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PdNi5 ALLOY: EFFECT OF THERMO-MECHANICAL TREATMENT ON MECHANICAL AND MICROSTRUCTURAL PROPERTIES[***]

Abstract

In this paper, the effect of thermomechanical processing on microstructure and mechanical properties of cold rolled samples of PdNi5 alloy was investigated for the purpose of its characterization. After melting and casting in a vacuum, a thermomechanical treatment was applied including the homogenization annealing in temperature range 800-1000^{o}C for 30, 60 and 90 minutes, cold rolling with deformation degrees of 60, 85 and 97%, recrystallization annealing in the temperature range of 200-1000^{o}C for 20, 30 and 40 minutes and electroresistant annealing at speed of 14, 16 and 24 meters per minute for the PdNi5 wire with diameter of 0.15 mm, and at speed of 18, 22 and 24 meters per minute for the PdNi5 wire with diameters of 0.111 and 0.08 mm with measurement of hardness, tensile strength, relative elongation and observing the structural changes using optical and SEM microscopy

The test results of influence of parameters of thermomechanical processing on the mechanical and structural properties of the PdNi5 alloy show that the process should be led in strictly defined conditions in order to be able to use this alloy for making catalyst-catchers in high-temperature catalytic processes in the production of nitric acid.

Keywords: *PdNi5 wires, catchment gauze, thermo-mechanical treatment*

INTRODUCTION

The high price of palladium is a limiting factor in the study of Pd-Ni alloys, so the number of scientific papers which include their characterization is relatively small. However, a widespread application of the platinum based alloys in the processes of catalysis, electronics industry, the jewelry industry, for production the medical and dental equipment, has led to a fact that researchers in many countries make the significant efforts to study this system alloys [1-7]. The binary phase diagram of the Pd-Ni system is shown in Fig. 1 [8]. It shows a complete solubility of components in the solid state, with minimum on the liquidus and solidus curve (1273^{o}C at 45at.% Pd) [8] without superlattices or intermediate phases [9]. In the alloys of Ni-Pd system, at cooling, surface-centered cubic α-solid solution is formed. As soon as is reached at cooling the area of interruption in solubility in the solid state is reached, at cooling, the surface-

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centered cubic α-solid solution decomposes into two also surface-centered cubic α - solid solutions of different composition: α_1 - solid solution is richer in nickel, and α_2 - solid solution is richer in palladium than it fits the overall composition of the alloy. Decomposition of surface-centered cubic α-solid solution on the two solid solutions of different composition but the same lattice, is the result of different lattice constants of the Ni (a = 0.35238 nm), and Pd (a = 0.38902 nm).

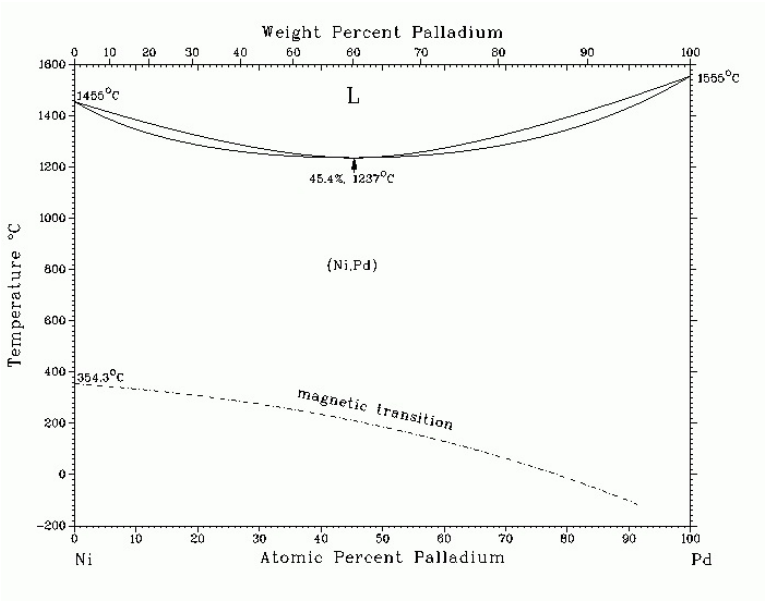


Figure 1 *The binary phase diagram of the system Pd-Ni*

Only a few papers have been found [10, 11] by the authors who dealt with Pd-Ni and thermo-mechanical treatment on the properties of PdNi5 alloy, and that is why this alloy was selected for the study in order to determine the optimal conditions for thermo-mechanical processing regime, so it could be used for making catalyst-catchers to capture the platinum in catalysis process at high temperatures.

Therefore, the object of this paper is to study the effect of the complex thermo-mechanical treatment on improvement the mechanical properties and electrical conductivity, as well as the structural changes occuring in the alloy. Keeping in mind the complex influence of deformation degree, annealing time, annealing temperature and texture on the recrystallization rate, and also on the recrystallized grain size and mechanical characteristics, the experiments with annealing time and annealing temperature change on the alloy Pd-5% mass Ni with different degree of deformation for further plastic processing in order to make yhe Pd-catalyst-traps, was carried out in this work.

EXPERIMENTAL

The binary Ni-Pd alloy with 5% mass nickel was obtained by melting of 99,99% purity palladium powder and 99,95% purity nickel as a sheet metal in the medium frequency induction furnace, in a MgO casting pot, sized $h_1 x h_2$ = 85x80 mm,

d_1xd_2 = 65x55 mm. In order to achieve better compacting of materials, Pd-powder and Ni-sheet metal were pressed on a hydraulic press with a force of 270 daN/cm^2. Casting temperature of PdNi5 alloy was 1520^{o}C. Molten batch was overheated before casting of 150-170^{o}C. Casting was done in a graphite mold, pre-heated at temperature of 350-400^{o}C. Samples were melted and cast in vacuum. All cast samples with a circular cross-section (Ø20 mm) were homogenized at 800, 900 and 1000^{o}C during 30, 60 and 90 minutes in an electric resistance furnace of chamber type LP08. All samples were quenched in water. After quenching, the samples were cold rolled on the stand rolls with calibrated rollers, system square-square, to the calculated dimensions of 11.2 mm; 6.8 mm and 2.3 mm with 60%, 85% and 97% reductions, respectively, with the inter-phase annealing for 15 minutes at 900°C followed by quenching in water. Heat treatment after rolling consisted of the recrystallization annealing the samples of PdNi5 alloy, in a wire form, in the electric resistance furnace of chamber type LP08 without protective atmosphere, at temperatures in the range 200-1000^{o}C during 20-40 minutes interval. All samples were quenched in water after annealing. The final wire drawing dimensions (Ø 0.15 mm, 0.11 mm and 0.08 mm) were achieved by drawing with 99% reduction. After reduction, all samples were exposed to the recrystallization annealing at the electrical resistance annealing speed from 14 m/min to 24 m/min for different annealing voltages from 20 V to 36 V.

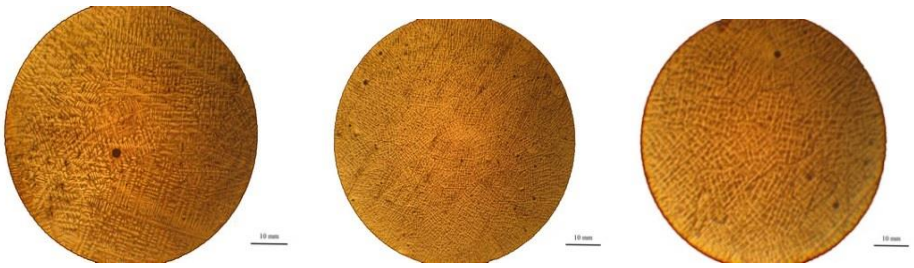
After the thermo-mechanical treatment, the values of hardness, tensile strength, elongation and electrical conductivity were measured and structural changes were observed by the optical and scanning electron microscopy. Hardness measurement was done on the combined device for measuring the hardness of Vickers and Brinell, WPM, Leipzig, Germany, at a load of 5 kgf and load duration of 15 s according to ASTM:E384, taking the 3-point average. Tensile strength and elongation were measured using a universal device for tensile testing, type „Mohr + Federhaf + Losenhansen“ – Manheim and testing machine Otto Wolpert up to 100 kg with the extent to 5 kg. Before testing, all samples were cut to a length of 150 mm. Electrical conductivity was measured using the Wheatstone bridge. Microstructural changes in the course of thermo-mechanical treatment were observed on a metallographic microscope EPYTIP 2, with magnification of 80 to 400 times and on a JEOL JSM-6610LV scanning electron microscope with an EDS detector. For the metallographic testing, samples were prepared according to the standard procedure - grinding, polishing (polishing machines ROWA E-KG) with 0.05 μm Al_2O_3 powder, and etched a few seconds with solution of 1 g CrO_3 +20 ml HCl to obtain a microstructure.

RESULTS AND DISCUSSION

I The effect of homogenization annealing on mechanical properties and microstructure

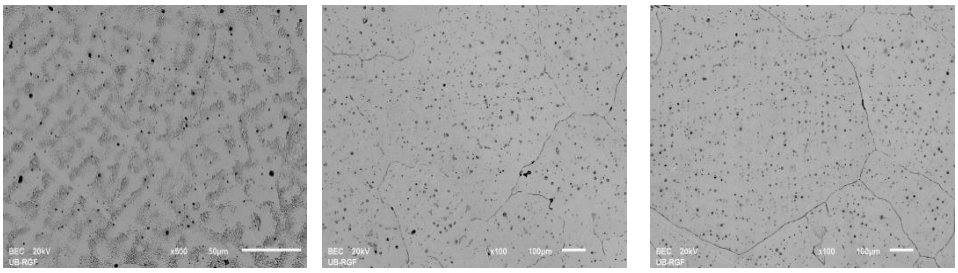
Figure 2 shows the optical microphotographs, while Figure 3 shows the scanning electron microphotographs of the alloy after different thermo-mechanical treatment. Microsrtucture of the alloy after homogenization annealing at 800^{o}C for 30 minutes is shown in Figures 2a and 3a. It is noted that the used heat treatment did not lead to degradation of cast dendritic structure. Homogenization annealing was carried out in order to eliminate a segregation and obtain a homogeneous structure [12]. Further increasing of the annealing temperature to 900^{o}C for 30 minutes (Figures 2b and 3b) led to some equalization of concentrations of alloying element. Dendrites form and their boundaries to the areas that solidified last, still exist, but the contrasts have de

creased and dendrites are just discernible. It is noticeable that duration of homogenization annealing (30 minutes at 900^{o}C) was not sufficient for complete homogenization of the structure, or complete breakdown of the dendritic branches. Furtherincreasing of the annealing temperature to 1000^{o}C, Figures 2c and 3c , 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 the literature data [13,14].



a) *b)* *c)*

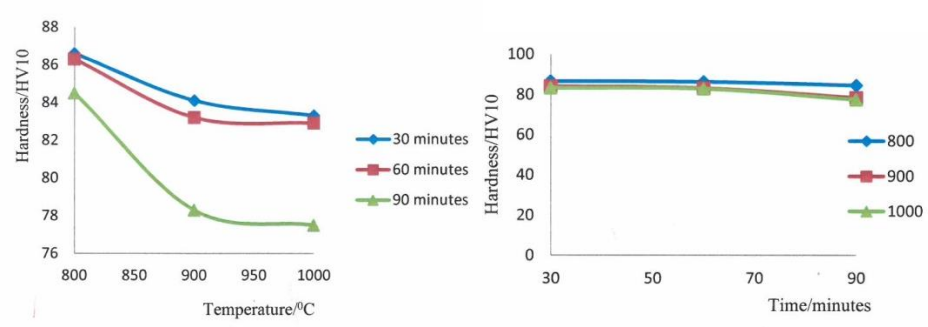
Figure 2 *Optical microphotographs of the alloy after homogenization annealing during 30 minute at: (a)800^{0}C, (b) 900^{0}C, (c) 1000^{0}C, 80x. The samples are quenched in water*



a) *b)* *c)*

Figure 3 *Scanning electron micrographs of the alloy after homogenization annealing during 30 minute at: (a)800^{0}C, (b) 900^{0}C, (c) 1000^{0}C*

Figure 4 shows the effect of different parameters of homogenization annealing on hardness values. An increase in the temperatures values contributes to a decrease in hardness values due to the equalization of concentration difference in the structure. Temperature influence in comparison with influence the time of homogenization annealing on a change of hardness values (Figures 4a and 4b) is significant. The cast samples have a highest hardness value 98 HV 10 and the annealed samples at 800^{o}C for 30 minutes have 86.6 HV 10. Further increase of temperature to 900^{o}C and 1000^{o}C leads to a decrease to 84.1 HV 10 and to 83.3 HV 10, respectively.



a) *b)*

Figure 4 *Effect of parameters of homogenization annealing on hardness values*

Figure 5 shows the effect of parameters of homogenization annealing on microhardness values. It can be observed that th microhardness values of homogenized samples decrease with increase of temperature and time of homogenization annealing. A sample after homogenization annealing at 1000°C for 90 minutes has minimum microhardness value (102.56 HV 0.15). According to the microhardness value of sample after homogenization annealing, it can be concluded that the microhardness at 800°C for 30 minutes decreases for 36%.

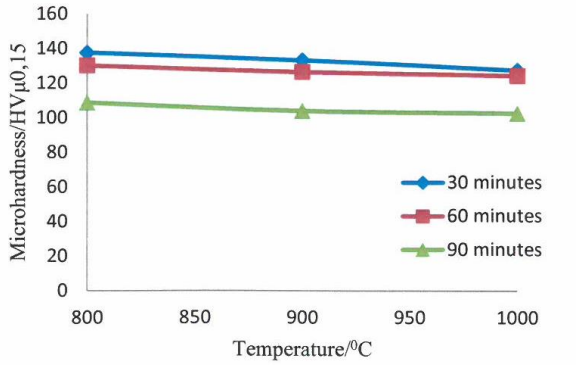


Figure 5 *Effect of parameters of homogenization annealing on microhardness values*

The effect of homogenization anneling on electrical conductivity values is shown in Figure 6. Pure metals have a proper and uniform crystal lattice, and therefore have a small electrical resistance. Additives in small quantities distort the crystal lattice, and increases electrical resistance. The same is also with the alloys from a solid solution, i.e. which together with the solidification are crystallized, and atoms are incorporated in a crystal lattice of the other element. The temperature increase leads to the intense thermal vibrations of atoms in the crystal lattice, but the mobility of conductive electrons is less due to the collisions with atoms of the crystal lattice. Comparative effect of these factors affects the electrical conductivity values as shown

in Figure 6. It can be observed that the electrical conductivity values slightly decrease with an increase of homogenization annealing time and temperature.

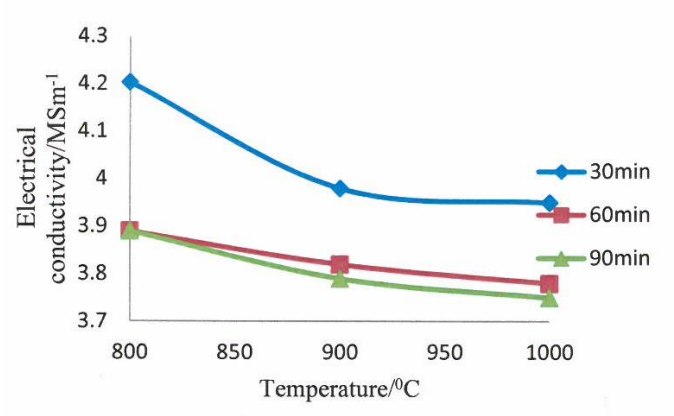


Figure 6 *Effect of parameters of homogenization annealing on electrical conductivity values*

II The effect of recrystallization annealing on mechanical properties and microstructure

Figure 7 shows the effect of annealing on the hardness values of finally rolled samples with 60%, 85% and 97% reduction. It can be seen that during annealing, the hardness values of the cold deformed alloy at temperatures below 400°C do not change, but internal stresses are removed.

In the temperature range from 400°C to 500°C, i.e. in the interval of recovery of crystals, there is a continuous decrease of hardness in samples deformed with lower degrees of deformation (60% and 85%), while in samples deformed with deformation degree of 97% this interval extends up to 600°C. In this temperature range, in addition to the removal of internal stresses, the recovery of crystal structure occurs by removal the small defects in the crystal lattice due to the increased rate of diffusion of atoms. In the area of recovery no changes in hardness of samples occur, given that there is no change in dislocation density, but only to their redistribution, so there is no change in the structure (Figure 7a). At 500°C (ε = (60 or 80)%) and at 600°C (ε = 97%) the hardness rapidly decreases indicating the occurrence of a texture change, i.e. a new structure appeared (Figure 7b). The newly formed structure, during the primary recrystallization process, is a polygonal and with the strain free grains. This character of change in mechanical properties in this temperature range is caused by reduction a dislocation density and removal the subgrain boundaries. Further increase in annealing temperature above the recrystallization temperature results in a gradual, but quite small, reduction of hardness, due to the increase in grain size, which is a sign of the secondary recrystallization (Figure 7c).

Hardness values after recrystallization annealing decrease with the increase of the cold plastic deformation degree.

Recrystallization temperature of pure palladium is around 500°C [12] and depending on the presence of impurities and de

formation degree. It is noted (Figure 6), that the joint effect of the alloying palladium with nickel and deformation degree effect in the Pd-Ni alloy, shifts the recrystallization temperature to even 600°C. With increasing deformation degree, recrystallization temperature shifts to the lower temperature values, as a results of the increased stored energy, which causes a smaller critical size of the nucleus and decrease in the activation energy for recrystallization, i.e., nucleation and growth of recrystallized grains become easier [12,15].

Microstructure of the PdNi5 alloy with 97% reduction after annealing at different temperatures for 30 minute is given in Figure 8. It was noted that to the annealing temperature of 500°C oriented deformation structure retains, in all samples (Figure 8a). Comparing to the structure of the cold-deformed samples of PdNi5 alloy, no change can be observed in the structure. The shape and size of grains correspond to the state after the end of the plastic deformation, and also the grid orientation of individual grains remains the basically retained [16]. By increasing the annealing temperature to 700°C, the elongated grains vanished, and the new polygonal grains were formed (Figure 8b). This is a distinctive sign of recrystallization. The increase in the annealing temperature at 900°C causes further growth of the grains (Figure 8c).

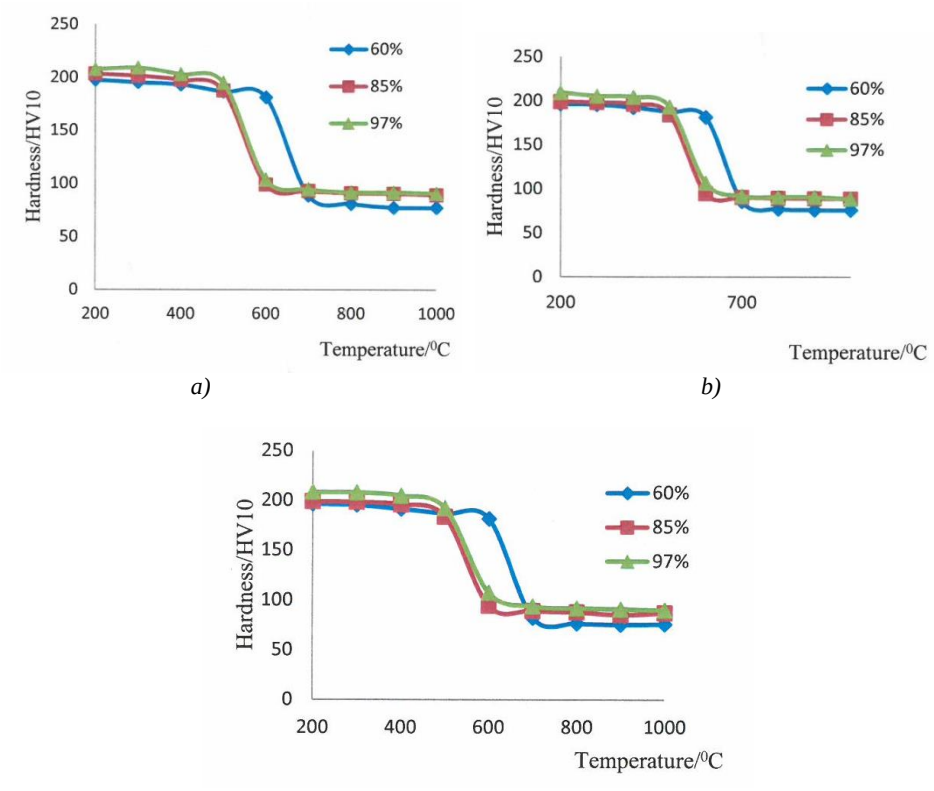
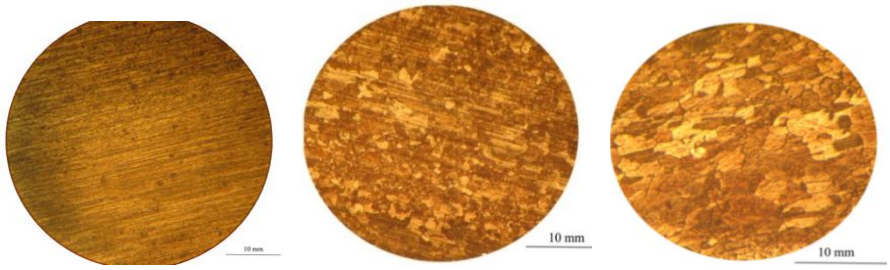


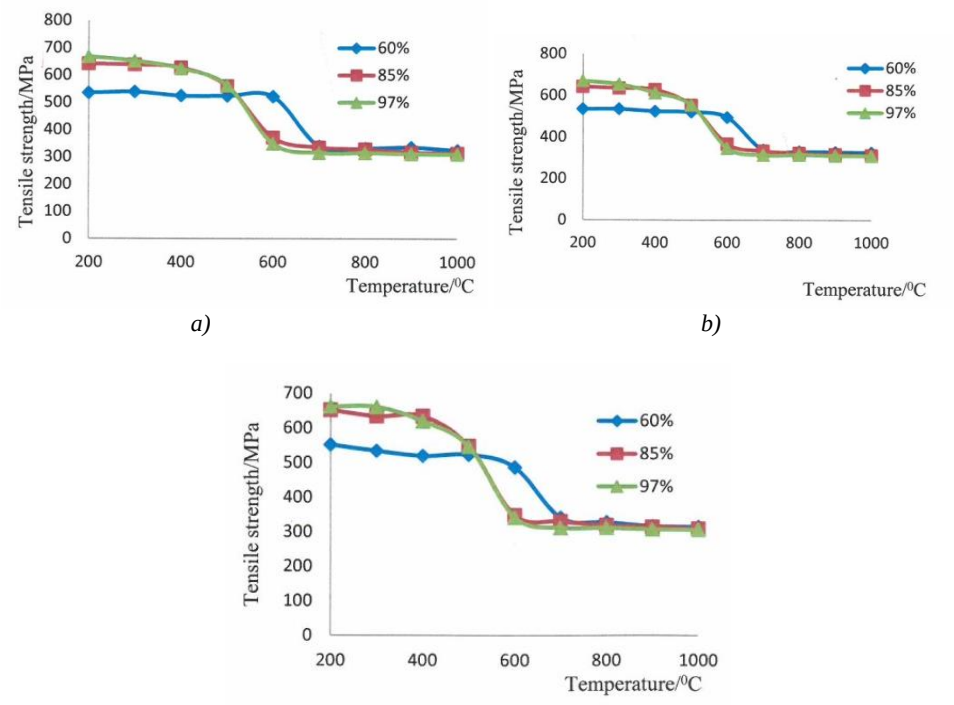
Figure 7 *Dependence of hardness, HV, PdNi5 alloy of deformation degree, annealing temperature and time: a) 20 minutes; b) 30 minutes; c) 40 minutes*



a) *b)* *c)*

Figure 8 *Optical microphotographs of the alloy with a deformation degree 97%, after annealing for 30 minutes at: (a)500^{0}C, (b) 700^{0}C, (c) 900^{0}C, 400x. The samples are quenched in water*

Figure 9. shows an effect of annealing on the tensile strength values of finally rolled samples with 60%, 85% and 97% reduction.



a) *b)*

c)

Figure 9 *Dependence of tensile strength PdNi5 alloy of deformation degree, annealing temperature and time: a) 20 minutes; b) 30 minutes; c) 40 minutes*

From the study results it can be seen that the tensile strength of cold-deformed and differently heated PdNi5 alloy samples in the form of wire, does not change continu

ously with increasing annealing temperature. Tensile strength virtually does not change to a temperature of 400°C, while in the temperature range 400-500°C there is a slight decline in R_m. This is a consequence of reducing the concentration and redistribution the errors in a lattice. At 500°C, there is a rapid decrease of tensile strength in samples deformed with a greater deformation degree (85% and 97%), while in samples deformed with adeformation degree of 60%, this change occurs at 600°C. This change takes place in a very narrow temperature range (500-600°C) or (600-700°C), and is a result of advancement the recrystallization process and formation of a new, undeformed structure, which is noted by metallographic examination (Figure 8). Further increase of annealing temperature above 600°C or above 700°C leads to grain growth, which causes a further slight decrease in tensile strength, due to occurrence the secondary recrystallization, or structure enlargement.

Figure 10 shows an effect of annealing on elongation values the finally rolled samples with 60%, 85% and 97% reduction.

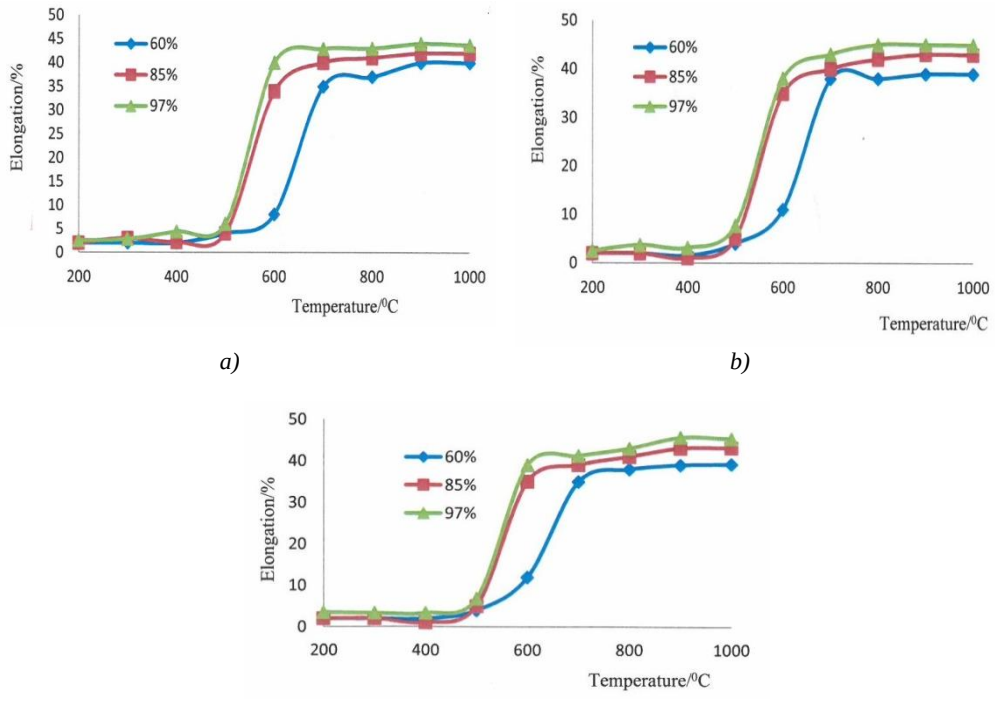


Figure 10 *Dependence of elongation PdNi5 alloy of deformation degree, annealing temperature and time: a) 20 minutes; b) 30 minutes; c) 40 minutes*

III The effect of electrical resisatnce annealing on mechanical properties

Figures 11 and 12 graphically present the dependence of tensile strength (Rm) and elongation (A) of drawn PdNi5 wires produced by high deformation (97%), on annealing voltage and speed after cold work.

It can be concluded from the results, shown in Figures 11a) and 12a), for the wire diameter 0.15 mm, that with the increase of voltage and resistance annealing speed, the values of tensile strength slightly decrease, while, at the same time, the relative elongation values slowly increase. The maximum values of elongation (46.5%) with acceptable value of tensile strength (321,45 MPa) for the aforementioned wire is achieved by annealing at voltage of 24V and speed of 24 m/min.

For the wire with diameter 0.11 mm (Figures 11.b) and 12.b)) values of tensile strength and elongation show a similar behaviour as for the wires of 0.15 mm in diameter. The maximum value of elongation (36.5%) with acceptable value of tensile strength (313.5 MPa) was achieved by annealing at voltage of 28V and speed of 18 m/min.

For the wire with diameter 0.08 mm with increasing voltage and resistance annealing speed, the values of tensile strength also slightly decrease while the relative elongation values rapidly increase (Figures 11c) and 12c)). The maximum value of elongation (35.5%) with acceptable value of tensile strength (286 MPa) was achieved by annealing at voltage of 32 V and speed of 18 m/min. This character of change the mechanical properties was caused by the consolidation of recrystallized structure.

For voltage values lower than 20 V, for wire of $\emptyset$ 0.15 mm, and 28 V for wires of $\emptyset$ 0.11 and 0.08 mm, as well as for the voltage values higher than 24 V and 36 V, the tensile strength and elongation show the values unsuitable for further use of wires for making palladium catalysts-catchers. Namely, the insufficient or excessive annealing of wire occurs, which results in the low values of tensile strength and elongation.

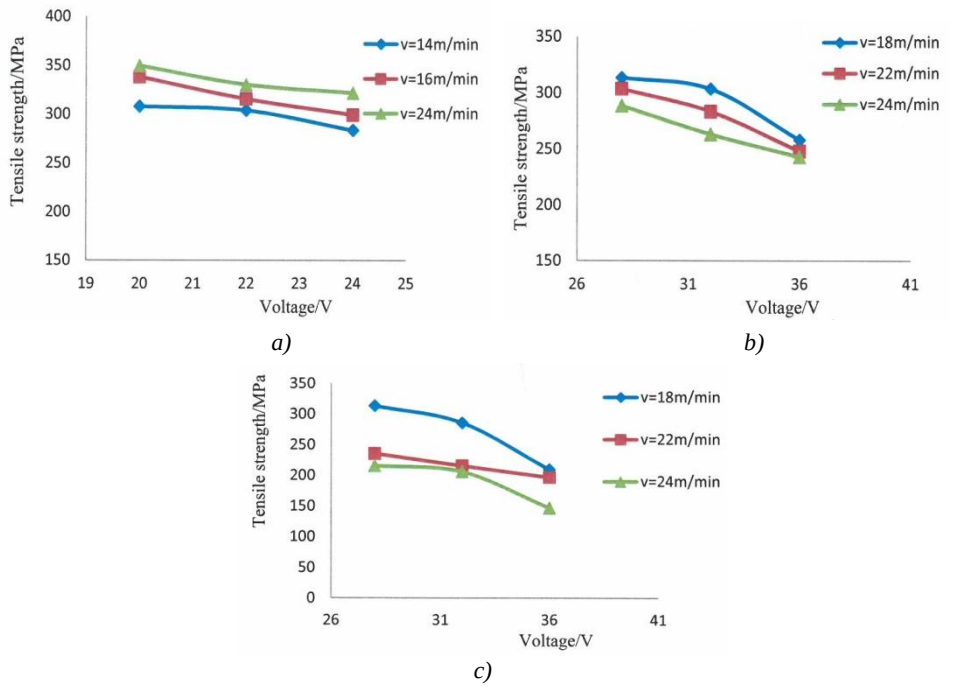


Figure 11 *Dependence of tensile strength drawn PdNi5 wire of different diameter of resistance annealing parameters: a) 0.15; b) 0.111; c) 0.08 mm*

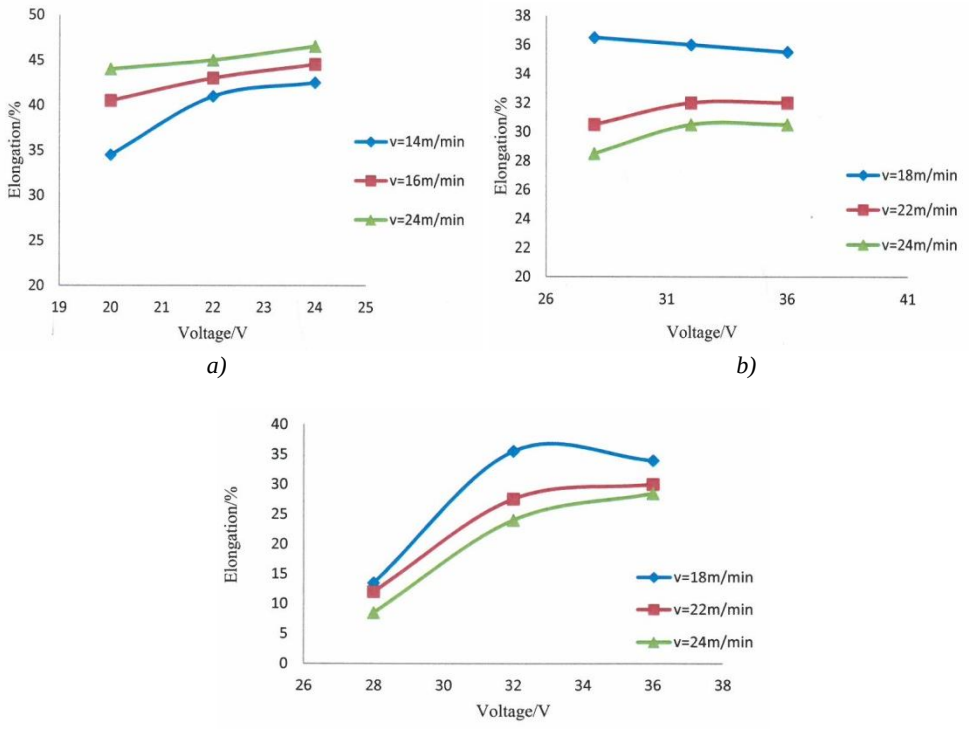


Figure 12 *Dependence of elongation drawn PdNi5 wire of different diameter of resistance annealing parameters: a) 0.15; b) 0.111; c) 0.08 mm*

CONCLUSION

Based on the study of the effect of thermo-mechanical treatment on the properties improvement and structural changes in the Pd-5 wt.% Ni alloy, it can be concluded that the best combination of properties of the final wire (diameter 0.08, 0.111 and 0.15 mm) was achieved in the following regimes of thermomechanical treatment:

- Regime of homogenization annealing (900^{o}C for 30 minute). With the selected regime of homogenization annealing, the values of hardness (84,1 HV), microhardness (133,32 HV) and electrical conductivity (3,9 MSm-1) allows further plastic processing.
- Regime of recrystallization annealing (900^{o}C for 30 minutes). With the selected regime of recrystallization annealing for sample deformed with the highest deformation degree (97%), the highest value of relative elongation (45%) is achieved, with very satisfactory values of tensile strength (310 MPa) and hardness (90,8 HV). For the samples deformed with lower deformation degrees, under the same annealing conditions, the relative elongation values are lower, while the values of tensile strength and hardness are slightly higher.

- Regimes of resistance annealing (U and v) are different depending on the final wire diameter. So,
  for Ø 0.15 mm U = 24 V and
  v = 24 m/min;
  for Ø 0.111 mm U = 28 V and
  v = 18 m/min;
  for Ø 0.08 mm U = 32 V and
  v = 18 m/min.

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