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Investigation of mechanical and structural characteristics of platinum and palladium at high temperatures

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ABSTRACT: In order to broaden future application of products based on platinum and palladium a comparative analysis of their high-temperature mechanical properties was performed. Platinum and palladium are of great importance and are widely used in chemical industry, electronics, for making laboratory dishes, to name a few. Mechanical properties of pure metals, such as: tensile strength, creep rate and rupture time were investigated using universal testing machine for tensile testing of materials. Microstructure of samples was investigated by optical microscopy. Based on obtained results it can be concluded that the platinum, compared to palladium, is superior for high-temperature applications.

KEYWORDS: Annealing; Creep; Deformation; Metals; Tensile test

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RESUMEN: *Estudio de las características mecánicas y estructurales del platino y paladio a altas temperaturas*. Se realiza un estudio comparativo de las propiedades mecánicas a alta temperatura del platino y paladio, con el fin de ampliar las aplicaciones de los productos basados en estos metales. El platino y el paladio son de gran importancia y se utilizan ampliamente en la industria química, electrónica y para la fabricación de placas de laboratorio, entre otras aplicaciones. Se estudiaron las siguientes propiedades mecánicas de los metales puros: resistencia a la tracción, velocidad de fluencia y tiempo de rotura bajo condiciones de fluencia. Para esas investigaciones se utilizó una máquina universal de ensayos para realizar los ensayos de tracción. La micro-estructura fue investigada por microscopía óptica. Basándose en los resultados obtenidos, se puede concluir que el platino, en comparación con el paladio, presenta mejores prestaciones para aplicaciones a alta temperatura.

PALABRAS CLAVE: Deformación; Ensayo de tracción; Fluencia; Metales; Recocido

1. INTRODUCTION

The interest in platinum and platinum alloys increases constantly, because the new areas of application are continuously discovered (Gavin, 2010). 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 (Preston, 1960; Fischer, 1992) and nitrogen fertilizers (Ning *et al*., 1996; Yuantao and Zhengfen, 1999; Trumić *et al*., 2009), production of thermocouples (Wu and Liu, 1997), production of automotive catalysts (Funabiki *et al*., 1991), jewelry (Biggs *et al*., 2005; Wright, 2002) and sensors (González-López *et al.*, 2010). Recently, glucose sensors based on nanoparticles of platinum alloys with Ru, Pd and Au, on the carrier of carbon, have been developed (Xiao *et al.*, 2009).

1.1. Platinum

The influence of cold deformation and annealing temperature on mechanical properties of platinum (samples with purity 99.5%, 99.9% and 99.99%) have been studied by Trumić *et al.* (2010) while Loginov *et al.* (2007) investigated rheological properties of 99.93 wt% Pt. It was found that the destruction of 99.5% pure Pt sample occurs at the annealing temperature of 650–680 °C. Samples of higher purity, with increasing annealing time, were maintaining mechanical properties. The deformation degree had almost no effect on recrystallization temperature of different purity platinum. Temperature dependence of thermodynamic and mechanical properties of six fcc transition metals (Ni, Cu, Ag, Au, Pt, Rh) were examined using Molecular Dynamics (MD) simulations by Cagin *et al.* (1999). Comparative analysis of high temperature strength of platinum and its binary alloys with low content of alloying element was done by Trumić *et al.* (2012). Considering that platinum is an active component of automotive three-way catalysts, Singh *et al.* (2008) investigated oxidation of carbon monoxide over Pt/Al_2O_3. Kim *et al.* (2011) examined propane combustion over Pt catalysts supported on various zeolites.

1.2. Palladium

Different ways of production of palladium nanoparticles production (Redon *et al.*, 2011; Desforges *et al.*, 2005), as well as palladium nanowires and nanorods (Bliznakov *et al.*, 2011) have been investigated. Ohm and Hill (2010) examined thermoelectric behavior of palladium, and Kordas *et al.* (2000) studied Pd thin film deposition on polymers from liquid precursors. Edwards and Hutchings (2008) wrote about recent progress in direct synthesis of hydrogen peroxide using supported palladium and gold–palladium alloy catalysts. Anodic passivation of palladium in alkaline medium was studied by means of different electrochemical techniques (García-Ochoa and Genescá, 2000).

The aim of this study is to investigate mechanical properties and structure of platinum and palladium at high temperatures.

2. MATERIALS AND METHODS

All experimental examinations which results are presented in this paper were performed on platinum samples of 99.95% purity and palladium 99.5% purity.

Platinum and palladium for preparation of all samples originate from production of electrolytic copper RTB group, Serbia, obtained as by-products, technical grade. With additional refinement at Institute of Mining and Metallurgy (Bor, Serbia) purity required for sample preparation was achieved. Impurities in samples were characteristic for raw material of Bor deposits: Pd, Ag, Au, Bi, Sb, As, Cu.

Melting of samples was carried out in a vacuum middle frequency induction furnace. Annealing of samples was carried out in an electro resistant furnace type LP08. For determination of high-temperature tensile strength of pure platinum and palladium in the temperature range 1100–1400 °C, samples of 1.3 mm in diameter and 50 mm long were used. Before testing, the samples were annealed at 1300 °C for 3 hours. Deformation rate in tests was 6 mm min^{-1}. For mechanical properties testing of the samples at high temperatures, a universal device for tensile testing of materials up to 1500 °C, by manufacturer Karl Frank, type 81221, was used. For testing time dependant strength and elongation at high temperatures, "Mayes" MK 2 TC/10 unit, was used. Chemical analysis of samples material was performed on atomic absorption spectrophotometer. Structure of the samples was examined using an optical microscope.

3. RESULTS AND DISSCUSION

In order to find new possibilities of platinum and palladium use, their mechanical properties at high temperatures were examined.

Dependence of a short time tensile strength (R_{100}) from temperature, for pure platinum and palladium are shown in Figure 1. Dependence of tensile high temperature strength (UTS) for pure Pt and Pd from temperature, in the temperature range 900–1200 °C, are shown in Figure 2.

From Figures 1 and 2, it can be concluded that short time tensile strength and tensile high-temperature strength of platinum have higher values

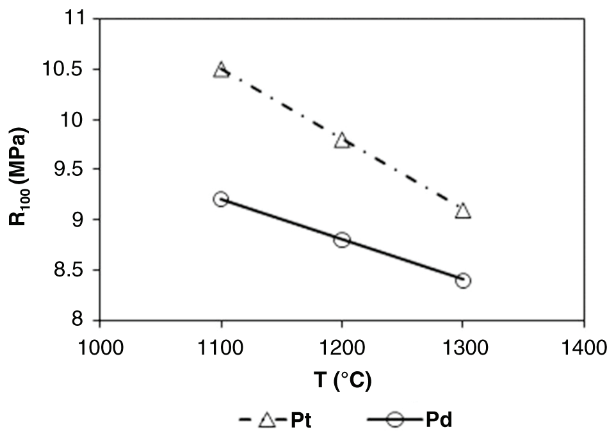

FIGURE 1. Dependence of short time tensile strength (R_{100}) Pt and Pd on temperature.

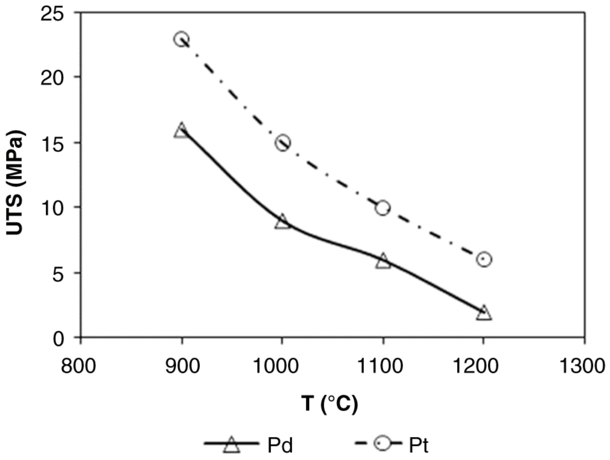

FIGURE 2. The dependence of tensile high temperature strength (UTS) Pt and Pd on temperature.

compared to the same mechanical properties of pure palladium. In temperature range 900–1300 °C, with temperature increase these mechanical properties decrease for both, platinum and palladium.

Test results of dependence of rupture time (t) of platinum and palladium in temperature range 1200–1400 °C, at a stress of 5 MPa, are shown in Figure 3. Values of rupture time of platinum and palladium in the temperature range 1200–1400 °C, at a stress of 5 MPa, showed significant decrease with increasing temperature, while values for platinum were significantly higher compared to that of palladium.

Test results of creep rate ($\dot{\varepsilon}$) of platinum and palladium at 1200 and 1300 °C, at a stress of 5 MPa, are shown in Table 1. Creep speed of platinum and palladium in temperature range 1200–1300 °C, at a stress of 5 MPa, increases with increasing temperature,

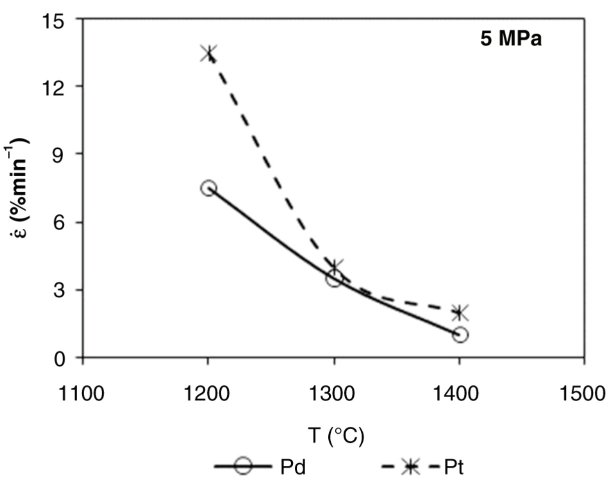

FIGURE 3. The dependence of the Pt and Pd rupture time from temperature, at a stress of 5 MPa.

TABLE 1. Creep rate values for Pt and Pd at 1200 and 1300 °C, at a stress of 5 Mpa

T (°C)	$\dot{\varepsilon}_{Pt}$ (% min^{-1})	$\dot{\varepsilon}_{Pd}$ (% min^{-1})
1200	0.2	0
1300	0.5	0.05

while values for platinum are significantly higher than values of creep rate for palladium.

It is characteristic for palladium that in the investigated temperature range (1200–1400 °C) creep resistance increases with increasing temperature, which can be explained by appearance of internal oxidation of metals or impact and effect of present impurities. The higher the creep resistance of palladium is, his rupture time in the temperature range 1200–1400 °C is significantly shorter compared with pure platinum (Fig. 3).

A relative elongation of platinum and palladium at a stress of 5 MPa was determined (Tables 2 and 3). From the obtained results it can be concluded that the relative elongation of platinum increases noticeably with temperature increase, while that increase in value for palladium is insignificant.

In order to investigate plasticity of palladium, fracture character at stretching in temperature range 500–1200 °C was determined. Characteristics of plasticity and fracture of the palladium samples with 2 mm in diameter after the high temperature stretching are given in Table 4.

For palladium, greatest plasticity was observed at 500 °C. At this temperature, with prolongation of stretching time, obtained values of elongation and reduction in cross-sectional area at fracture are almost 3 times lower.

Further increasing of temperature to 700 °C reduces the plasticity of palladium. In the temperature range 900–1250 °C palladium has the lowest values of relative elongation and characteristic

TABLE 2. Relative elongation of platinum (strain 5 MPa)

T (°C)	Elongation (%)
1100	28
1400	55

TABLE 3. Relative elongation of palladium (strain 5 MPa)

T (°C)	Elongation (%)
1100	23
1200	28
1300	28

TABLE 4. Plasticity and fracture characteristics of palladium samples after the high temperature tensile tests

T (°C)	$\sigma^{\S}$ (MPa)	$t^{\dagger}$ (h)	$A^{\dagger\dagger}$ (%)	$f^{\ddagger}$ (%)	Fracture character
500	61	Instant fracture	94	89	Plastic, primarily within the crystal.
500	23	181	28	36	Plastic, primarily intercrystalline.
700	35	Instant fracture	42	88	Plastic, primarily intercrystalline.
700	14	1416	–	–	No fractures, intercrystalline cracks were observed on the surface.
900	8.5	137	4.4	2.0	Brittle fracture, intercrystalline.
1250	1.2	115	3.5	–	Brittle fracture, intercrystalline.

$\sigma^{\S}$: Strain; $t^{\dagger}$: Time untill break; $A^{\dagger\dagger}$: Elongation; $f^{\ddagger}$: Surface reduction at fracture

intercrystalline fracture, which is in agreement with literature data (Savickij *et al.*, 1975; Ritvin, 1987).

These observed changes in plasticity of palladium in temperature range 500–700 °C can be explained by forming of solid palladium oxide (Ritvin and Medovoj, 1974), while at temperatures above 900 °C, changes are influenced by increased absorption of gases (Ritvin, 1987).

Based on the obtained results it can be concluded that palladium is much less resistant to high temperatures compared to platinum.

It was found that at a constant creep rate of 0.5% h^{-1}, changes within the platinum grain occur at temperatures lower than 500–700 °C, while at the same conditions for palladium, at temperatures lower than 600–800 °C (Savickij *et al.*, 1975; Ritvin, 1987).

Our contribution to the study of creep mechanism of metals with a face centered cubic lattice, consisted in examining changes in pure platinum microstructure at a stress of 1–13 MPa in the temperature range 1350–1400 °C. The microstructure of platinum, deformed at a stress of 1 MPa at a temperature of 1350 °C is shown in Figure 4.

Based on the obtained microstructure of platinum, it can be concluded that as a result of high-temperature creep, straight lines and wavy traces of deformation occurs in microstructure of grains. In first case, creep traces pass through grain boundaries (Fig. 4a), in second case they weaken (Fig. 4b), while in the third case they almost don't reach grain boundaries (Fig. 4c). In Figure 4a sliding lines are visible almost on the entire grain surface, in Figure 4b they are present only in grain center, while in Figure 4c they are not noticeable. It was concluded that they appear as a result of changes within grains or due to deformation processes which results in moving of grain boundaries. Dashed, wavy, and sometimes almost straight creep lines can be observed in platinum grains after high-temperature creep at 1350 °C at a stress of 5 and 13 MPa (Fig. 5).

Based on the presented results, it can be concluded that metal evaporation contributes to changes in microstructure of platinum grains at high-temperature creep. As a result of metal evaporation, there are micro geometric changes in microstructure; there is a grain boundary etching and appearance of parallel lines in grains. In terms of short-term heating (a few seconds or minutes), at moderate temperatures (below 1000 °C) micro changes in structure develop slightly and practically don't show

a) b) c)

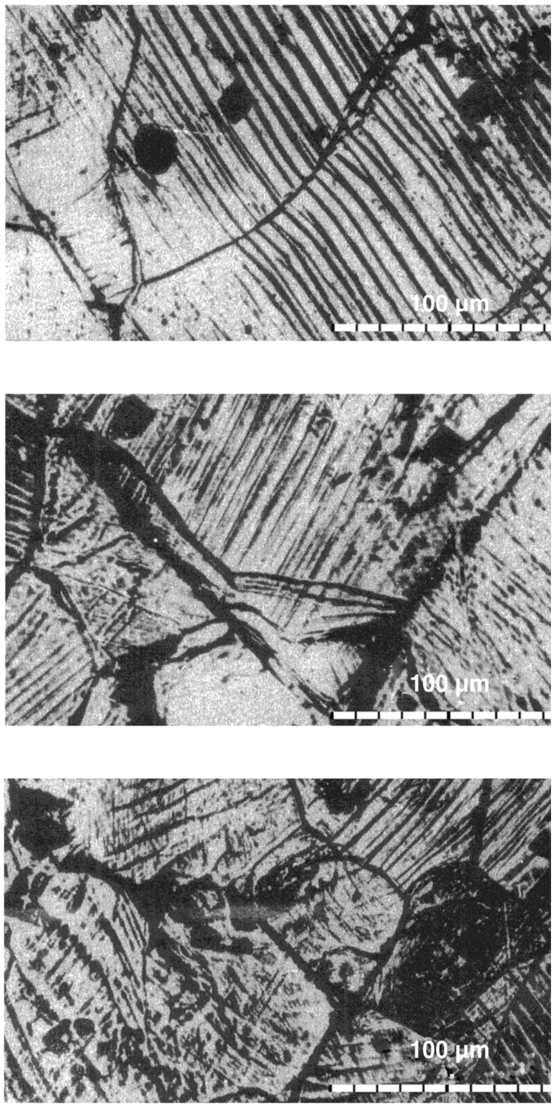

FIGURE 4. Microstructure of platinum after creep lasting 1 hour, at a stress of 1 MPa at 1350 °C (a, b and c).

a)

b)

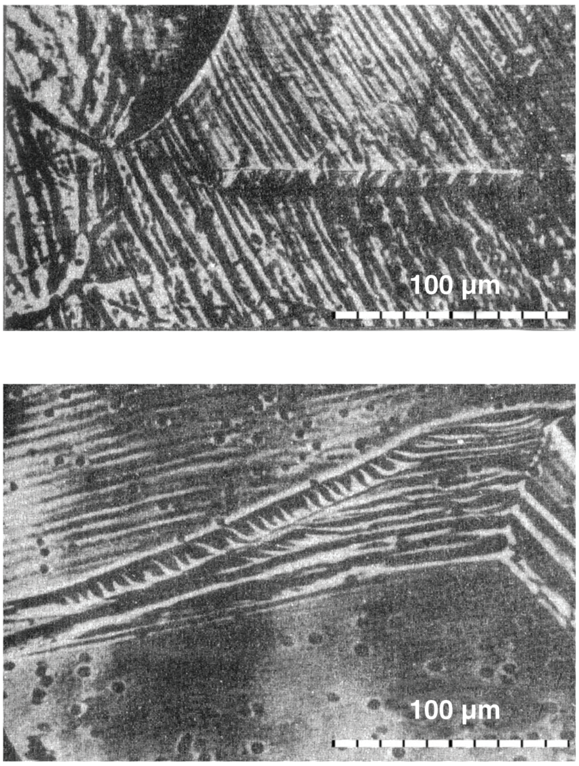

FIGURE 5. Platinum microstructure after creep at 1350 °C: a) at a stress of 5 MPa for a period of 1 hour and b) at a stress of 13 MPa for a period of 10 minutes.

any significant impact on high temperature stability of platinum. Prolonged heating (several hours or more) at temperatures greater than 1000 °C, can lead to a pronounced structural changes, weakening of grain boundaries and accelerated destruction of metals at strain.

4. CONCLUSIONS

The paper presents a comparative analysis of high-temperature characteristics of pure platinum and palladium. Based on obtained results it can be concluded that:

- Values of short time tensile strength and high-temperature tensile strength of pure platinum are higher compared to the same values for palladium.
- In temperature range 900–1300 °C investigated mechanical properties decrease for both, platinum and palladium.
- Rupture time for platinum and palladium in temperature range of 1200–1400 °C, at a stress of 5 MPa, decreases with increasing temperature. Values for platinum are higher in comparison to that of palladium.
- Creep rate of platinum and palladium in temperature range 1200–1300 °C, at a stress of 5 MPa, increases with increasing temperature. Values for platinum are much higher compared with those for pure palladium.
- Relative elongation of platinum increases sharply in temperature range 1100–1400 °C, at a stress of 5 MPa. For palladium, under same conditions, elongation increasing is negligible.
- Maximum plasticity of palladium was observed at 500 °C.
- Increasing the temperature to 700 °C reduces the plasticity of palladium.
- In the temperature range 900–1250 °C palladium has the lowest values of relative elongation and typical intercrystalline fracture.
- When strained at 1 MPa at a temperature of 1350 °C for one hour, in the microstructure of platinum grain, straight and wavy traces of deformation appear.
- After a high-temperature creep of platinum at 1350 °C at a stress of 5 and 13 MPa, dashed, wavy and very often straight creep lines in certain areas of platinum grains appear.
- At temperatures up to 1000 °C, after brief heating of platinum and palladium, changes in microstructure of grains are negligible and do not significantly affect the high temperature characteristics of these metals.
- At temperatures above 1000 °C, with prolonged heating of platinum and palladium, significant changes in surface structure occur, resulting in a weakening of grain boundaries and accelerated destruction of metals at strain.
- Based on overall consideration of obtained results of the high-temperature strength of platinum and palladium, it can be concluded with certainty that platinum, at temperatures over 1000 °C and under different stresses, is superior to palladium.

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