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Pt-Rh ALLOYS: INVESTIGATION OF TENSILE STRENGTH AND ELONGATION AT HIGH TEMPERATURES

STOPY Pt-Rh: BADANIE WYTRZYMAŁOŚCI NA ROZCIĄGANIE I WYDŁUŻENIA W WYSOKICH TEMPERATURACH

In this paper are presented investigation results of tensile strength and elongation of selected alloys from Pt-Rh system. Samples with the content of rhodium in a concentration range of 7-40% (wt.) were studied. Studies were performed in the temperature range 1100-1500°C at a stress of 2-20 MPa. A universal device for measuring hardness was used to measure the Vickers hardness. For investigation of time strength and elongation at high temperatures, the device Mayes MK2 TC/10 was used. It was found that the value of tensile strength increases with increasing rhodium content, and decreases with increasing temperature. Elongation decreases to 7% Rh, then increases with increasing rhodium content to 15% and then slowly decreases again. With increasing temperature there is a slight increase in elongation.

Keywords: Pt-Rh alloys, high temperature, tensile strength, elongation

W pracy przedstawiono wyniki badań wytrzymałości na rozciąganie i wydłużenia wybranych stopów z układu Rh-Pt. Zbadane zostały próbki z zawartości rodu w zakresie 7-40% wag. Pomiar twardości Vickersa przeprowadzono w zakresie temperatur 1100-1500°C, przy naprężeniu 2-20 MPa, przy użyciu uniwersalnego urządzenia do pomiaru twardości. Do badania wytrzymałościna rozciąganie i wydłużenia w wysokich temperaturach zastosowano urządzenie Mayes MK2TC/10. Stwierdzono, że wytrzymałość na rozciąganie zwiększa się wraz ze wzrostem zawartości rodu i zmniejsza się wraz ze wzrostem temperatury. Wydłużenie zwiększa się wraz ze wzrostem zawartości rodu od 7% do 15%, a następnie powoli zmniejsza się ponownie w zakresie od 15% do 40% rodu. Wraz ze wzrostem temperatury obserwowany jest niewielki wzrost wydłużenia.

1. Introduction

The interest in platinum and platinum alloys increases constantly, because the new areas of application are continuously discovered [1]. Today, platinum alloys, due to their characteristics such as high strength, good workability and mostly corrosion resistance at high temperatures, are present in different areas such as production of glass [2,3] and nitrogen fertilizers [4-6], production of thermocouples [7], production of automotive catalysts [8], jewelry [9,10] and so on. Recently, glucose sensors based on nanoparticles of platinum alloys with Ru, Pd and Au, on the carrier of carbon, have been developed [11]. Of all platinum alloys, currently, most widely used are alloys of platinum with rhodium, which application range of temperature extends up to 1600°C.

Platinum and its alloys represent a major challenge for researchers and up to date a number of metallurgical aspects of behavior or characteristics have been studied, such as:

(i) the influence of cold deformation and annealing temperature on mechanical properties of platinum [12], and rheological properties of 99.93 wt% Pt [13]. It was found that the destruction of 99.5% pure Pt occurs at the annealing temperature of 650-680°C. Samples of higher purity, with increasing annealing time, were maintaining the mechanical properties. The deformation degree had almost no effect on the recrystallization temperature of different purity platinum.

(ii) Pt-Rh, Pt-Pd, Pd-Rh and Pt-Pd-Rh phase diagrams were investigated using Monte Carlo simulation method in combination with MEAM method and optimized parameters [14], and also the influence of Rh on the surface distribution in Pt-Pd-Rh alloy was monitored [15].

Number of authors worked on the development of platinum alloys thermodynamic database [16-18]. Thermodynamics and phase equilibrium of binary Pt-Rh system were studied by Jacob et al. [19]. Rdzawski and Stobrawa [20] have developed two new Pt-Rh alloys: PtRh10 with 0.2% of yttrium for use in glass industry, and PtRh10 with 5 ppm of boron for applications in nitrogen fertilizers production. Also, new materials for high temperature aplictions were developed, based on dispersion strengthened platinum [21], on dispersion-strengthened PtRh5 alloy [22] and on dispersion-strengthened PtRh10 alloy [23]. All are strengthened by the incorporation of a fine dispersion of zirconium oxide within the metal/alloy matrix. Zhang et al. [24] have examined how platinum dispersion strengthening by small amount of yttrium and zirconium influence the microstructure and mechanical properties, wherein it has been conclud-

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ed that the addition of these elements improves the properties of platinum at room and elevated temperatures, and that the alloying with both elements simultaneously is more efficient. Microstructural analysis of selected platinum alloys used in industry and jewelry making (including PtRh10 and PtRh30), has been performed by Battaini [25]. Fischer et al. [26] have studied the stress-rupture strenght and creep behaviour of platinum, Pt-Rh and Pt-Ir alloys, dispersion hardened platinum materials, rhodium and iridium. The oxidation of ammonia on PtMe (Me = Ir, Rh, Pd, Ru) [27] for developing ammonia based fuel cells, have been examined. The aim of this study is investigation of the tensile strength and elongation of the selected alloys from Pt-Rh system at high temperatures, under different loads.

2. Experimental

Platinum and rhodium for alloys production have been obtained as a side product in production of electrolytic copper RTB, Serbia. By additional refinement, the necessary purity (99.95% for Pt and 99.5% for Rh) has been achieved. The composition of the investigated samples is listed in TABLE 1. Impurities in the investigated samples were characteristic for the raw material from deposits of Bor – Pd, Ag, Au, Bi, Sb, As, Cu. Melting of the samples was performed in mid-frequency induction furnace. Annealing of samples was carried out in a resistance furnace, type LP08. For hardness testing (HV), tensile strength (R_m), as well as elongation (A) of pure platinum and Pt-Rh alloys, at different temperatures and in different strains, following samples had been used: a) sheet of 1.5 mm in thickness and b) wire of 2 mm in diameter. To measure the Vickers hardness, a universal device for hardness measurement, by manufacturer Karl Frank, type 38532, was used. For testing the tensile strength and elongation, at high temperatures, the device Mayes MK2 TC/10 was used. Chemical analysis of material for samples was performed on an atomic absorption spectrophotometer.

TABLE 1

The composition of investigated samples (in weight %)

Alloy	Pt (wt. %)	Rh (wt. %)
Pt	100	0
PtRh7	93	7
PtRh10	90	10
PtRh15	85	15
PtRh20	80	20
PtRh40	60	40

3. Results and discussion

In order to supplement the existing database of platinum and platinum metals, originating from the site of Bor, Serbia, influence of change in rhodium content as alloying element on the tensile strength and elongation, were investigated, as important parameters of high-temperature strengthening of platinum. Rhodium content in the samples tested was: 7, 10, 15,

20 and 40%. To determine the hardness, an investigation of samples of pure Pt and Pt alloys with rhodium content of 7, 10, 15 and 20%, at room temperature, was performed (Fig. 1.).
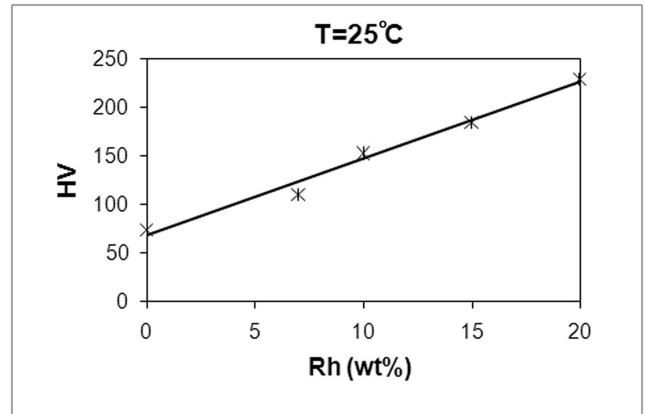

Fig. 1. Dependence of hardness (HV) of platinum and investigated Pt-Rh alloys from rhodium content at 25°C

Based on the dependence shown in Fig. 1., it was observed that hardness increases almost linearly with increasing rhodium content in the alloy.

In Fig. 2a it is presented the dependence of tensile strength (UTS) of the alloys of Pt-Rh system from the rhodium content in the temperature range 1100-1400°C. In the same temperature range elongation values (A) for pure platinum and investigated Pt-Rh alloys as a function of rhodium content, were determined (Fig. 2b).
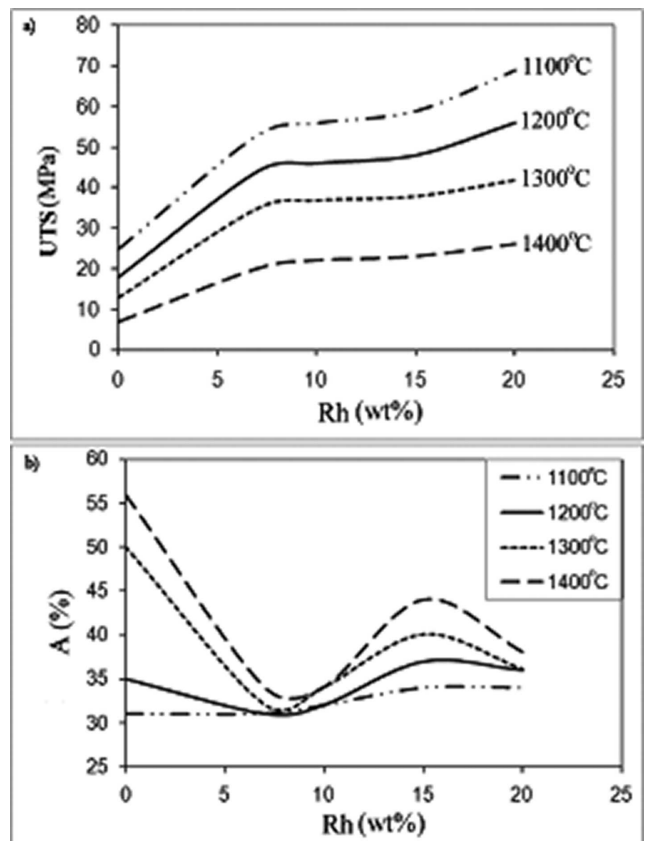

Fig. 2. Dependence of: a) tensile strength (UTS) and b) elongation (A) of investigated Pt-Rh alloys from rhodium content at different temperatures

Based on the dependence shown in Fig. 2 (a and b) it was observed that a value of tensile strength increases with increasing rhodium content in the alloy, while the value of the elongation decreases to 7% Rh, then increases with increasing rhodium content to 15% and then slowly decreases again. Regarding the influence of temperature on the change of tensile strength of the studied alloys, it can be concluded, based on the dependences shown in Fig. 2a, that tensile strength decreases significantly with increasing temperature. Elongation of investigated Pt-Rh alloys increases with increasing temperature (Fig. 2b), however this increase is not as pronounced.
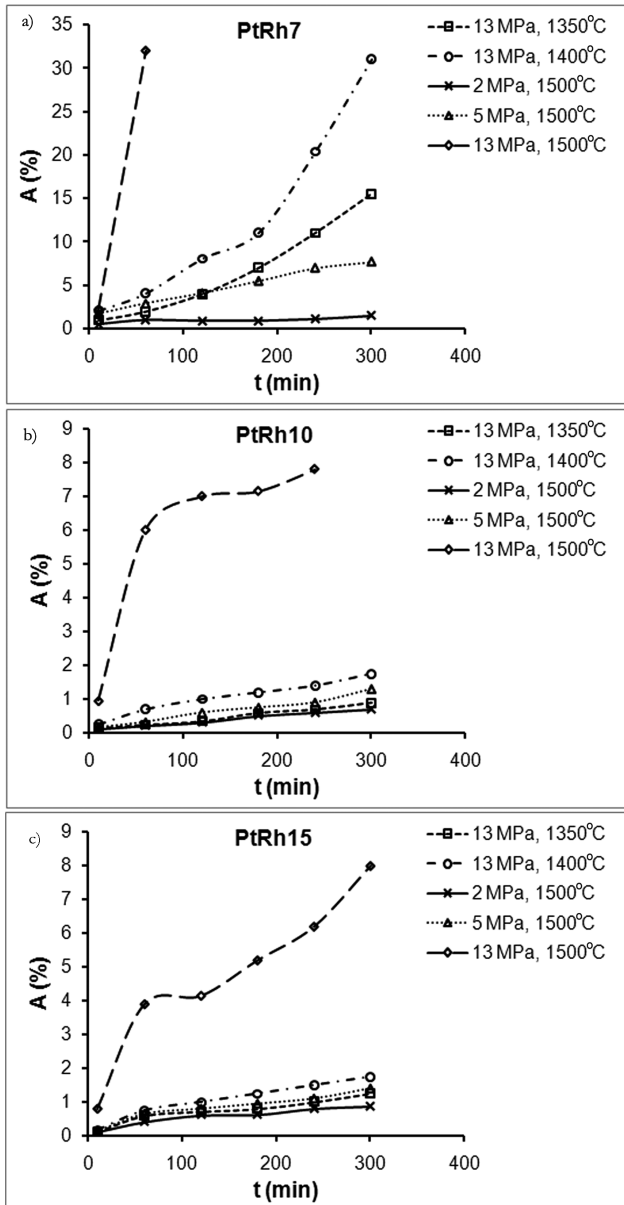

Fig. 3. Dependence of elongation (A) of the strain time at a load of 13 MPa at 1350°C, 1400°C and 1500°C, as well as the load of 2 and 5MPa at 1500°C for: a) PtRh7, b) PtRh10 and c) PtRh15

In order to study the time strength and resistance of alloys of the Pt-Rh system at high temperatures, creep curves were recorded for alloys samples with 7, 10 and 15% Rh, at testing time of 5 hours. Dependence of elongation (A) from the test period, at a stress of 13 MPa at temperatures of 1350-1500°C, as well as at a stress of 2 and 5 MPa at 1500°C for PtRh7

sample is shown in Fig. 3a. Dependence of elongation (A) of the test period, at a stress of 13 MPa and at temperatures of 1350-1500°C, as well as at a stress of 2 and 5 MPa at 1500°C for PtRh10 sample is shown in Fig. 3b, and for sample PtRh15, under the same conditions, in Fig. 3c.

Based on the dependence of the elongation change during the 5-hour stretching of platinum alloys with 7, 10 and 15 % Rh, presented in Fig. 3 (a, b, c), it was observed that all creep curves have parts with a constant strain rate. With increasing temperature at constant strain, the highest elongation of samples is for composition PtRh7, while for the other alloys with 10 and 15 % Rh elongation is significantly reduced.

In Fig. 4. it is given the elongation change of PtRh7 samples depending on the testing period, at a stress of 5 MPa at temperatures of 1300 and 1400°C.
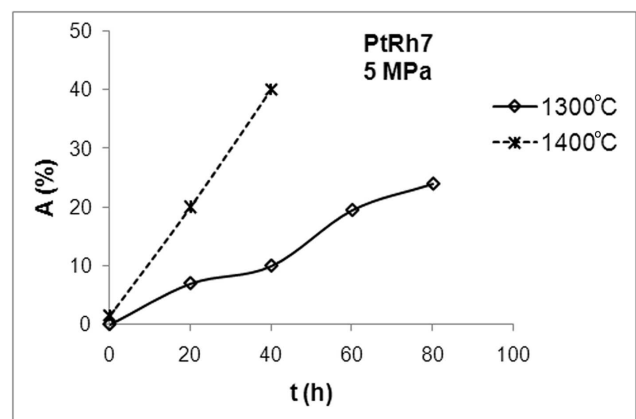

Fig. 4. Dependence of elongation (A) of the testing period, at a stress of 5MPa at 1300°C and 1400°C, for PtRh7 alloy

Based on the dependence shown in Fig. 4, it was observed that the creep curves for PtRh7 alloy at a stress of 5 MPa are characterized by almost linear increase in elongation with increasing the testing period, while the increase in temperature leads to a significant increase in stretching values.

The results in elongation changes of PtRh7 samples as a function of testing time at a stress of 1 MPa, at various temperatures, are shown in Fig. 5. After five hours of testing samples were cooled to room temperature, elongations were measured, and then the same samples were again subjected to 1MPa stress at different temperatures and the examinations continued.
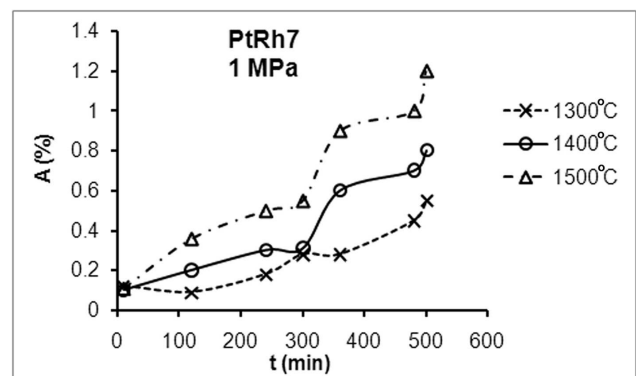

Fig. 5. Dependence of elongation (A) of the testing period, at a stress of 1MPa, at temperatures of 1300, 1400 and 1500°C for PtRh7 alloy

During the 5-hour elongation measurement of samples at a constant stress of 1 MPa, it was observed that with the temperature increase the elongation slightly increases. After termination of stress, cooling samples and repeating the measurement procedure there was a rapid increase of elongation at all temperatures tested.

In all cases where the high temperature testing was interrupted after a certain time interval (5 hours), the shape of creep curves of platinum alloys with 7% Rh depended only on whether the sample had a break in the stress or not. It is noticeable that for the samples, which in cooling had a break in the stress, the creep curves have bends at all test temperatures. Creep curves were practically straight for the case of testing samples without breaking strain, as shown in Fig. 4.

In Fig. 6a it is presented the dependence of elongation of PtRh40 samples of the testing period, at a stress of 14.1 MPa and 20 MPa, at a temperature of 1220°C, while Fig. 6b presents the dependence of elongation of the PtRh40 alloy of the testing period at a stress of 14.1 MPa and 20 MPa at a temperature of 1450°C.
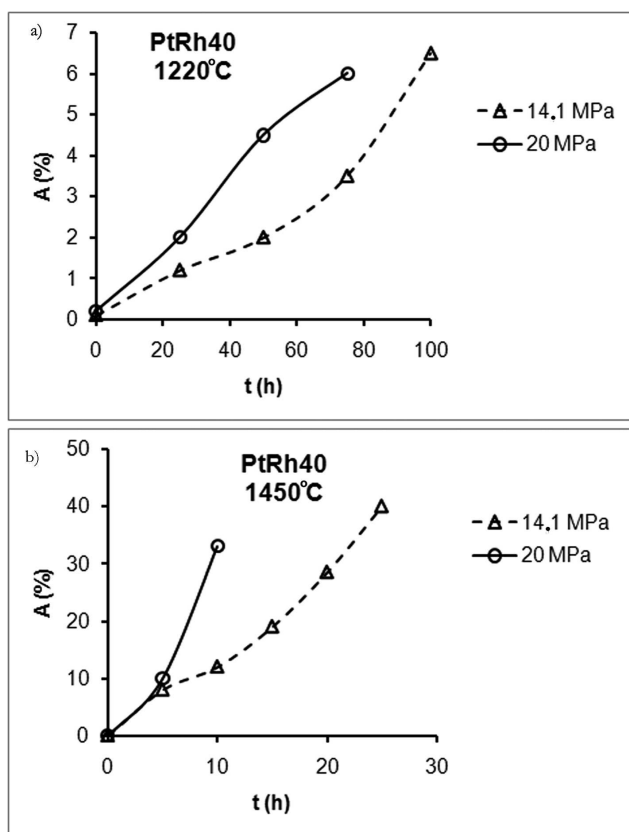

Fig. 6. Dependence of elongation (A) of the testing period at a stress of 14.1 MPa and 20 MPa for the PtRh40 alloy at: a) 1220°C b) 1450°C

Based on the presented results it was observed that with increasing rhodium, values for hardness, tensile strength and elongation increase proportionally. It was particularly observed the effect of platinum hardening with rhodium, at high temperatures (1300 and 1400°C). Tensile strength of platinum with 20% Rh is nearly 3 to 3.5 times higher compared to pure platinum, while the addition of 7% Rh increases the tensile strength of platinum two times in all testing temperatures, and even three times at 1400°C.

Reduction in tensile strength can be expected at rhodium content higher than 30%. This may be explained by the decrease in plasticity of Pt-Rh alloys with high content of rhodium. For this reason, the practical applications have platinum alloys with 5, 7, 10, 13 and 15% Rh.

Based on the size of the atomic diameters of precious metals [28], rhodium stands out as a metal which significantly increases the effect of platinum hardening.

If a melting temperature of alloying element is higher (Pt-1768°C, Rh-1960°C [28]) the stronger the interatomic connection of that element with the basic metal is [29], and the greater the strengthening with that alloying element is, which was confirmed by our results.

By increasing concentrations of metals with higher melting temperature than platinum, the tensile strength increases proportionally, while reducing the creep rate of alloys based on platinum [29]. In our case, by increasing the concentration of rhodium, the interatomic bond forces and high temperature resistance of platinum alloys increase.

An important mechanism in platinum strengthening, using platinum group metals (primarily rhodium), at high temperatures, which controls the creep process, is blocking (preventing) the movement of dislocations. In blocking the movement of dislocations due to the accumulation of rhodium atoms, the lattice errors energy reduces and for the further realization of the creep process additional (critical) strain is necessary. When forming a solid solution of platinum with rhodium, where there is a big difference in the values of lattice defects energy of basic and alloying element ($\gamma_{Pt} = 120$ kJ/m^2 and $\gamma_{Rh} = 180$ kJ/m^2) [29], any increase in the concentration of rhodium results in solid solution strengthening, as after all, our results have confirmed.

For most of the platinum alloys which form a continuous series of solid solutions, it can be assumed that the higher the concentration of alloying element is, as well as greater difference in lattice errors energy of platinum and that element, the greater the strengthening of platinum-based solid solution is.

About the value of the lattice errors energy of platinum and its alloys can be judged based on the dislocation structure, as shown in study [30].

By alloying platinum with rhodium the size of the cavity decreases almost twice, leading to distortion of the perfect dislocation structure: cavities have broken boundaries, isolated dislocations within holes are fixed. When alloying platinum with rhodium, a dislocation structure with a fairly uniform distribution of dislocations can be formed, as well. Such a change of dislocation structure of platinum testifies of reducing the lattice errors energy of the dislocation structure. As a result, the speed of high-temperature creep of platinum when alloying with rhodium is significantly reduced.
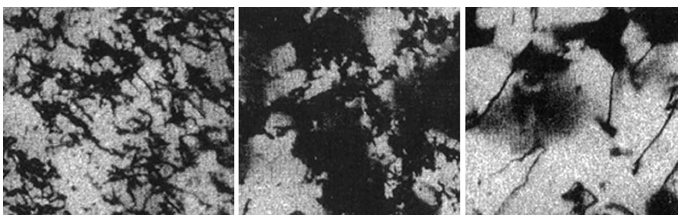

Fig. 7. The dislocation structure of the sample with composition PtRh10, with deformation degree of 6% [30]

4. Conclusion

Hardness testing at room temperature was performed, as well as tensile strength and elongation of selected Pt-Rh system alloys containing rhodium to 40%, in the temperature range of 1100-1500°C, at different stresses.

Based on obtained results, it was concluded that the hardness of investigated alloys, at room temperature, increases proportionally with increasing rhodium content.

The values of tensile strength increase with increasing rhodium content in the alloy, and significantly decrease with increasing temperature.

As opposed to that, the elongation decreases to 7% Rh, then increases with increasing rhodium content of 15% and then slowly decreases again. With increasing temperature there is a slight increase in elongation.

For PtRh40 alloy creep curves have the form characteristic for creep of pure metals, where plastic deformation at high temperatures is controlled by creep dislocation mechanism.

By increasing rhodium content, the resistance of Pt-Rh system alloys at high temperatures increases, which is explained, on one hand, with the high melting temperature of rhodium, and, on the other hand, with small difference in atomic diameters of platinum and rhodium.

Acknowledgements

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