow dissociation of adsorbed hydrogen molecules is the rate-determining step. During prolonged absorption, the absorption rate is determined by the slow diffusion of H$^+$ ions within the crystal lattice of cobalt. Palladium catalyses the absorption of hydrogen by dissociating the adsorbed hydrogen molecules more rapidly on its own atoms located on the surface of Co powder than on those of cobalt. The catalysis of the dissociation reaction, enables H$_2$ absorption into Co-0.003 Pd powder to occur at lower temperatures, with the substantially higher absorption enthalpy. The absorption enthalpy is higher at lower temperatures, since a decrease of the temperature results in a more rapid decrease of the H$^+$ ions enthalpy in cobalt powder compare to the enthalpy of H$_2$ molecules in the gas phase. The presented results show that Co-0.003Pd, exhibits high hydrogen absorption/desorption rate and high hydrogen storage capacity, which makes it suitable for the use in environmentally friendly energy generation processes, thus ensuring effective preventive protection of human health.

5. Acknowledgements

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6. References

0,003Pd праху на нижим температурама уз знатно већу ентазију апсорпије. Резултати овог истраживања омогућавају интеграцију технолошких истраживања и истраживања у домену очување јавног здравља, чиме се омогућава превентивна заштита здравља кроз очување човекове околине.

Кључне речи: кобалт, паладијум, апсорција/десорција водоника, процеси добијања енергије који не загађују животну средину