Rapidly quenched Pd$_{47}$Ni$_{47}$Si$_{6}$ based alloy for application as a brazing material.

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Abstract. Fabrication conditions of the Pd$_{47}$Ni$_{47}$Si$_{6}$ amorphous ribbons designed for functional application as a filler metal in joining metallic elements have been developed. Particular attention in developing fabrication technology was drawn to the question of elimination of ribbon contamination with carbon, the presence of which has disadvantageous effect on the quality of the amorphous PdNiSi brazes. Thermodynamic properties of the PdNiSi braze were examined and its characteristic temperatures $T_S$ and $T_L$ have been determined. Density and resistivity of the ribbons have been measured. Moreover, brazing tests were conducted using the brazing alloys fabricated under this work, designed for joining such metals as ST3S constructional steel, tungsten, molybdenum and tantalum. The strength tests were also carried out confirming very good functional properties of the developed brazing alloy.

1. Introduction

The palladium-based brazing alloys, similarly as the brazes based on other metals but containing this element, are characterized by very good capacity of wetting majority of metals and high corrosion resistance. Therefore, in spite of their high price, they are increasingly used for brazing nickel and its alloys, beryllium, gold, zirconium, tungsten, tantalum and heat-resistant alloys operating at high temperatures [1]. An additional advantage of palladium alloys is that they can be fabricated by melt-spinning method in a form of thin ribbons. This fabrication method is significantly more economical comparing to the traditional one (melting and plastic working) and besides, the yield achieved using this method is very high, reaching about 95 %. Due to the use of very thin ribbon the brazing process is very cost-effective in reference to electricity and material consumption. This makes that these alloys are becoming increasingly attractive from scientific point of view and potential applications [2-4].

The aim of this work was to determine fabrication conditions of the Pd$_{47}$Ni$_{47}$Si$_{6}$ [wt %] brazing alloys in a form of amorphous ribbons, examination of their properties and an assessment of the possibility of using them for joining metal components designed for high-temperature operation.
2. Experimental
The Pd$_{47}$Ni$_{47}$Si$_{6}$ [wt %] amorphous ribbons were cast from master alloys prepared from Pd, Ni and Si, 99.9 % in purity. The melting process was conducted in a vacuum induction furnace using the graphite crucible and ceramic crucible from Al$_2$O$_3$. After casting at the temperature of about 1600°C the charge of a mass of about 0.6 kg was subjected to refining carried out at the temperature of about 1200°C, and then liquid metal was poured into cylindrical mould. Chemical composition of the ingots was checked by means of X-ray micro-analysyer and then they were used to fabricate PdNiSi ribbons by rapid quenching on the surface of rotating copper wheel [5]. The obtained ribbons were subjected to XRD examination aimed at checking their amorphousness, and their chemical composition was determined by means of X-ray micro-analysis. Moreover, calorimetric examination was made in order to analyse the process of ribbon melting and solidification and to determine characteristic temperatures of solidus $T_s$ and liquidus $T_L$. The X-ray Photoemission Spectroscopy method (XPS) was used to determine the contents of carbon and oxygen over the whole ribbon volume. Besides, resistivity and density of the ribbons were determined. Finally, tests were carried out by means of the Instron machine to check the strength of joints made between different metal components using the PdNiSi braze.

3. Result and discussion
Determination of fabrication conditions of the Pd$_{47}$Ni$_{47}$Si$_{6}$ ribbons.
As a results of tests carried out, the following main parameters of ribbon casting were determined:

- mass of a charge - 0.6 – 0.7 kg,
- linear speed of a wheel - 44 m/s,
- charge temperature during casting - 1463 K
- dimensions of quartz crucible nozzle - 21 mm × 0.9 mm
- distance between the nozzle and wheel surface - 0.4 mm

The ejecting pressure was changed within a range from 20 to 30 kPa depending on required thickness of a ribbon.

The ribbons were cast using process parameters listed above, whereas during the first series of tests master alloy was prepared in a graphite crucible, and then in alundum crucible. The ribbons obtained were 30 and 40 µm in thickness, respectively. Their chemical composition was determined by means of X-ray micro-analysyer showing that there was very high concentration of carbon and oxygen at the surface of 30 µm thick ribbon (master alloy from graphite crucible), and only trace amounts of C and O were found in the 40 µm thick ribbon. Therefore, the PdNiSi ribbons with high contents of C and O were examined by XPS method. The dependence of intensity of C and O presence on a sample surface on sputtering time is shown in Fig. 1. After removal of a sample layer corresponding to the time of 10 min, the content of carbon dropped to about 15 % of the atomic concentration, and the oxygen content dropped to zero. After 50 minutes of sputtering, the carbon content was at the level of 2.5 %. It should be expected, therefore, that carbon was present over the whole sample volume, and it originated from the graphite crucible used to fabricate master alloys. Further examination was made using only the ribbons containing trace amounts of C and O on their surface.

Fig. 2 shows diffraction pattern obtained for the Pd$_{47}$Ni$_{47}$Si$_{6}$ ribbon at the range of 2θ angle from 20° to 120°, in which diffraction lines are not present. The X-ray examination showed that the ribbon contained only amorphous phase.
The dependence of intensity of carbon and oxygen presence on a sample surface on sputtering time.

Figure 2. Diffraction pattern obtained for the Pd$_{47}$Ni$_{47}$Si$_6$ ribbon at the range of 20° to 120°.

Figure 3. The DTA diagram for the Pd$_{47}$Ni$_{47}$Si$_6$ ribbon.

The DTA diagram for the Pd$_{47}$Ni$_{47}$Si$_6$ ribbon is presented in Fig. 3. It shows that no phase transformations take place during heating the sample, and a regular-shaped peak evidencing the presence of a single peak appears during melting. However, solidification of a sample during DTA analysis proceeds much slower than during melt-spinning process, which makes that multi-phase structure of an alloy is revealed.

Table 1. Physical properties of the Pd$_{47}$Ni$_{47}$Si$_6$ amorphous brazing ribbons.

| ribbon thickness (µ) | ribbon width (mm) | density (g/cm$^3$) | resistivity ($\mu\Omega\times$cm) | $T_S$ (K) | $T_L$ (K) |
|----------------------|-------------------|-------------------|-----------------|---------|---------|
| 40±2                 | 21                | 9.285             | 91.0            | 809.3   | 821.7   |
| 30±2                 | 20                | 9.18              | 92.0            | 828.2   | 835.9   |

Brazing tests for the developed Pd$_{47}$Ni$_{47}$Si$_6$ alloy were carried out on rods from ST3S constructional steel, 15 mm in diameter, and on rings 15 mm in diameter made from sheets of tungsten, molybdenum and tantalum, 0.1 mm thick. Fig. 4 shows layout of joined metals and Pd$_{47}$Ni$_{47}$Si$_6$ braze. The brazing process was conducted using induction heating at 1223 K, in an atmosphere of argon.

Parameters of the brazing process were the following:

- heating power - 1 – 1.3 kW; f = 30kHz,
argon flow pressure - 4.5 kPa,
brazing temperature - 1223 K,
brazing time - 300 s.

Results from the strength tests performed for four samples are presented in Table 2.

Table 2. Results from strength tests for brazed pieces acc. to the layout shown in Fig. 4

| Sample No | ST3S | W  | Mo | Ta |
|-----------|------|----|----|----|
| Strength (MPa) | 108 | 57 | 21 | 5.4 |

The sample No 1 consisting of two rods from ST3S steel joined with the PdNiSi braze exhibits very high strength reaching about 50% of the breaking strength of the ST3S steel rods. Sample No 2, in which tungsten ring was inserted between the braze and steel rod, has twice smaller breaking strength than sample No 1. This effect may result from deformation of a tungsten ring (0.1 mm thick) causing that the forces act upon the joint under different angles. Further strength decrease found in case of the samples No 3 and 4 can be partly explained similarly as for sample No 2, whereas almost four-fold lower strength of a joint with W (sample No 4) compared to that with Mo (sample No 3) can result from much higher plasticity of W compared to Mo.

4. Conclusions

Fabrication conditions of the Pd$_{47}$Ni$_{47}$Si$_{6}$ braze in a form of ribbons, about 20 mm wide and from 30 to 40 µm thick, have been developed. The XPS examination showed that graphite crucible cannot be used to prepare master alloys, since during smelting process graphite atoms embed into the whole alloy volume, and consequently, the ribbon obtained by melt-spinning contains an excessive amount of C.

It was also found that the PdNiSi ribbons cast from master alloys prepared in alundum crucibles contain only trace amounts of carbon. Main physical properties of the ribbons have been determined, and preliminary tests with joining rods from ST3S steel, W, Mo and Ta by means of the PdNiSi braze have been carried out confirming very good breaking strength of the joined metal components.

5. References

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