

The influence of melting atmosphere and casting on the mechanical and structural characteristics of palladium-nickel alloy

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The main aim of the research, presented in this paper, is to analyze the structural conditions of the PdNi5 alloy depending on the applied melting atmosphere and casting, as well as monitoring changes in the structural and mechanical properties of PdNi5 alloys after homogenization annealing in order to obtain the required quality castings for further plastic processing - rolling. In one case, the melting and casting of the alloy was done in medium frequency induction furnace in an charcoal atmosphere, while in the second, in a vacuum atmosphere. Hardness and the content of C, H, S were determined, and structural analysis of the cast samples using SEM and EDS analysis, was performed. Furthermore, after homogenization annealing at 800°, 900° and 1000°C, lasting 90 minutes, the hardness was determined and structural analysis with an optical microscope was performed and samples are subjected to plastic processing – rolling, with deformation degrees $\epsilon = 92\%$. Based on the analysis of the results, it was found that the melting and casting in vacuum with optimum heat treatment, could be applied to obtain satisfactory castings and structural characteristics for further plastic processing - rolling. The results presented in this paper may offer further knowledge of the effects various parameters have on the properties of palladium-nickel alloy.

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1. Introduction

The high cost of palladium and its extensive use in catalysis, electronic and electric devices, jewelry, medical and dental equipment, resulted in the fact that the manufacturers and researchers in many countries make significant efforts in order to get better knowledge of the properties of pure palladium and palladium alloys [1-3].

Softer than platinum, ductile and resistant to oxidation and high temperature corrosion, palladium is useful in eliminating harmful emissions produced by internal combustion engines. Autocatalysts are by far the largest user of palladium; autocatalysts convert over 90 percent of hydrocarbons, carbon monoxide and oxides of nitrogen produced in the exhaust from gasoline engines into carbon dioxide, nitrogen and water vapor [4].

Palladium and its alloys may be used as a contact material in electronics and telecommunications as they have good thermal stability and low contact resistance [2,3]. The good thermal stability as well as low contact resistivity could be realized simultaneously with the Pd / Ni contact).

Change of electrical resistivity with temperature above the Currie point (the temperature at which ferromagnetic substances turn into paramagnetic) does not depend on palladium concentration in the alloy [5].

Phase diagram of binary system Pd-Ni is shown in the figure 1. It shows a complete solubility of components in the solid state, with minimum on the liquidus and solidus curve (1273°C at 45% Pd) [6] without superlattices or intermediate phases [7]. This alloy is therefore called pseudoeutectic. Large range order in the alloys of Pd-Ni system was not found, while the short-range order is present at room temperature during isochronous annealing [8].

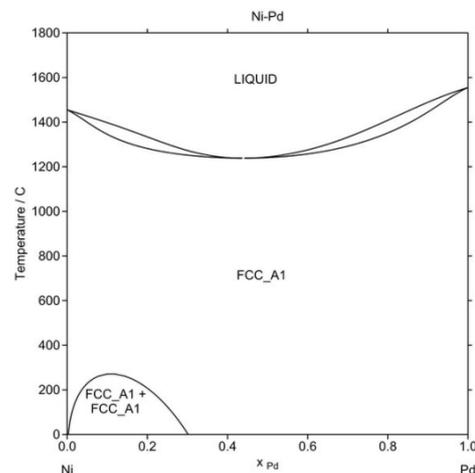


Fig. 1. Phase diagram of binary system Pd-Ni [6].

The magnetic transformation extends from the Ni side up to the Pd side at continuous decrease in temperature. Electric and magnetic behavior of the system Ni-Pd alloys were studied in the papers [8,9]. Perpendicular magnetic anisotropy of Pd/Ni-multilayers (MLs) with (111) and (100) orientations strongly depends on the crystal orientation.

The surface structure and condition of Pd-Ni alloys were studied using various techniques. The alloys of this system have expressed tendency towards segregation of palladium at lower temperatures and lower contents of palladium [10].

Relative thermodynamic properties of Ni-Pd system alloys were investigated by Bidwell and Speiser [11] who tested the thermodynamic properties of this system in the temperature range 700-1200°C. Based on studies, it was concluded that the excess entropies of mixing are positive for all compositions. This is considered to be the primarily result of ferromagnetic properties of the alloys.

The authors M.Kasprzak et al [12], observed that during diffusion annealing the microstructure is completely transformed so the new grains are formed at the interface and they are distinguished in composition. Formation of a globular grain, in contrast to the former columnar microstructure, can be seen.

The rapid solidification of Pd-Ni alloys is studied with the constant-pressure and constant-temperature (TPN) and the constant-volume and constant-temperature (TVN) molecular dynamics technique to obtain an atomic description of glass formation in the alloy [13]. Relation between the cooling rate and glass transition temperature was also studied. The results show that the atomic mismatch and having the eutectic composition are important parameters to form glassy state.

Thermal conductivity of Ni with the addition of elements, building a continuous series of solid solutions, was investigated by Terada and coauthors [14]. Reduction of thermal conductivity by alloying is analogous to the horizontal distance of the alloyed element of nickel in the periodic table, while cold rolling has no effect on thermal conductivity. At medium concentrations of the alloying element (Pd), the linear dependence of heat capacity on temperature is disrupted, what can be attributed to the disruption of short-range order [15].

Pd-Ni alloys are also used as cathode catalysts in direct methanol fuel cells [16], as electrocatalysts for

oxygen reduction in the acidic media [17], hydrogen-permeable membrane applied on porous carriers [18,19]. Also, Pd-Ni alloys are used in the production process of nitric acid as the Pd-catalyst-trap. The role of Pd-catalyst-trap consists in reduction of volatile platinum oxide from gas flow to the metal form and retention of platinum metal on the surface of Pd catalyst-trap. Pd-Au alloys [20,21] were previously used for making Pd-catalyst-trap, until nowadays when the alloys of Pd-Ni system are used [22,23].

The aim of this study was to investigate the influence of atmosphere during smelting and casting on mechanical and structural characteristics of PdNi5 alloy, and represents a contribution to the study of this system.

2. Experimental work

All experimental investigations which results are presented in this paper, were carried out on samples of the following labels: PdNi5-I, PdNi5-II, PdNi5-III, PdNi5-IV, PdNi5-V, PdNi5-VI, Pd-purity 99,99% and Ni-purity 99,95%. The nickel content in all samples was 5% wt.

Palladium, used for making all the samples, originating from the RTB Borproduction of electrolytic copper, was obtained as a by-product. The additional refining treatment in the Mining and Metallurgy Institute was carried out in order to increase the purity of palladium. Impurities in the samples were: Ag, Cu, Fe, As, Sb and Bi.

In order to achieve better compacting of materials, Pd-powder and Ni-sheet metal were pressed on hydraulic press with a force of 270 daN/cm².

Melting of PdNi5 alloy was carried out in the medium frequency induction furnace, in a MgO casting pot, size $h_1 \times h_2 = 85 \times 80$ mm, $d_1 \times d_2 = 65 \times 55$ mm. Casting temperature of PdNi5 alloy was 1520°C. Molten batch was overheated before casting for 150-170°C. Casting was done in graphite mold, pre-heated at temperature of 350-400°C. Samples PdNi5-I, PdNi5-II and PdNi5-III were melted under a protective layer of charcoal while the samples PdNi5-IV, PdNi5-V and PdNi5-VI were melted and cast in vacuum.

The basic characteristics of melting and casting samples are given in Table 1.

Table 1. The basic characteristics of melting and casting

Melting and casting under protective layer of charcoal						Melting and casting in vacuum	
PdNi5-I		PdNi5-II		PdNi5-III		PdNi5-IV, V, VI	
Sample mass, g	Casting time, s	Sample mass, g	Casting time, s	Sample mass, g	Casting time, s	Sample mass, g	Casting time, S
255.1	4.73	250.1	5.2	283.1	2.2	260.5	3.4

Annealing of samples was carried out in an electric resistance furnace of chamber type LP08.

Chemical analysis of cast samples was done on the atomic absorption spectrometer (AAS, Produced by: Perkins & Elmer, Model: 403, Detection limit: <0, 0001 g/dm³). Analysis of samples on the content of carbon, hydrogen and sulfur was carried out on a device CHNOS Elemental Analyzer, model VARIO Macro cube, manufacturer Elementar Analysensysteme GmbH. Hardness measurement was done on the combined device for measuring the hardness of Vickers and Brinell, WPM (Werkstoffprüf-maschinen), Leipzig, Germany, with hardness range of 5 to 250 daN, taking a 10-point average.

Microstructure testing of the alloy was done on samples with diameter of 20mm and 5 mm in height. The samples were prepared according to standard procedure - grinding, polishing (polishing machines ROWA E-KG) with 0,05 μm Al₂O₃ powder and etched a few seconds with HNO₃ solution (samples melted and cast under a layer of charcoal) and solution of HCl: HNO₃ = 1.5:1 (samples melted and cast in vacuum). After heat treatment these samples were etched in a solution of 1 g CrO₃ +20 ml HCl to obtain microstructure. Optical microscopy was performed on metallographic microscope EPYTIP 2, with magnification 200x. The general morphology of the samples was tested using the scanning electron microscopy (SEM model: JEOL JSM - 6610LV). The energy-dispersive spectrometer (EDS) was used to determine the chemical composition of the cast and the phases present in the system Pd-Ni.

3. Results and discussion

In order to obtain casts with satisfactory mechanical and structural characteristics for further plastic processing -rolling, the comparative analysis of melting and casting of alloys was done, under a protective layer of charcoal, in one case, and in a vacuum, in the second case.

Palladium and nickel are metals, which in the solid state build a continuous series of solid solutions (Fig. 1).

The structure of palladium-nickel alloy [24] is single-phase and consists of polyhedral surface-centered cubic grains of α-solid solution. Polyhedral structure of the solid solution occurs only when solidification is slow, so the concentration differences arose during crystallization could equate by diffusion. Otherwise, due to the rapid solidification of the melt in graphite molds, as in our case, there is a crystal segregation that in the metallographic

cross section can be identified by stratified built inhomogeneous dendrites, as shown in Fig. 2.

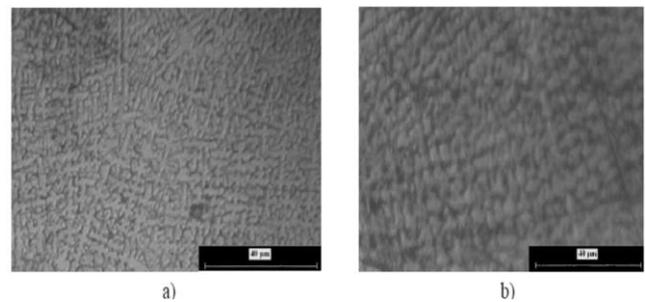


Fig- 2.95%Pd+5%Ni. Cast state. Inhomogenous α-solid solution. Crystal segregation. a) Melting and casting under the protective layer of charcoal PdNi5-II; b) Melting and casting in vacuum PdNi5-IV.

Soft, i.e. nickel poorer primary and secondary dendrite branches are clearly distinguished from solid, nickel richer inter-dendritic areas. Segregation in solid solution is as more pronounced as the cooling rate is higher and the rate of diffusion is lower, which is confirmed by our results.

For the purpose of comparative analysis of the mechanical and structural characteristics of PdNi5 alloy, they were melted and cast under a protective layer of charcoal, and in vacuum, and the content of carbon, hydrogen and sulfur in the alloys after melting and casting was determined.

Table 2 shows the results of testing of carbon, hydrogen and sulfur content in cast samples.

Table 2. Content of C,H and S in cast samples.

Samples	C(%)	H(%)	S(%)
PdNi5-I	0,1	0,015	0,143
PdNi5-II	0,11	-	-
PdNi5-III	0,95	-	0,049
PdNi5-IV,V,VI	-	-	-

Based on the results presented in Table 2, it can be concluded that the samples PdNi5-I,-PdNi5-II, PdNi5-III (melting and casting under a protective layer of charcoal), absorbed carbon from the charcoal and graphite molds, while in samples PdNi5-IV, PdNi5-V, PdNi5-VI (melting and casting in vacuum) there were no traces of carbon.

The results of measuring the hardness of cast samples are given in Table 3 and SEM and EDS results of samples PdNi5-II and PdNi5-IV are shown in Fig. 3.

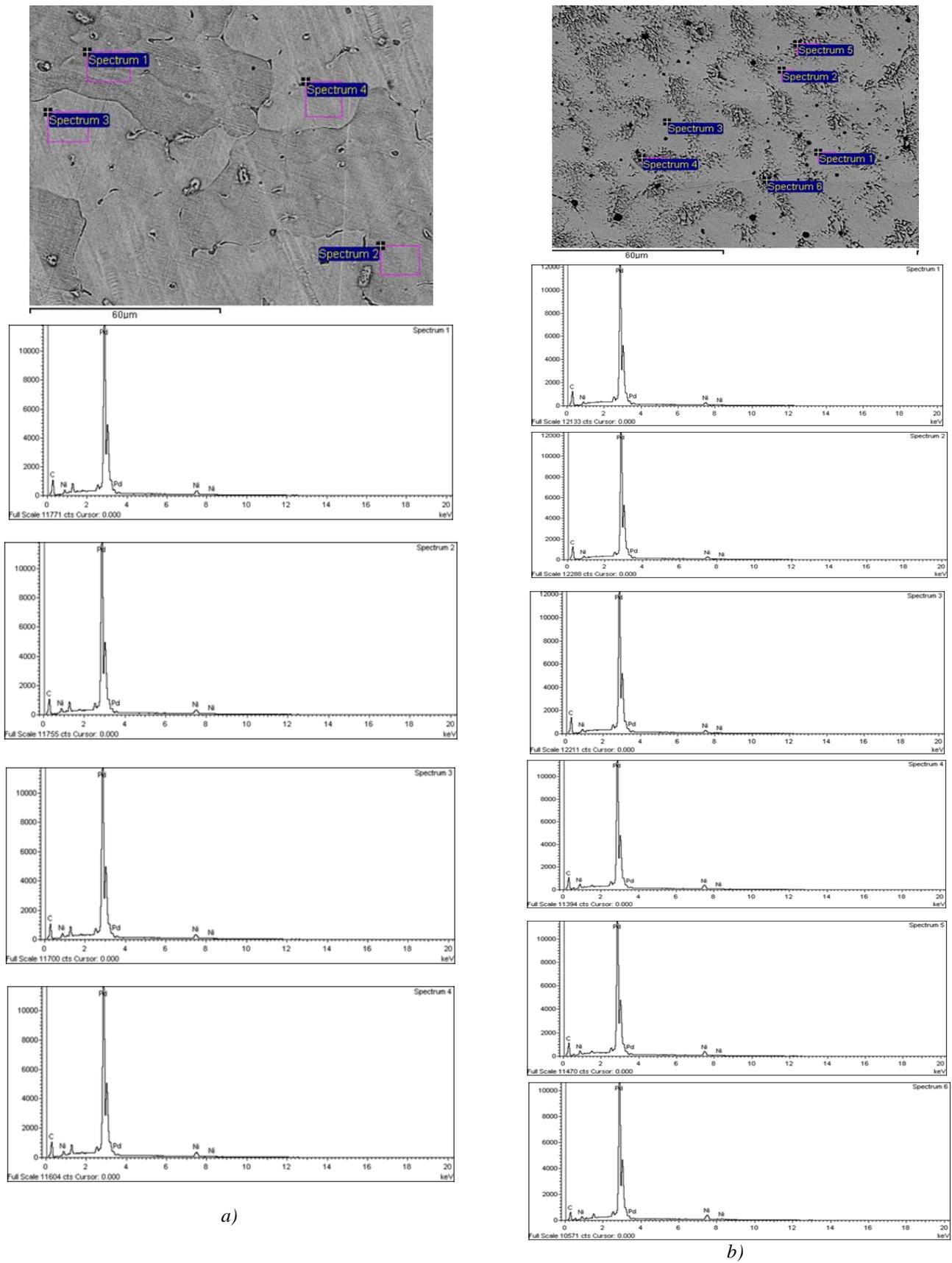


Fig. 3. SEM photos and EDS results of samples PdNi5-II and PdNi5-IV; a) Alloy PdNi5, melted and cast under a charcoal layer. The alloy quenched at 1550°C in water. Carbide precipitates at grain boundary and inside a grain. b) Alloy PdNi5, melted and cast in vacuum, the alloy quenched at 1550°C in water.

Table 3. Hardness values of cast samples

Samples	Hardness, HV/20 daN	Hardness, HV/10 daN
PdNi5-I	105,2	
PdNi5-II	105,1	
PdNi5-III	105,1	
PdNi5-IV		98,2
PdNi5-V		97,5
PdNi5-VI		99,3

Based on the results, it can be concluded that the melting and casting of PdNi5 alloy in a protective charcoal atmosphere caused carbon diffusion from the protective atmosphere into the alloy and creating of carbide crystals, so instead of a homogeneous solid solution, as was observed in the case of melting and casting in vacuum, an inhomogeneous alloy was obtained (α -solid solution + carbide crystals).

As a rule, an increase in temperature increases the ability of a metal to build solid solutions. Enhanced oscillations of atoms around the rest position [24], caused by a temperature rise, slacken the grid, so that the grid disturbances, caused by installing foreign atoms, can be reduced.

Temperature dependence of the solubility of the solid solution is often given by Van't Hoffovom equation[24]:

$$\log(X\%) = A - \frac{B}{T} \quad (1)$$

where: X - content of dissolved element in solid solution, at%.,

T - absolute temperature, K,

A, B - empirical constants for solid solutions.

Fig. 4. provides a basic flow of solubility line a-b in $T-C_b$ diagram, corresponding to equation (1) [25].

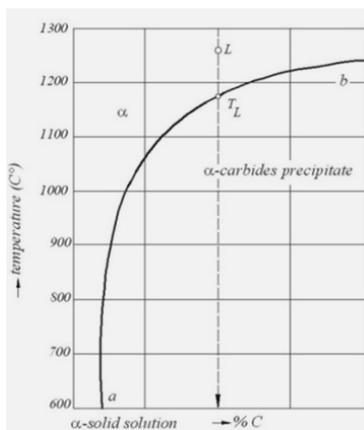


Fig. 4. Flow of solubility line a-b of solid solution [25].

In our case, it is a palladium-nickel solid solution, indicating temperature-dependent solubility for metal compound with carbon, so-called carbide. Homogeneous solid solution, α -phase, is stable only above the solubility line a-b. In the case of equilibrium, at temperatures below the line a-b, beside α -solid solution, the carbide crystals are also present. The alloys are heterogeneous then.

In order to create and extract carbide crystals at cooling down the α -solid solution, carbon atoms that are in the α -homogeneous solid solution evenly spaced, have to move a certain distance within the crystal lattice. This movement of atoms occurs by diffusion [24], so that the temperature and time, according to equation (2), play an important role in segregation:

$$X^2 = 2Dt = 2D_0 e^{-\frac{Q}{RT}} \cdot t \quad (2)$$

where: D_0, D – diffusion constants, $cm^2 \cdot s^{-1}$,
 Q - activation energy of diffusion, J/mol,
 R - universal gas constant, 8,314 J/molK,
 T - temperature, K,
 t - time, s.

If α -solid solution is quenched from phase field of solid solution, in water, then the time available for the diffusion is too short for atoms to move enough to extract. By quenching, the α -homogeneous solid solution, thermodynamically stable only at temperatures above the solubility line a-b, is obtained at room temperature also in a homogeneous state, and deposit formation is suppressed. The overall carbon remains dissolved in the α -solid solution [24,25].

Solid solutions, such as the solution obtained in our conditions, that due to the rapid cooling are not in balance, which are more alloyed than it corresponds to the equilibrium conditions, are referred to as oversaturated solutions. The movement speed of atoms at room temperature is very low, hence oversaturated solid solutions can stand, at appropriate low temperatures, arbitrarily long time without making deposits.

In order to eliminate crystal segregation of PdNi5 alloy casts, melted and cast under a protective layer of charcoal, and in vacuum, the samples were subjected to homogenization annealing. The annealing was performed at 800°C, 900°C and 1000°C for 90 minutes. Metallographic photos of structures of samples PdNi5-II and PdNi5-IV are shown in Figs. 5 and 6.

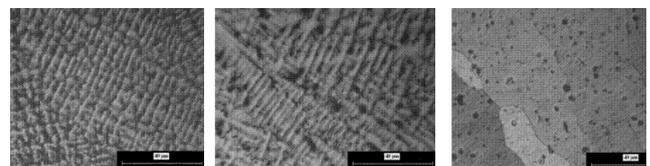


Fig. 5. Microstructure of the PdNi5-II sample after homogenization annealing at various temperatures for 90 minutes.

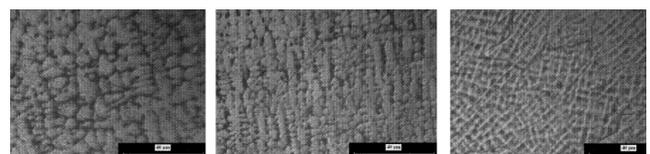


Fig. 6. Microstructure of the PdNi5-IV sample after homogenization annealing at various temperatures for 90 minutes.

Based on the presented results for the sample PdNi5-II, we come to the conclusion that if the oversaturated solid solution is annealed at higher temperatures, as soon

as it passes a critical temperature the formation of deposits occurs. The amount and size of deposit depend on the temperature and annealing time. The higher the temperature and the longer the annealing time, the closer the alloy to the equilibrium and the larger the precipitate crystals.

If the alloy is annealed at 800°C, numerous very fine carbide crystals occur in the α -solid solution, (Fig. 5a). The precipitate has particularly segregated on the sliding planes. That way a different grid structure of twinning lamellas clearly comes to the fore. Raising the annealing temperature to 900°C, (fig. 5b) causes rougher carbide precipitate. It is clear that the position of carbide rods is approximately dependent on α -solid solution. Annealing temperature of 1000°C, (fig. 5c) causes coagulation of carbide particles. Carbide precipitate isolates at the grain boundaries as well as inside the grains themselves.

In solid solutions which solubility is dependent on temperature, the state of the structure depends on the cooling rate and subsequent annealing [24,25]. The higher the cooling rate, the less precipitate extract, and a greater saturation of solid solution. In contrast, the higher the temperature and the longer the annealing time, the fully the balance restores, what have been confirmed by the results for PdNi5 alloy melted and cast in a protective charcoal atmosphere.

Fig. 6 from a to c show the effect of different annealing temperature on the removal of crystal segregation in PdNi5 alloys, melted and cast in vacuum. Annealing at 800°C for 90 minutes led to some equalization of concentrations of alloying element in the central part of the crystal, which solidified first, and the crystal areas which solidified last (Fig. 6 a). Dendrites form and their boundaries to the areas that solidified last still exist, but the contrasts have decreased. After annealing for 90 minutes at 900°C dendrites are just discernible, (Fig. 6 b). Further increasing of the annealing temperature to 1000°C, (Fig. 6 c), leads to a solid solution grain boundaries become clearly marked. It can also be seen that the orientation of dendrites inside a grain is always the same, but considerably varies from grain to grain, showing a good agreement with literature data [24,25].

The results of hardness measurements of the investigated samples after homogenization annealing at 800°C, 900°C and 1000°C for 90 minutes are shown in Fig. 7.

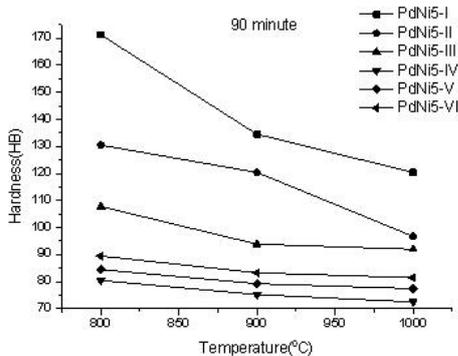


Fig. 7. Dependence of hardness, HB, of alloy PdNi5 on temperature, after 90 minutes of annealing.

Based on the presented results of hardness depending on the annealing temperature (Fig. 7), it can be concluded that the hardness of the alloy increases as much as the amount of extracted carbide increases. The α -solid solution has a lowest hardness value, $HB=105,1 \text{ N/mm}^2$. Samples PdNi5-II annealed at 800°C and then quenched in water, have hardness value of $130,5 \text{ N/mm}^2$, while quenched from 900°C have hardness value of $120,4 \text{ N/mm}^2$, and quenched from 1000°C have hardness value of $111,8 \text{ N/mm}^2$.

Measuring the hardness of the sample PdNi5-IV (melting and casting in vacuum) led to the following results: Samples quenched from 800°C have hardness value of $84,5 \text{ N/mm}^2$, quenched from 900°C $79,3 \text{ N/mm}^2$, while samples quenched from 1000°C have hardness value of $77,5 \text{ N/mm}^2$. The hardness value for α -solid solution was $98,2 \text{ N/mm}^2$.

With the aim of further comparative analysis of the influence of the melting atmosphere and casting of PdNi5 alloy on further behavior during plastic processing, after the homogenization annealing, the samples were subjected to rolling with total deformation degree of $\epsilon=92\%$.

The results of plastic processing of PdNi5 alloys are shown in Figs. 8 and 9.

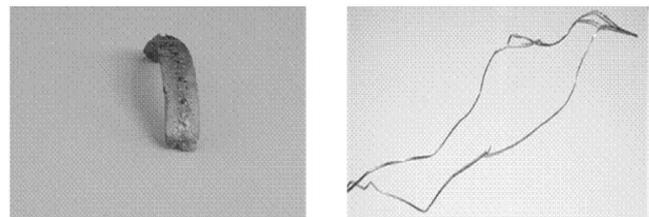


Fig. 8. View of the PdNi5-II sample (melting and casting in the charcoal atmosphere) after rolling.



Fig. 9. View of the PdNi5-IV sample (melting and casting in the vacuum atmosphere) after rolling.

Based on the results shown in Fig. 8, it can be concluded that the alloy PdNi5 melted and cast in the protective charcoal atmosphere, due to absorption of carbon, is not suitable for further plastic processing. The sample showed strong porosity after the rolling, which caused a splitting of the sample along the length.

PdNi5 alloy melted and cast in vacuum had a pronounced plasticity during rolling processing. The result

of good work ability was obtaining a wire (Fig. 9) with satisfactory mechanical properties.

Based on the investigation of the influence of the melting atmosphere and casting of PdNi5 alloy, it can be concluded that melting and casting of that alloy in vacuum leads to obtaining castings with good mechanical and structural properties suitable for further plastic processing (Fig. 9).

For further researches, based on the results presented in this paper, it is necessary to do mathematical modeling of technological process of PdNi5 wire production, so the hardness, tensile strength and elongation values, which are the key factor in the application of catalysts made of palladium-nickel wires, could be reliably predicted with the choice of operating parameters of the process. Mathematical modeling would be performed using multiple linear regression (MLRA), Simplex method, or Artificial Neural Networks (ANNs) [26-30].

4. Conclusion

The paper presents the results of a comparative analysis of the mechanical and structural characteristics of the PdNi5 alloy melted and cast in the charcoal atmosphere and vacuum, in order to obtain satisfactory quality castings for further plastic processing.

Based on the results, the following can be concluded:

All the samples obtained in charcoal atmosphere and in vacuum, cast in a graphite mould and cooled in water, have a very pronounced dendritic structure.

The samples obtained by melting and casting in the charcoal atmosphere, due to absorption of carbon, have higher hardness values than samples obtained in a vacuum atmosphere, where there is no record of the carbon presence.

For samples obtained in the charcoal atmosphere, selected regime of homogenization annealing led to the segregation of carbide particles in the solid solution, which resulted in hardness increase. Further plastic processing (rolling, 29 % ϵ) resulted in a cracking patterns due to the high porosity and the carbon presence. Any change in the regime of plastic processing would not lead to the achievement of better results.

The best structural and mechanical properties were obtained by the samples from the vacuum atmosphere, with the selected regime of homogenization annealing ($T=900^{\circ}\text{C}$ and $t=90\text{ min}$). With the selected regime of plastic processing (rolling, 29 % ϵ) the wire with satisfactory mechanical properties was obtained, which was the goal of the work.

The above results, can be on the one hand, considered as a contribution to the characterization of PdNi5 alloy, bearing in mind that the above alloy hasn't been investigated enough from the point of determination of structural and mechanical properties depending on the melting atmosphere and casting, and on the other hand, are important for the selection of the optimal technology for obtaining products based on these alloys.

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References

- [1] G. Slavkovic, B. Trumic, D. Stankovic, Mining engineering, **2**, 181 (2011)
- [2] M. Antler, The Application of Palladium in Electronic Connectors, Platinum Metals Rev. **26**(3), 106 (1982).
- [3] H. W. Jang, H. K. Cho, J. Yong Lee, Jong-Lam Lee, Microstructural and Electrical Investigation of Low Resistance and Thermally Stable Pd/Ni Contact on p-Type GaN, J. Electrochem. Soc. **150**(3), G212 (2003).
- [4] S. Dragulović, Z. Ljubomirović, Z. Stanojević Šimšić, V. Conić, S. Dimitrijević, V. Cvetkovski, V. Trujić, Optoelectron Adv. Materials – Rapid Comm. **5**(12), 1370 (2011)
- [5] K. Ikeda, Electrical Resistivity and Ferromagnetism in Ni-Pd Alloys, Journal of Applied Physics, **62**(11), 4499 (1987).
- [6] <http://resource.npl.co.uk/mtdata/phdiagrams/nipd.htm>
- [7] P. V. Petrenko, A. V. Gavriljuk, N. P. Kulish, N. A. Mel'nikova, Yu. E. Grabovskii, The Physics of Metals and Metallography, **108**(5), 449 (2009).
- [8] H. Takahashi, S. Fukatsu, S. Tsunashima, S. Uchiyama, Journal of Magnetism and Magnetic Materials, **104–107**(3), 1831 (1992).
- [9] A. Tari, B. R. Coles, Journal of Physics F: Metal Physics, **1**(6), L69 (1971).
- [10] S. Helfensteyn et al., Applied Surface Science, **212–213**, 844 (2003).
- [11] L. R. Bidwell, R. Speiser, Acta Metallurgica **13**(2), 61 (1965).
- [12] M. Kasprzak, D. Baither, G. Schmitz, Acta Materialia, **59**(4), 1734 (2011).
- [13] S. Ozdemir Kart, M. Tomak, M. Uludogan, T. Cagin, Turk J Phys. **30**, 319 (2006).
- [14] Y. Terada, K. Ohkubo, T. Mohri, Journal of Applied Physics, **81**(5), 2263 (1997).
- [15] J. Tomiska, J. Qing, R. Luck, Zeitschrift fur Metallkunde **84**(11), 755 (1993).
- [16] J. Zhao, Electrochimica Acta **55**, 1756 (2010).
- [17] G. Ramos-Sánchez, H. Yee-Madeira, O. Solorza-Feria, International Journal of Hydrogen Energy, **13**(33), 3596 (2008).
- [18] S. E. Nam, K. H. Lee, Journal of Membrane Science, **170**, 91 (2000).
- [19] Ø. Hatlevik, S. K. Gade, M.K. Keeling, P. M. Thoen, A. P. Davidson, J. D. Way, Separation and Purification Technology, **73**, 59 (2010)

- [20] B. Trumić, D. Stanković, V. Trujić, J. Min.Metall. Sect. B. **45**(1), 69 (2009).
- [21] Y. Ning, Z. Yang, H. Zhao, Platinum Metals Rev.**40**(2), 80 (1996).
- [22] R. Kraehnert, M. Baerns, Applied Catalysis A: General **327**, 73 (2007).
- [23] B. Trumic, D. Stankovic, V. Trujic, J. Min.Metall. Sect. B. **45**(1), 79 (2009).
- [24] Hermann Schumann, Metallographie, Leipzig, VEB Deutscher Verlag für Grundstoffindustrie, 1975.
- [25] E. Savitsky, V. Polyakova, N. Gorina, N. Roshan, Physical metallurgy of platinum metals, Translated from Metallovdennije platinovyh metallov, Metalurgiya Publishers, Moscow, 1975.
- [26] Ž. Živković, I. Mihajlović, Đ. Nikolić, Serbian Journal of Management, **4**(2), 143 (2009).
- [27] P. Đorđević, I. Mihajlović, Ž. Živković, Serbian Journal of Management, **5**(2), 189 (2010).
- [28] I. Mihajlović, N. Štrbac, P. Đorđević, A. Ivanović, Ž. Živković, Serbian Journal of Management, **6**(2), (2011), pp.135-144.
- [29] S. Ivanov, E. Požega. Sci. Sinter. **40**(2), 197 (2008).
- [30] S. Lj. Ivanov, Lj. S. Ivanić, D. M. Gusković, S. A. Mladenović. Hem. ind. **66**(4), 601 (2012).

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