PREPARATION AND CHARACTERIZATION OF AMORPHOUS AND NANOCRYSTALLINE PALLADIUM ALLOYS

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Several phosphorus-free Palladium alloys are obtained from the PaNiSi, PaNiCuSi, PdNiSiSb, PdNiCuSiSb, PdNiCuSb systems. Differential scanning calorimetry is used to investigate the thermal behaviour of alloy $Pa_{40}Ni_{40}Si_{20}$. The amorphous properties of the alloys are determined by X-ray analysis using a Bruker D8 Advance automatic X-ray powder difractometer with CuKα radiation (Ni filter) and a solid state sensitivity detector LynxEye. Data on the glass forming ability of the alloys is obtained and the possibility of replacing phosphorus with silicon and/or antimony is proven. Experiments are conducted with different rates of cooling of the alloys and the rates at which amorphous or nanostructure occur are identified. Data is obtained indicating that both optimization of the composition and appropriate fluxing can be expected to produce a bulk amorphous alloy from the PdNiCuSb system.

Keywords: palladium alloys, amorphous state, nanostructure, glass-forming ability.

1. INTRODUCTION

Some of the newest and most intensively studied materials are amorphous metal alloys, also known as metallic glass. Due to the unique atomic arrangement in their structure compared to the crystalline materials, the amorphous

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alloys have outstanding mechanical properties such as high yield strength (~ 2 GPA) [1] and a wide range of tensile strength (2000–5500 MPa) [2, 3]. These unique properties make these new materials extremely interesting and justify the great interest from the researchers over the past two decades. In addition to the so-called “two-dimensional” metallic glass ribbons whose thickness does not exceed 30 µm, amorphous alloys of up to several centimeters have been produced in the past decades. Today, the alloy $Pd_{43}Ni_{10}Cu_{27}P_{20}$ can be obtained in amorphous state at a critical cooling rate in the range of 0.33 K/s [4] and thickness up to 8 cm [5].

Metal foams generally find more and more engineering application, which is largely due to the relatively high strength combined with the very low specific weight. This unique combination of properties makes the foam an attractive structural material that imitates the mechanical properties of some natural materials, such as wood or bone [6]. Bulk amorphous metal foams can be transformed into construction materials of a new generation. The preparation of amorphous or nanocrystalline foams takes place in two stages: synthesis of suitable bulk alloys, and their subsequent foaming. This is the reason why the production and characterization of amorphous and nanocrystalline alloys is a task of great interest for the researchers.

It is known [7, 8] that bulk metallic glasses are obtained from three- and more component systems. Successful production of amorphous metal foams has so far been achieved with a limited number of palladium alloys, e.g. $Pd_{43}Cu_{27}Ni_{10}P_{20}$ [9] and $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ [10]. Those alloys contain phosphorus as a glass-forming element that allows the production of amorphous metal even from a three-component alloy at low cooling rates of 10^2–10^3 °C/s, *Fig. 1.*

The alloys of the palladium phosphorus system are extremely difficult to obtain due to the high vapor pressure of phosphorus at alloying temperatures, *Fig. 2.* In addition, phosphorus is hazardous to work due to its easy flammability and toxicity. It is therefore necessary to explore the possibilities for synthesis of several types of phosphorus-free palladium alloys and their ability to form amorphous alloys.

2. EXPERIMENT

Palladium alloys are synthesized from high purity 99.99 components by induction melting in protective atmosphere of argon (purity 99.999). Ribbons 30–50 µm thick are obtained by melt-spinning method. The alloy is inductively melted in a quartz ampoule and the molten metallic jet is ejected through a

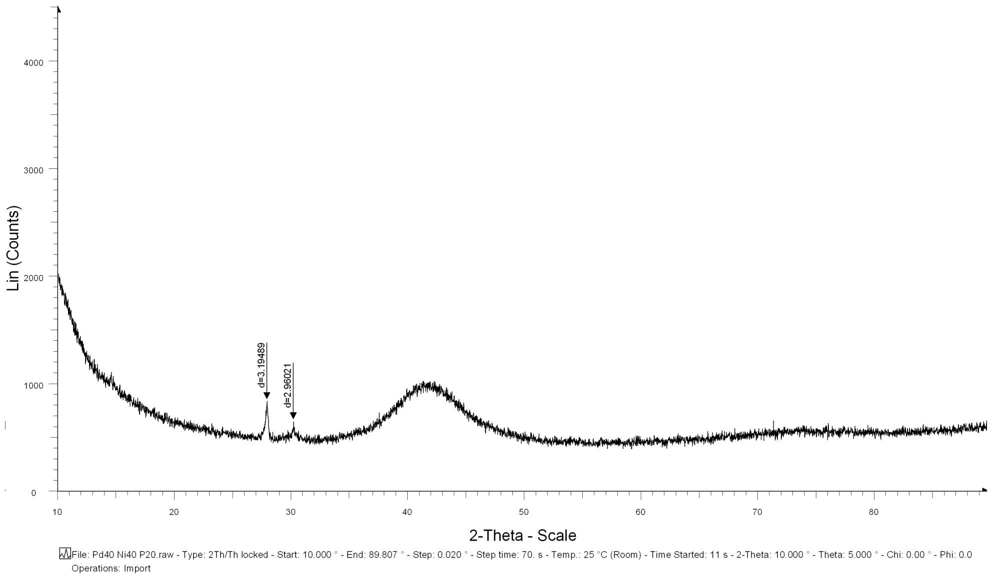

Fig. 1. X-ray diffraction pattern of amorphous palladium alloy ribbon with composition $Pd_{40}Ni_{40}P_{20}$

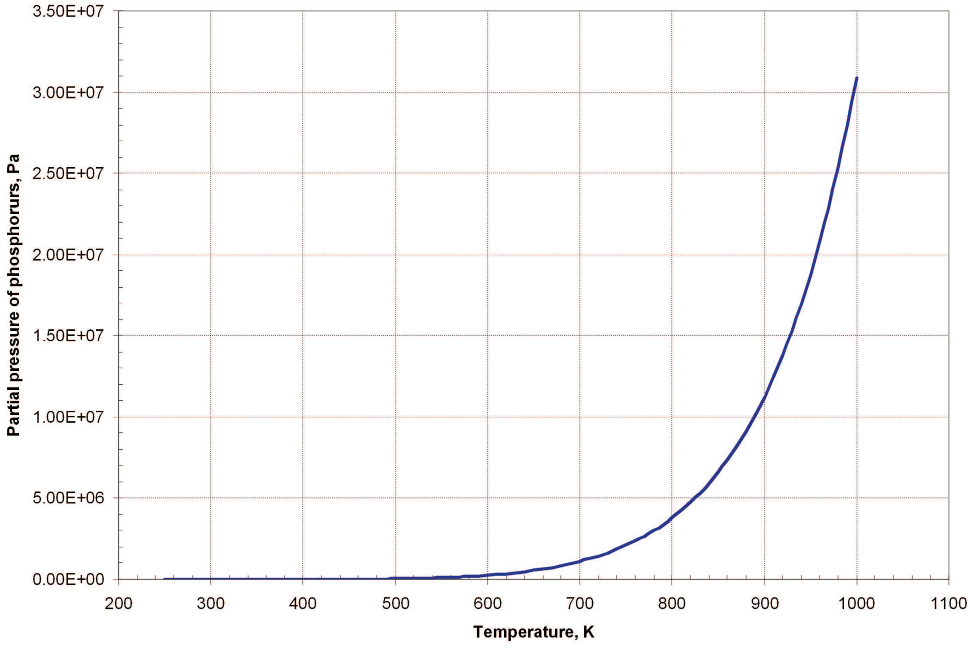

Fig. 2. Partial pressure of saturated phosphorus vapors at different temperatures

nozzle on a metal disk rotating at an appropriate speed allowing cooling rate of 10^5–10^6 K/s. Bulk metal alloys of diameters 4 and 7 mm are also produced by induction melting in a quartz ampoule but are cooled in water at room temperature with cooling rate 10^2–10^3 K/s.

The thermal properties of alloy $Pa_{40}Ni_{40}Si_{20}$ are investigated with SETSYS 2400 computerized thermal installation SETARAM, France. The results obtained are processed with specialized software (Calisto, v. 1.062).

The amorphous and crystalline alloys are characterized by X-ray analysis using Bruker D8 Advance automatic X-ray powder difractometer with CuKα radiation (Ni filter) and solid state sensitivity detector LynxEye. The X-ray spectrum is recorded in the angular range of 5.3 to 80° 2θ with step 0.02° 2θ. The qualitative phase analysis is carried out using Diffraction Data Center (PDF) PDF-2 (2009) with DiffracPlusEVA software package.

The chemical compositions of the ligatures obtained and the metallic glasses are determined using Energy Dispersive X-ray microanalysis (EDAX). It was found that the composition of the alloys corresponds to the target composition.

3. RESULTS AND DISCUSSION

3.1. Alloy $Pa_{40}Ni_{40}Si_{20}$

The possibility of replacing phosphorus with silicon, which also has a high glass formation ability, was studied. *Figure 3* shows the X-ray diffraction pattern of the ribbon obtained, which is typical for an amorphous alloy. The amorphous alloy ribbon is annealed in Differential Scanning Calorimetry apparatus (DSC) and the characteristic peaks were established, *Fig. 4*. Three exothermic and two endothermic peaks are observed on the DSC curve. The exothermic peaks show the thermal effect of crystallization of the amorphous alloy. There are three phases crystallizing at 424 °C, 522 °C, and 617 °C, respectively. The endothermic peaks occur at 716 °C and 851 °C, respectively. The particularity of the alloy is the presence of a phase melting first at 716 °C, after which the remaining solid phase melts at 851 °C. The bulk amorphous alloys typically crystallize as deep eutectics. The presence of three-crystalline phases, one of which has a lower melting temperature, means difficult or impossible glass forming of the alloy at larger sizes of 30–50 µm and at lower cooling rates of 10^5–10^6 K/s. This assumption is confirmed by the X-ray analysis. The alloy is inductively melted in a quartz ampoule of 7 mm diameter under argon and is quenched in water together with the ampoule. Crystalline structure is observed on the X-ray diffraction pattern of the alloy, *Fig. 5*.

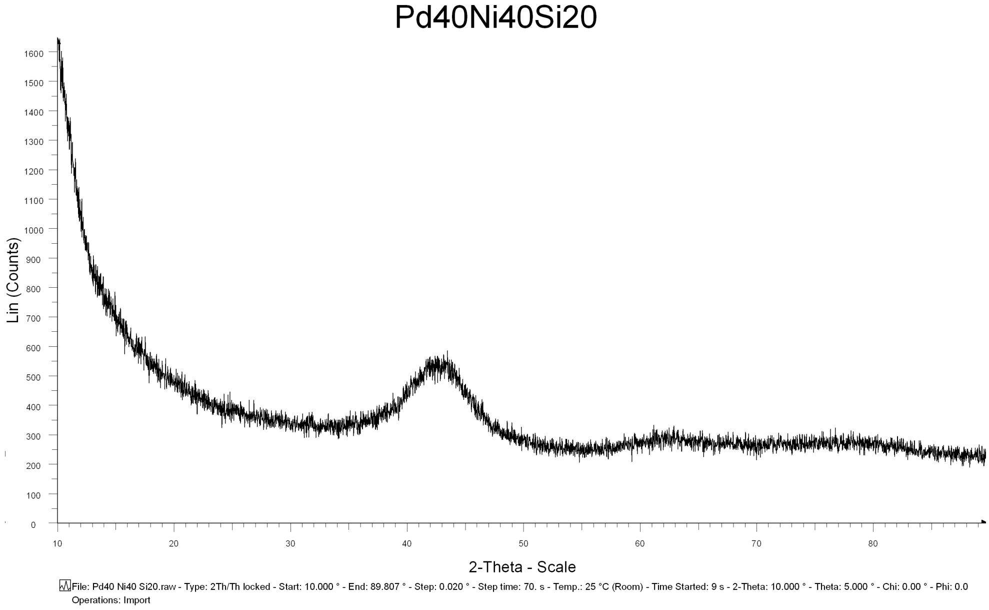

Fig. 3. X-ray diffraction pattern of amorphous palladium alloy ribbon with composition $Pd_{40}Ni_{40}Si_{2O}$

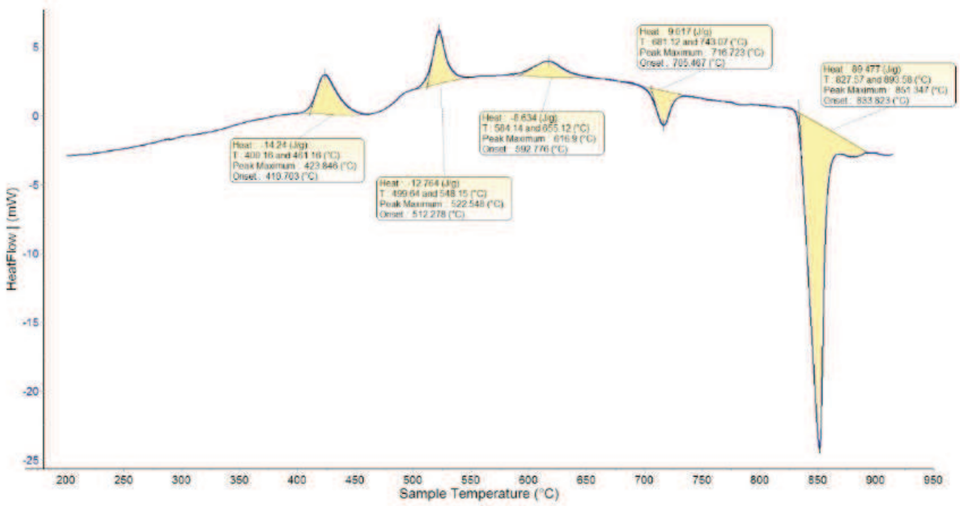

Fig. 4. Differential scanning calorimetry of amorphous ribbon of alloy $Pd_{40}Ni_{40}Si_{20}$

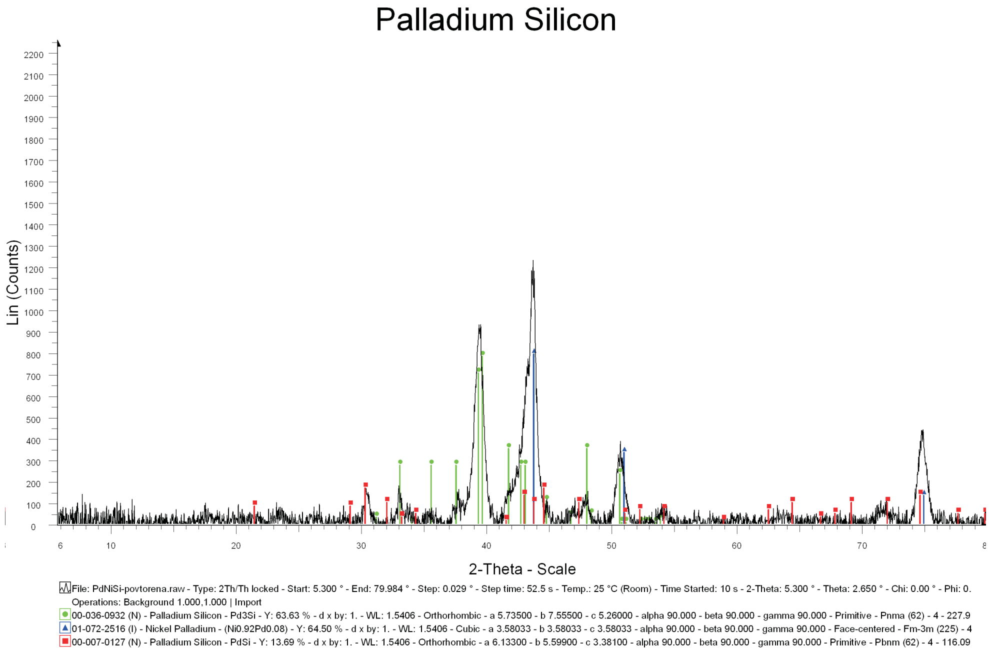

Fig. 5. X-ray diffraction pattern of water-quenched alloy $Pd_{40}Ni_{40}Si_{20}$, diameter 7 mm

The alloy $Pa_{40}Ni_{40}Si_{20}$ is not amorphous upon quenching with cooling rates of 10^2–10^3 °C/s and 7 mm diameter.

3.2. Alloy $Pd_{43}Ni_{10}Cu_{27}Si_{20}$

Since the more complex alloy systems have a better glass forming ability, the alloy has been complicated by adding a fourth component. In *Figure 6* the X-ray diffractogram of the obtained ribbon is shown. A distinct diffraction halo with maximum of about 48° (2θ) is observed, indicating the amorphous structure of the resulting material. The alloy is again melted and quenched in water in quartz ampoules with diameters of 4 mm and 7 mm. The X-ray diffractograms of alloy samples with diameters 7 mm and 4 mm are shown in *Figs 7* and *8*, respectively. On the X-ray diffractogram of water quenched alloy $Pd_{43}Ni_{10}Cu_{27}Si_{20}$ of diameter 7 mm crystalline phases and several broad peaks are observed indicating presence of nano-sized phases or amorphous zones in the structure. Phase size is: Cu_3Pd – 19 nm; (CuNiPd) 0.3333 – 10 nm; Pd_2Si – 12 nm. In the 7 mm ampoule the cooling rate is lower than the critical and

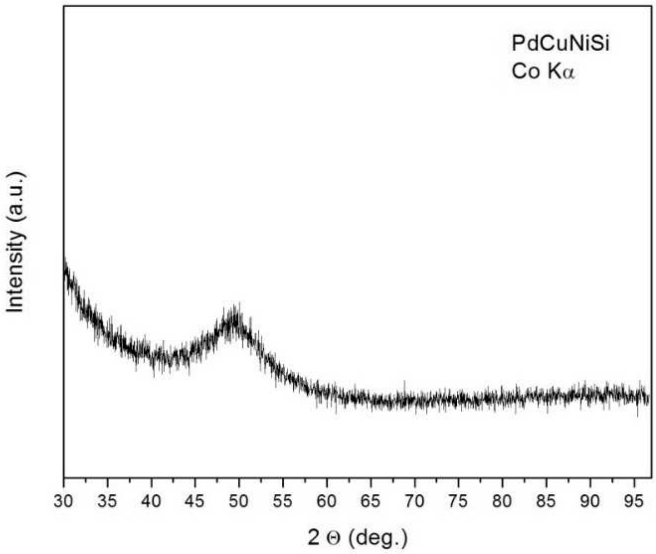

Fig. 6. X-ray diffraction pattern of amorphous palladium alloy ribbon with composition $Pd_{43}Ni_{10}Cu_{27}Si_{20}$

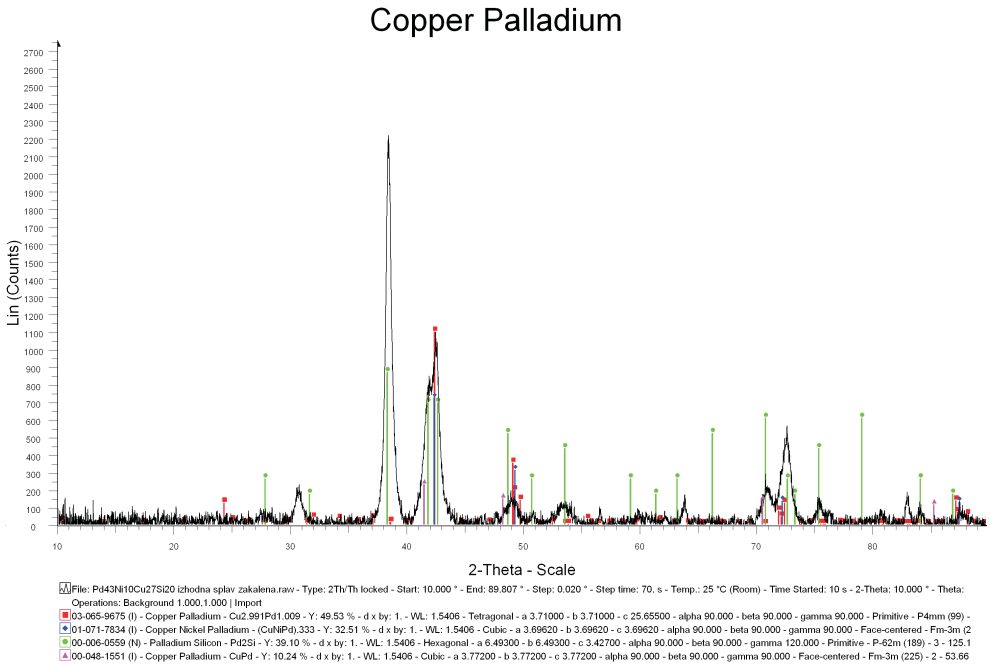

Fig. 7. X-ray diffraction pattern of water-quenched alloy $Pd_{43}Ni_{10}Cu_{27}Si_{20}$, diameter 7 mm

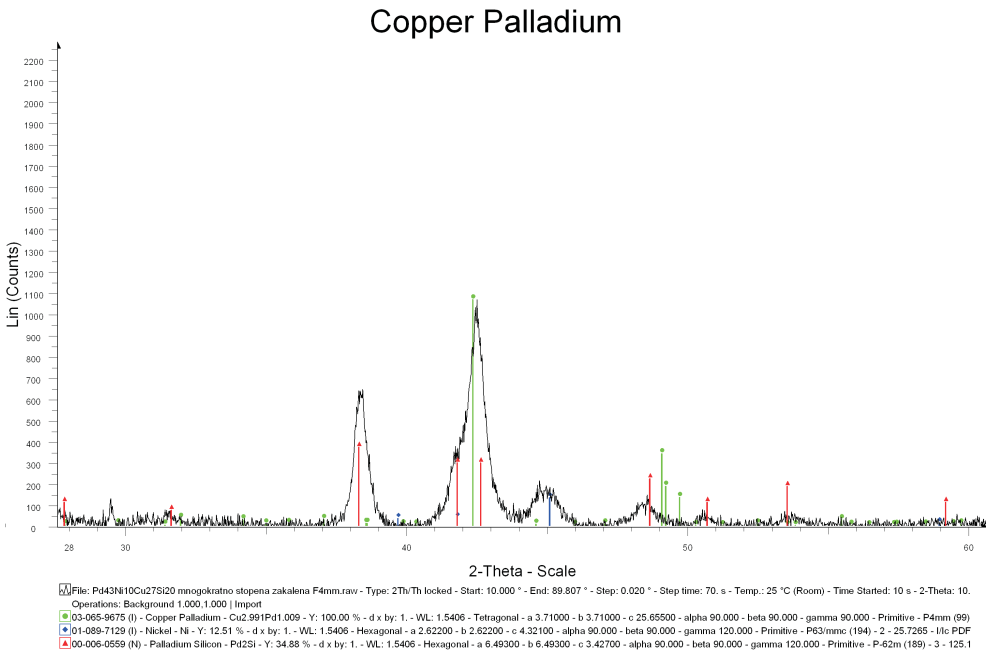

Fig. 8. X-ray diffraction pattern of water-quenched alloy $Pd_{43}Ni_{10}Cu_{27}Si_{20}$, diameter 4 mm

the alloy is not completely amorphous. In *Figure 8* crystalline phases and several broad peaks are also observed, which indicates the presence of nano-sized phases or amorphous zones in the structure. The size of the phases is: Cu_3Pd – 18 nm; Pd_2Si – 7 nm; the phase (CuNiPd) 0.3333 is not observed. There is tendency of both crystallites to become smaller plus suppression the crystal growth of some phases. However, complete amorphous structure is not achieved. At this diameter the alloy has a mixed crystalline/amorphous structure with nano-sized crystallites.

3.3. PdNiSiSb alloy

The alloys are further complicated by antimony. To 4.2374 g of alloy $Pd_{40}Ni_{40}Si_{20}$, 0.8464 g of antimony is added under B_2O_3 flux and is dried at about 200 °C. The alloying temperature is 1200 °C. The finished alloy is melted in a quartz ampoule of diameter 7 mm and quenched in water. The X-ray diffractogram of the alloy is shown in *Fig. 9*

The alloy is crystalline. Phases of NiPdSi, NiPd, PdSb, and PdSi are observed. To obtain amorphous or mixed amorphous nanocrystalline microstructure higher cooling rates are required.

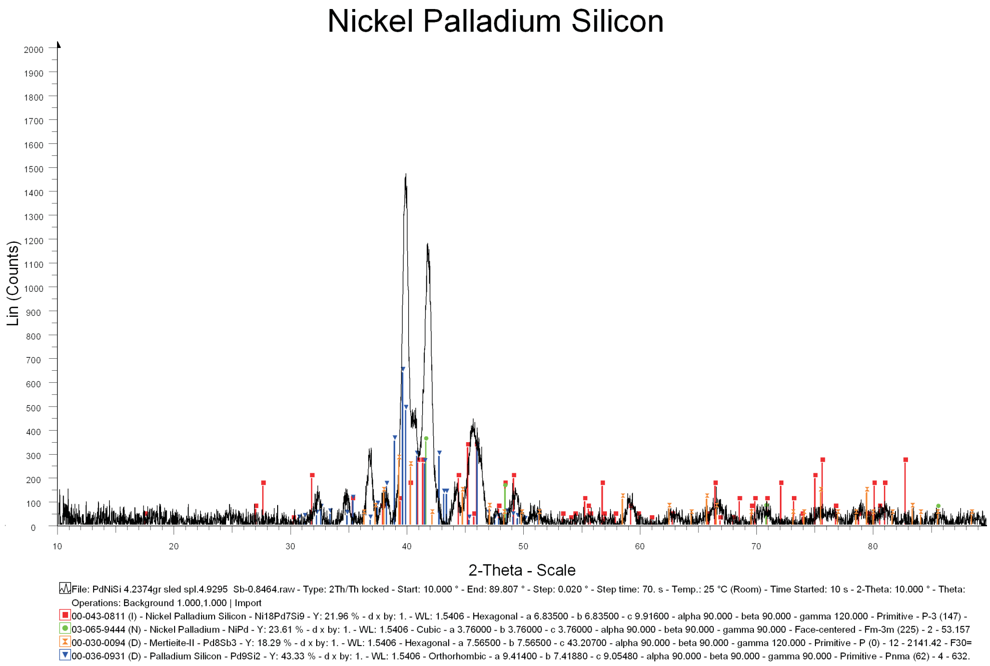

Fig. 9. X-ray diffraction pattern of water-quenched alloy PdNiSiSb, diameter 7 mm, fluxing with B_2O_3

3.4. PdNiCuSiSb alloy

To 9.5 g of alloy $Pd_{43}Ni_{10}Cu_{27}Si_{20}$, 2.129 g of antimony is added at alloying temperature 1200 °C under a flux of B_2O_3 and is dried at about 200 °C. The finished alloy is melted in a quartz ampoule of diameter 7 mm and hardened in water. The X-ray graph of the hardened alloy is shown in *Fig. 10.* The alloy is crystalline. Phases of PdSi, NiPd, CuNiPd, NiPdSi, and PdSb are observed.

3.5. $\mathbf{Pd_{42}Ni_{10}Cu_{27}Sb_{21}}$ alloy

Since silicon raises the alloying temperature and prevents foaming, a non-silicon $Pd_{42}Ni_{10}Cu_{27}Sb_{21}$ alloy is synthesized. It contains antimony and is

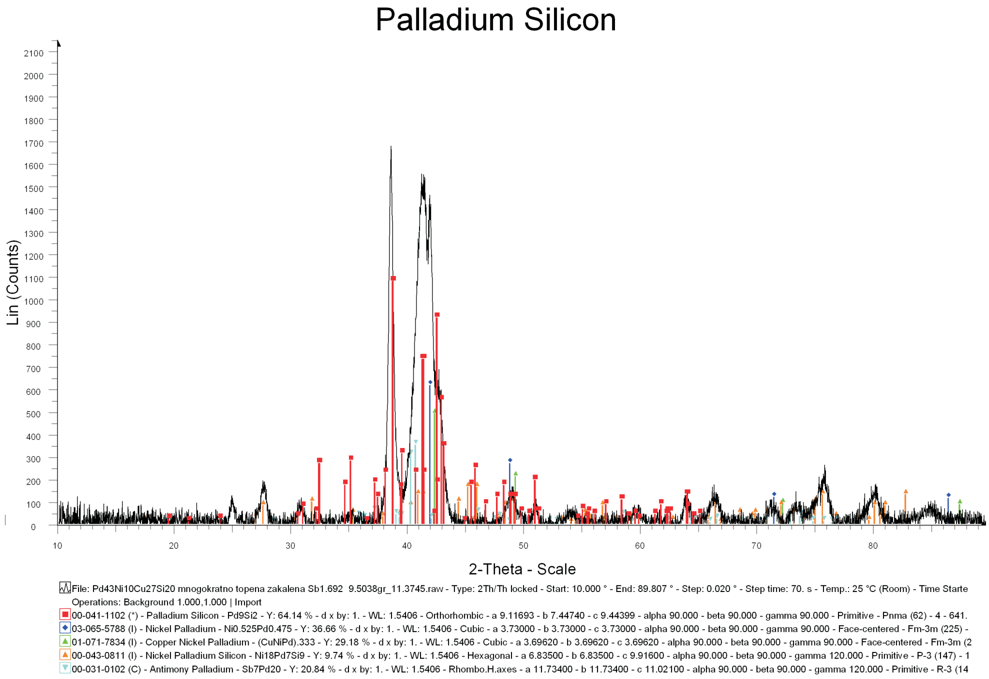

Fig. 10. X-ray diffraction pattern of water-quenched alloy PdNiCuSiSb, diameter 7 mm, fluxing with B_2O_3

close in composition to alloy $Pd_{43}Ni_{10}Cu_{27}P_{20}$, which allows producing amorphous bulk samples. The antimony has in the order lower partial pressure than the phosphorus at the synthesis temperature as shown in *Fig. 11.* Antimony belongs to the same group in the Periodic Table of Elements as Phosphorus and our hypothesis is that it could replace it as a glass-forming component. The alloy is obtained by alloying the components in a quartz ampoule under argon in induction furnace and refined in pre-dried B_2O_3 at 1200–1300 °C for about 5 minutes. *Figure 12* shows the X-ray diffraction pattern of the 7 mm diameter hardened alloy. Here crystalline phases and several broad peaks are observed too, indicating nano-sized phases or amorphous zones in the structure.

Amorphous or nanocrystalline alloys can be obtained if the melt is clean and free of crystallites of high-melting compounds, mainly oxides. The crystallization nuclei are removed from the melt of $Pd_{42}Ni_{10}Cu_{27}Sb_{21}$ alloy by fluxing with B_2O_3 for 10 minutes at 1200 °C in a 7 mm diameter quartz ampoule, after which the alloy is quenched in water.

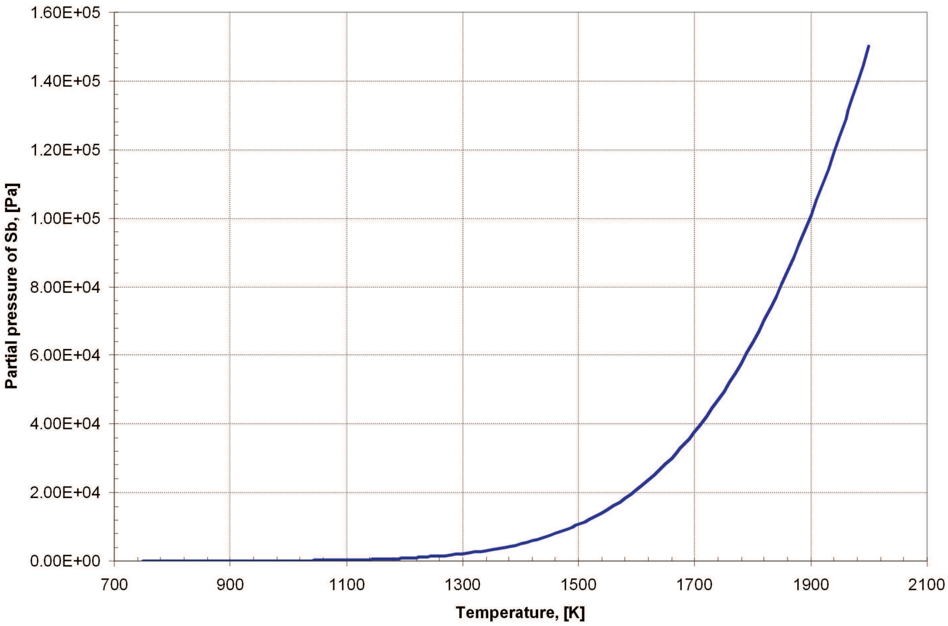

Fig. 11. Partial pressure of saturated antimony vapors at different temperatures

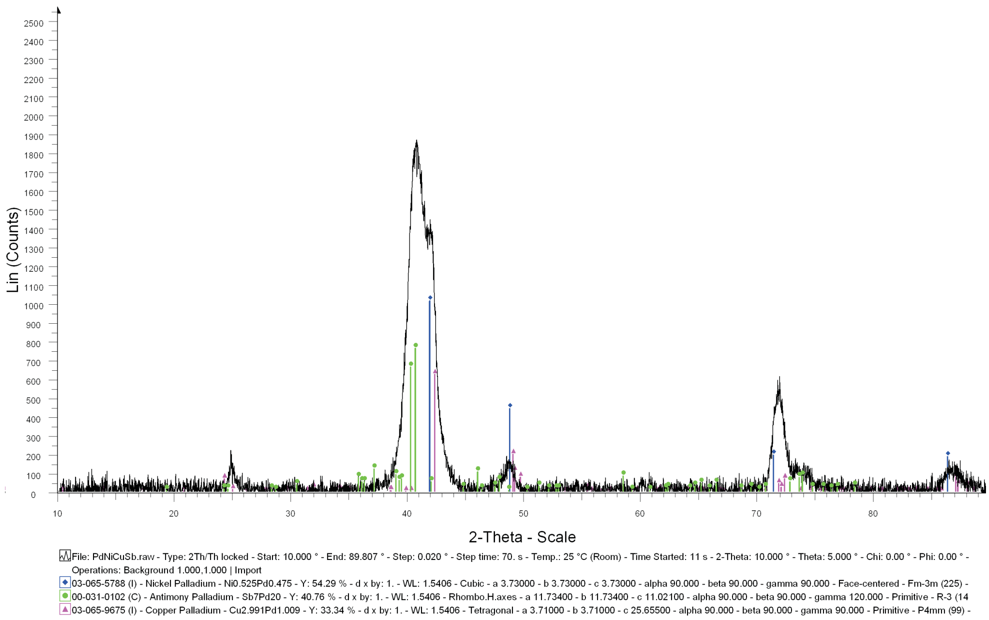

Fig. 12. X-ray diffraction pattern of water-quenched alloy $Pd_{42}Ni_{10}Cu_{27}Sb_{21}$, diameter 7 mm

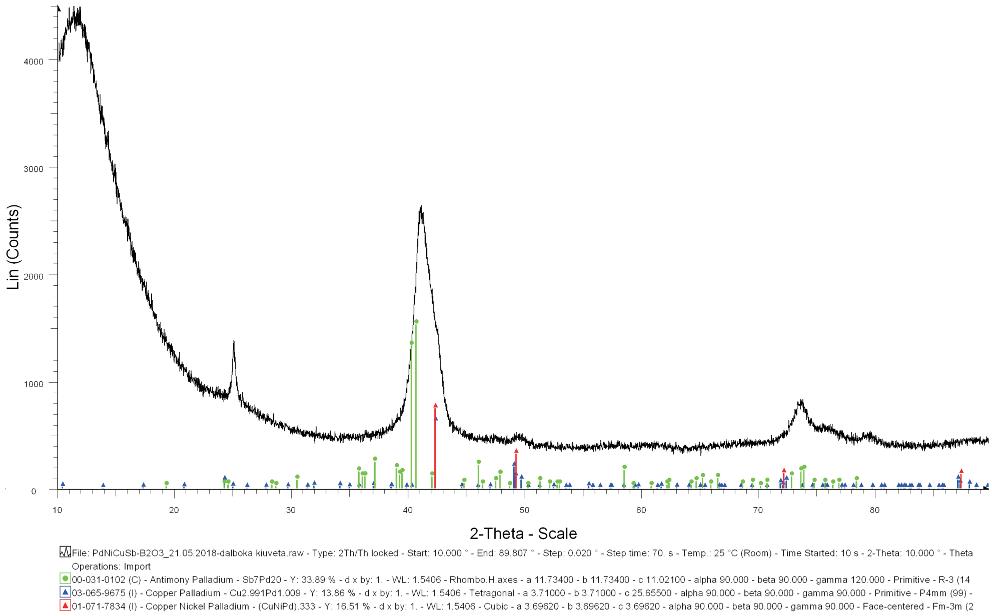

Fig. 13. X-ray diffraction pattern of water-quenched alloy $Pd_{42}Ni_{10}Cu_{27}Sb_{21}$, diameter 7 mm, additional fluxing with B_20_3

Nanocrystalline structure and occurrence of more amorphous areas are observed, *Fig. 13.*

4. CONCLUSION

- Palladium amorphous alloys $Pa_{40}Ni_{40}Si_{20}$ and $Pd_{43}Ni_{10}Cu_{27}Si_{20}$ free of phosphorus are obtained.
- The $Pa_{40}Ni_{40}Si_{20}$ and $Pd_{43}Ni_{10}Cu_{27}Si_{20}$ alloys are amorphous at cooling rates of 10^5–10^6 K/s.
- At cooling rates, 10^2–10^3 K/s the alloys have nanostructure with crystallite size between 7 and 20 nm.
- The alloy $Pd_{42}Ni_{10}Cu_{27}Sb_{21}$ can be partially amorphous at cooling rates of 10^2–10^3 K/s.
- Upon optimization of the composition and suitable fluxing, a bulk amorphous alloy from the PdNiCuSb system can be expected.

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ПОЛУЧАВАНЕ И ОХАРАКТЕРИЗИРАНЕ НА АМОРФНИ И НАНОКРИСТАЛНИ ПАЛАДИЕВИ СПЛАВИ

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Резюме. Получени са няколко безфосфорни паладиеви сплави от системите PaNiSi, PaNiCuSi, PdNiSiSb, PdNiCuSiSb, PdNiCuSb. С диференциална сканираща калориметрия е изследвано термичното поведение на сплав $Pa_{40}Ni_{40}Si_{20}$. Аморфността на сплавите е определена чрез рентгенографски анализ, извършен с автоматичен прахов рентгенов дифрактометър Bruker D8 Advance с CuKα лъчение (Ni филтър) и регистрация от твърдотелен позиционно-чувствителен детектор LynxEye. Получени са данни за стъклообразуващата способност на сплавите и е доказана възможността за замяна на фосфора със силиций и/или антимон. Проведени са експерименти с различни скорости на охлаждане на сплавите и са установени скоростите, при които се получава аморфна или наноструктура. Получени са данни, които показват, че, при оптимизиране на състава и подходящо флюсоване, може да се очаква получаване на обемна аморфна сплав от системата PdNiCuSb.

Ключови думи: паладиеви сплави, аморфно състояние, наноструктура, стъклообразуваща способност.

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