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Optimisation of the Recrystallisation Annealing Regime of Pd-5Ni Alloy

Using experimental design and statistical analysis to understand the metallurgical properties of palladium alloy for ammonia oxidation catchment gauze applications

By Aleksandra T. Ivanović* and Biserka T. Trumić
Mining and Metallurgy Institute (IRM) Bor, Zeleni bulevar 35, Bor, Serbia

Email: aleksandra.ivanovic@irmbor.co.rs

Svetlana Lj. Ivanov and Saša R. Marjanović
University of Belgrade, Technical Faculty in Bor, VJ 12, Bor, Serbia

Milorad M. Zrilić and Tatjana D. Volkov-Husović
University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia

Branka B. Petković
Faculty of Natural Science and Mathematics, University of Priština, Lole Ribara 29, Kosovska Mitrovica, Serbia

In this paper, changes in the mechanical properties of Pd-5Ni alloy are analysed after recrystallisation annealing in order to determine the optimal conditions for a thermomechanical processing regime for this alloy. The temperature and annealing time were varied and the resulting changes in hardness, tensile strength, relative elongation and proof strength were monitored. By using the simplex-lattice method and analysing experimental data, a fourth degree mathematical model-regression polynomial was defined and isolines of changes in the mechanical properties of the investigated alloys were designed depending on the conditions of heat treatment after rolling.

Introduction

Metal meshes, usually of platinum-rhodium or platinum-rhodium-palladium alloy, are used as ammonia oxidation catalysts for the production of nitric acid. These catalysts are exposed to very rigorous conditions: high temperature, high pressure, gas turbulence and the influence of oxygen, which can lead to rapid destruction of the catalysts and the reduction of their service life. Depending on the operating conditions in the reactor (temperature, pressure and ratio of oxygen to NH_3), losses of platinum group metals (pgms) from the catalytic meshes occur due to the formation of volatile oxides PtO_2, PdO and RhO_2 which are taken away by the gas stream (1, 2). Empirically, these losses are in the range 0.035–0.065 g/t_{HNO_3} for reactors operating at atmospheric pressure, or 0.32–0.39 g/t_{HNO_3} for reactors working under high pressure. Most of these losses are irreversible, and only 35–40% of the metal can be recycled by periodic cleaning of gas installations of adhered dust, and replacing and processing of the filter filling.

In order to reduce such incurred losses of platinum metals, due to their high cost (3), manufacturers and researchers in many countries have made significant efforts to develop processes for the efficient capture and recycling of products of oxidation of platinum metals resulting from the production of nitric acid, and in other, related, high-temperature catalytic processes (4). One of these methods is the use of Pd catchment gauzes or recovery gauzes arranged in conjunction with conventional Pt catalysts. The role of the Pd catchment gauze is to reduce the volatile PtO_2 from the gaseous stream to metal form, and retain the Pt metal on the surface of the Pd.

By placing the Pd catchment gauze just behind the platinum catalysts in the reaction zones, the resulting volatile PtO_2 reacts with Pd according to Equation (i):

$$2Pd + PtO_2 \rightarrow Pt + 2PdO \qquad \text{(i)}$$

Due to the higher affinity of Pd for oxygen relative to Pt, when there is contact between PtO_2 and Pd there is an exchange of oxygen.The Pt metal is then caught on the surface of the Pd mesh and kept there. Incorporation of Pt in the surface layers of the Pd catchment gauzes is further supported by the oxidation and evaporation of the alloying element in the Pd alloy at the temperature of ammonia oxidation, which assists in the retention of Pt on the Pd catchment gauze. These are the basic assumptions about the mechanism by which the process of capturing Pt using Pd catchment gauzes takes place.

Initially the catchment gauzes were made from palladium-gold alloys (4–6), while more recently palladium-nickel alloys have been used (7). Pd-Au catchment gauzes have a relatively short service life and can withstand only two campaigns before their complete destruction (1). Because of the short lifetime of the Pd-Au gauze and the high cost of both Au and Pd (up to 50% of the investment in Pt), Pd-Ni catchment gauzes are an attractive alternative. Compared to Au, Ni has a lower cost and produces comparable catalytic activity when used as an alloying element with Pd. The mechanical properties of Pd can be significantly improved by alloying with Ni and applying an appropriate thermomechanical treatment regime. Pd-Ni alloys in the solid-state create a continuous series of solid solutions (8).

The aim of this study was to determine the optimal recrystallisation parameters for annealing the Pd-5Ni alloy by testing the dependence of the mechanical and structural properties on the temperature and time of recrystallisation annealing. This will allow alloys of satisfactory mechanical properties to be obtained for further cold plastic processing or rolling. In this paper, the simplex method (9,10) was applied for the selection of an optimal heat treatment regime after rolling, for which previous studies at IRM Bor enabled selection of the factors and their levels (11). The simplex plans by Scheffe (12–14) were used to devise suitable experimental space allowing complex models of the investigated dependencies to be obtained (15–22).

Table I Results of X-ray Analysis of the Pd-5Ni Alloy Sample

Elements	Pd-5Ni alloy
% Pd	95.00
% Ni	5.00

Experimental

For the preparation of the samples, Pd powder of 99.99% purity and Ni in the form of thin sheets of 99.95% purity were used. The Ni content in the prepared samples was 5% by weight. Starting materials were first compressed on a hydraulic press in order to achieve better compactness of the material, and then the melting and casting of the samples were performed in a medium frequency induction furnace, in a magnesium oxide pot of dimensions $h_1 \times h_2 = 85 \times 80$ mm, $d_1 \times d_2 = 65 \times 55$ mm, under vacuum. The melting point of the Pd-5Ni alloy is 1520ºC. Prior to casting, the batch was overheated between 350–400ºC. To control the composition of the cast alloy an X-ray fluorescence analyser Niton^{TM} XL3t-950 was used. Homogenisation annealing was performed in an electric resistance furnace chamber type LP08 at 900ºC for 30 min. After that, rolling of samples was performed in duo-stand rolls with calibrated rollers of cross-sectional dimension 1.7 × 1.7 mm (with 97% reduction) and with intermediate annealing (900ºC, 15 min). Thermal treatment of the Pd-5Ni alloy samples after rolling in the form of a wire consisted of recrystallisation annealing and was performed in accordance with the given regimes (**Table II**).

The optimisation parameterswere Vickers hardness (HV), ultimate tensile strength (R_m), yield strength ($R_{p0.2\%}$), and relative elongation (A). Influential factors are recrystallisation annealing temperature (T) and recrystallisation annealing time (τ). For each combination of factors three repeated readings in a random order were performed. To select the optimum heat treatment conditions after rolling a simplex plan with fifteen experimental points and a fourth degree polynomial for the mathematical model were applied. Hardness measurements were performed on a combined instrument for measuring

Table II Matrix of Plan of the Experiment, Heat Treatment Regimes and the Results of the Experiment

Serial number of experiment	Coded values of factors			Regimes of recrystallisation annealing		Mean values of mechanical properties			
	x_1	x_2	x_3	T, ºC	τ, min	HV	R_m, MPa	$R_{p0.2\%}$, MPa	A, %
1	1	0	0	750	20	120.33	306	120	34
2	0	1	0	750	40	113	304	134	48
3	0	0	1	950	30	87.33	296	132	45
4	0.5	0.5	0	750	30	113	306	130	47
5	0.5	0	0.5	850	25	118.33	296	137	45
6	0	0.5	0.5	850	35	99.6	298	130	46
7	0.75	0.25	0	750	25	119	314	142	45
8	0.25	0.75	0	750	35	113	314	145	39
9	0.75	0	0.25	800	22.5	120.67	308	149	42
10	0.25	0	0.75	900	27.5	113.67	303	128	38
11	0	0.75	0.25	800	37.5	106	303	145	39
12	0	0.25	0.75	900	32.5	87.3	314	142	45
13	0.5	0.25	0.25	800	27.5	117.33	314	142	45
14	0.25	0.5	0.25	800	32.5	108.37	305	145	43
15	0.25	0.25	0.5	850	30	100.33	314	132	47
K_1	0.16	0.15	0.69	887.5	30	97	298	131	47
K_2	0.459	0.166	0.375	825	27.5	117	304	134	48

the Vickers hardness and Brinell hardness, from WPM (Werkstoffprüfmaschinen), Germany, with a hardness measurement range from 5 to 250 daN. Determination of tensile strength, relative elongation and yield strength (system responses) were performed on an Instron® 1332 materials testing machine of 100 kN. The tubes of test material were clenched by mechanical jaws and stretched at a rate of 10 mm s^{-1}. Before testing all tubes were cut to a length of 150 mm.

Mathematical processing of data obtained using the simplex method was performed with the help of specially developed software in the Delphi programming environment. Using the above software, mathematical models to describe the influence of annealing parameters on the hardness of the Pd-5Ni alloy were obtained. The adequacy of the model was determined on the basis of Student's criteria in control points (12, 13, 19, 20, 22, 23).Examination of the microstructure was performed on samples measuring 1.7 × 1.7 mm, which were prepared according to standard procedure: grinding, polishing (Zentrifugenbau RÖWAG polishing machine) with 0.05 μm Al_2O_3 powder and etched for a few seconds with a solution of 1 g CrO_3 + 20 ml HCl. Optical microscopy was performed on a metallographic microscope Epytip 2 (Carl Zeiss Jena, Germany), at 400× magnification. Changes in grain size with increasing temperature were monitored using the program Image-Pro® Plus for image analysis.

Results and Discussion

The X-ray spectrum of the sample of Pd-5Ni alloy is shown in **Figure 1**, and the results of the analysis are given in **Table I**. The results and analysis of the spectrum show that the cast alloy contains 95% Pd and 5% Ni, and hence it can be concluded that there was no loss or contamination of the alloy during casting.

Table II shows a matrix of the simplex plan of the experiment with 15 experimental points and heat treatment regimes and the results of the experiment.

By analysing the experimental results using specially developed software in the Delphi programming

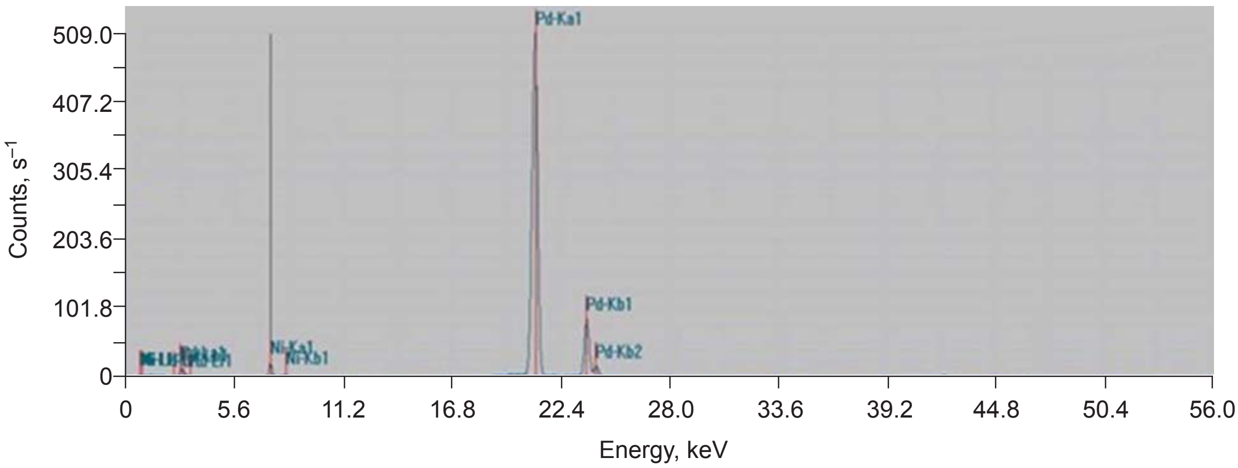

Fig. 1. The X-ray spectrum of the sample of Pd-5Ni alloy

environment, the dependence of the system response (HV, R_m, $R_{p0.2\%}$, A) on the input factors (temperature and annealing time) was obtained in the form of Equations (ii)–(v):

$$Y_{HV} = 120.33x_1 + 113x_2 + 87.33x_3 - 14.66x_1x_2 + 58x_1x_3 - 2.26x_2x_3 + 12.453x_1x_2(x_1 - x_2) - 50.667x_1x_3(x_1 - x_3) + 31.28x_2x_3(x_2 - x_3) + 44.453x_1x_2(x_1 - x_2)^2 + 52.587x_1x_3(x_1 - x_3)^2 - 65.947x_2x_3(x_2 - x_3)^2 + 541.520x_1^2x_2x_3 + 1.653x_1x_2^2x_3 - 797.68x_1x_2x_3^2 \qquad \text{(ii)}$$

$$Y_{Rm} = 306x_1 + 304x_2 + 296x_3 + 4x_1x_2 - 20x_1x_3 - 8x_2x_3 - 5.33x_1x_2(x_1 - x_2) - 80x_2x_3(x_2 - x_3) + 176x_1x_2(x_1 - x_2)^2 + 176x_1x_3(x_1 - x_3)^2 + 213.33x_2x_3(x_2 - x_3)^2 + 576x_1^2x_2x_3 - 368x_1x_2^2x_3 - 613.33x_1x_2x_3^2 \qquad \text{(iii)}$$

$$Y_A = 34x_1 + 48x_2 + 45x_3 + 24x_1x_2 + 22x_1x_3 - 2x_2x_3 + 69.33x_1x_2(x_1 - x_2) + 50.667x_2x_3(x_2 - x_3) - 40x_1x_3(x_1 - x_3) - 74.667x_1x_2(x_1 - x_2)^2 - 77.33x_1x_3(x_1 - x_3)^2 - 88x_2x_3(x_2 - x_3)^2 - 376x_1^2x_2x_3 + 40x_1x_2^2x_3 + 272x_1x_2x_3^2 \qquad \text{(iv)}$$

$$Y_{Rp0.2\%} = 120x_1 + 134x_2 + 132x_3 + 12x_1x_2 + 44x_1x_3 - 12x_2x_3 + 18.7x_1x_2(x_1 - x_2) + 10.67x_2x_3(x_2 - x_3) + 144x_1x_3(x_1 - x_3) + 298.67x_1x_2(x_1 - x_2)^2 + 90.67x_1x_3(x_1 - x_3)^2 + 272x_2x_3(x_2 - x_3)^2 - 141.33x_1^2x_2x_3 + 744x_1x_2^2x_3 - 317.33x_1x_2x_3^2 \qquad \text{(v)}$$

To check the adequacy of the selected models the control points $K_1(0.16;\ 0.15;\ 0.69)$ and $K_2(0.459;\ 0.166;\ 0.375)$ were used, where additional tests were performed under the following experimental conditions: T_1 = 887.5ºC, τ_1 = 30 min and T_2 = 825ºC, τ_2 = 27.5 min. The analysis showed the adequacy of the fourth degree model for all observed mechanical properties by Student's criteria for the credibility coefficient 0.995 and 14 levels of freedom in the control points (t_k(за $К_1$_0.94157; за$К_2$_2.49087) < t_{kr}(0.995; 14)_2.98). On the basis of these checks it can be claimed with a probability of 99.5% that the adopted mathematical model is adequate and that the model parameters are relevant to the selected heat treatment regime.

Certain mechanical properties are changed variously under the influence of the diffusion processes that take place during annealing (11, 24, 25).

Using Equations (ii)–(v) and specially developed software in the Delphi environment, isoline diagrams of level $Y_i = f(x_1, x_2, x_3)$, i = HV, R_m, $R_{p0.2\%}$, A were constructed. Isolines represent the set of temperature and time points which give the same values for the optimisation parameters. Changes in the mechanical properties of the investigated alloy correspond to the lines appearing at a given level within the system, depending on the conditions of heat treatment after rolling (**Figure 2**).

The results of mathematical processing confirm that the changes in mechanical properties (HV, R_m, A, $R_{p0.2\%}$) of Pd-5Ni alloy at a constant deformation degree of 97% depend strictly on the temperature and annealing time, defined by a fourth degree regression polynomial according to Equations (ii)–(v). Analysis of

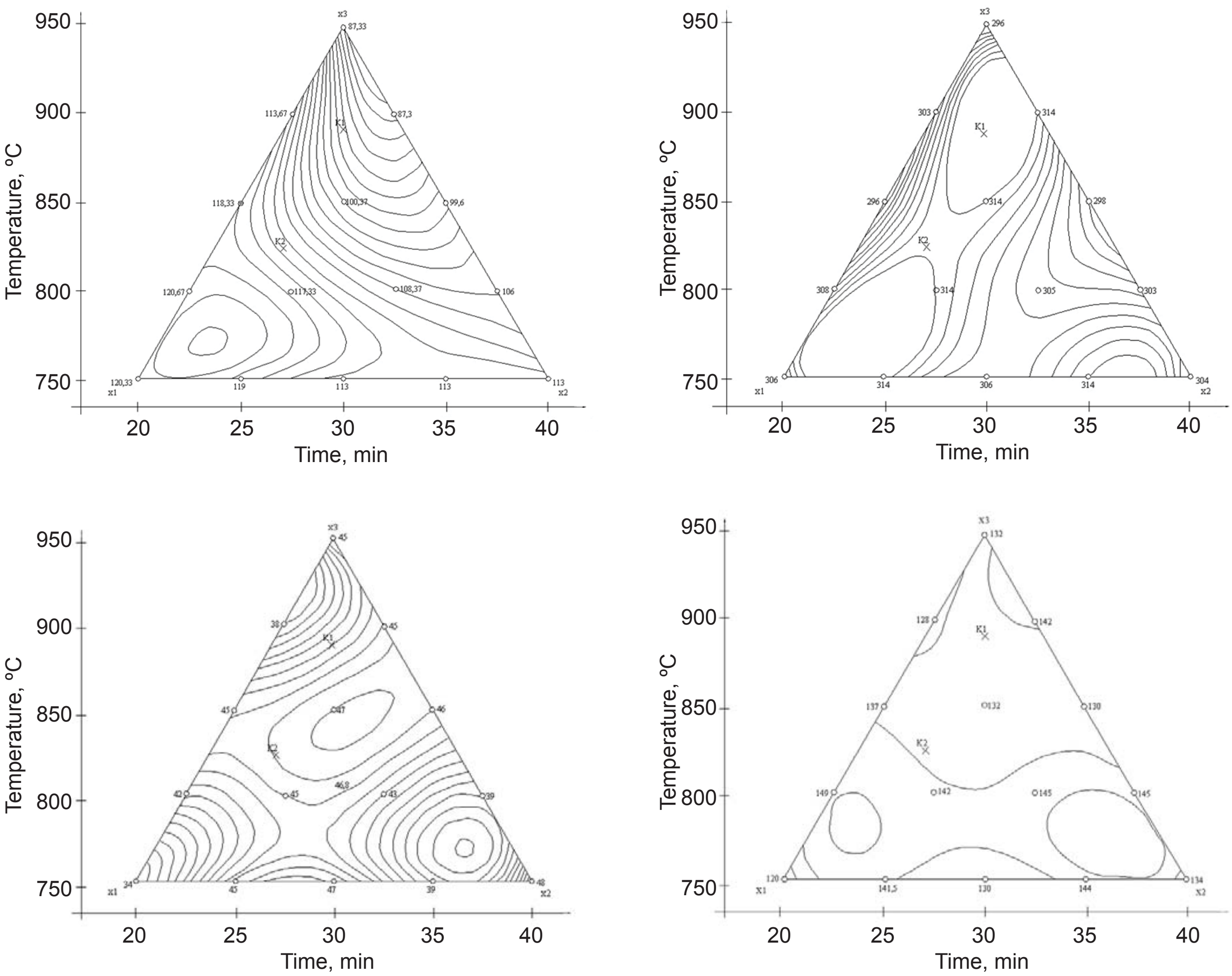

Fig. 2. Dependence of the mechanical properties of heat-treated alloy Pd-5Ni, at constant deformation degree of 97%, as a function of time and annealing temperature (◦ = experimental point; • = computational point; K = control point): (a) simplex triangle of hardness changes (HV); (b) simplex triangle of changes of tensile strength (R_m); (c) simplex triangle of changes of relative elongation (A); and (d) simplex triangle of changes of proof strength ($R_{p0.2\%}$)

the investigation results shows that the alloy annealed at 900ºC for 30 min has satisfactory values for hardness (HV = 89.9), ultimate tensile strength (R_m = 308 MPa), yield strength ($R_{p0.2\%}$ = 134 MPa) and elongation (A=49%), which is a key factor in the application of palladium gauzes for 'capture' of platinum at high temperatures.

Figure 3 shows the structural changes which occur during annealing of the Pd-5Ni alloy after cold rolling at a constant deformation degree of 97% depending on the temperature at a constant time (30 min). The polyhedral grain structure characteristic of a plastically deformed and then annealed alloy can be seen.

Recrystallisation grain size depends on the annealing temperature at a constant time (30 min), and as a rule, the higher the annealing temperature the larger the recrystallised grain, at the same degree of deformation (25). This was confirmed by our results (**Figure 4**).

Based on the investigations performed here, parameters for recrystallisation annealing of Pd-5Ni alloy can easily be set to provide adequate mechanical and structural characteristics for use as a catchment gauze in the catalytic oxidation of ammonia (26–28). For economic and technological reasons the following parameters were chosen as optimal for further plastic

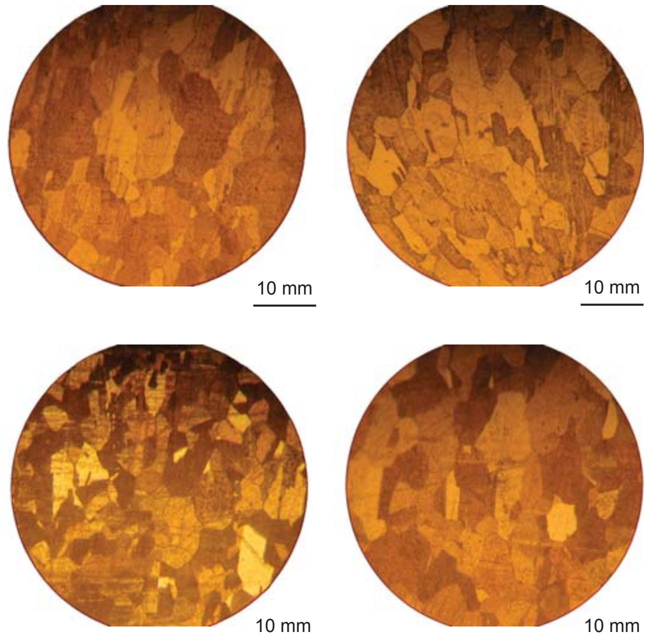

Fig. 3. Microstructure of Pd-5Ni alloy, after rolling and annealing at: a) 820ºC; b) 850ºC; c) 900ºC; and d) 950ºC. All magnifications are 400×

processing: annealing temperature of 900ºC, annealing time of 30 min.

Conclusions

This paper describes the application of experimental design and statistical analysis in studying the effects of recrystallisation annealing parameters on the mechanical properties of Pd-5Ni alloy. The simplex method was used to plan experiments examining the impact of changes in process variables (temperature and annealing time) on the mechanical and structural properties of the Pd-5Ni alloy at a constant deformation degree of 97%. A fourth degree empirical mathematical model was defined to describe the process, on which basis the values of HV, R_m, A, $R_{p0.2\%}$ within the selected values of temperature and annealing time could be predicted. The optimal conditions at the recrystallisation annealing were found to be: recrystallisation annealing temperature of 900ºC and time of 30 min at which satisfactory values for hardness (HV = 89.94), ultimate tensile strength (R_m = 308 MPa) and yield strength ($R_{p0.2\%}$ = 134 MPa) were achieved at a maximum relative elongation (A = 49%).

The above results could be considered a contribution to the characterisation of Pd-5Ni alloy, and are also of importance for selecting the optimal technology to obtain products based on this alloy. However it should be noted that the above alloy has not yet been sufficiently investigated in terms of the determination of structural and mechanical properties depending on the applied thermomechanical processing regime, and further work is recommended in this area.

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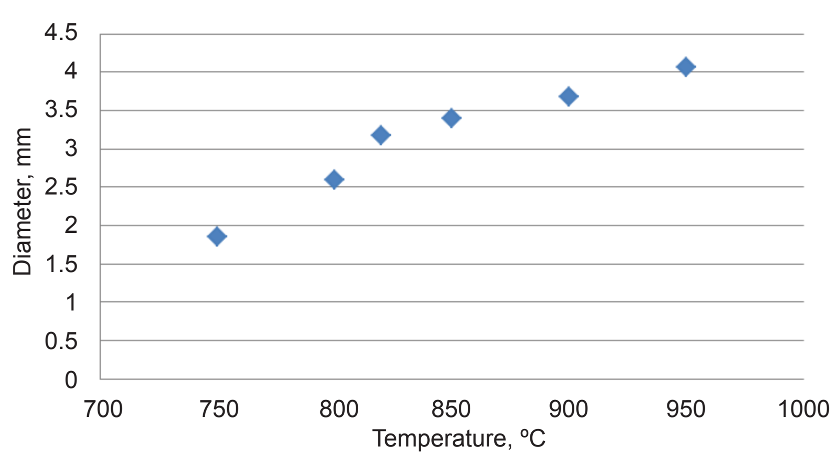

Fig. 4. Change in the size of recrystallised grains with temperature for τ = 30 min

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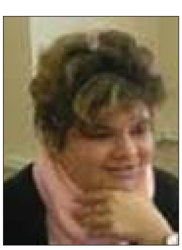
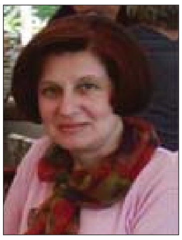


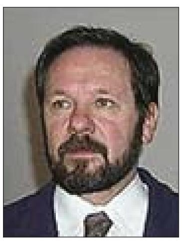
Aleksandra Ivanović is a Research Fellow at the Institute of Mining and Metallurgy (IRM) Bor, Serbia. She recieved her PhD degree from the University of Belgrade, Technical Faculty, in Bor in 2014. Her subjects of interest are processing of platinum metals, mathematical modelling and characterisation of alloys.

Biserka Trumić is a Senior Research Fellow at the IRM Bor. She recieved her PhD degree from the University of Belgrade, Technical Faculty, in Bor in 2001. Her subjects of interest are processing of platinum metals, high-temperature catalysis of ammonia on Pt-Rh-Pd catalysts and characterisation of alloys.

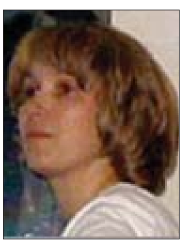


Svetlana Ivanov is an Associate Professor at the University of Belgrade, Technical Faculty in Bor, Department of Metallurgy, where she recieved her PhD degree in 1998. Her subjects of interest are heat treatment and plastic processing of non-ferrous metals, chemical-thermal treatments of metal powder samples, mathematical modelling, characterisation and testing of metallic materials.

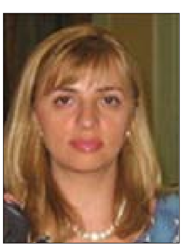
Saša Marjanović is an Assistant Professor at the University of Belgrade, Technical Faculty in Bor, Department of Metallurgy, where he recieved his PhD degree in 2010. His subjects of interest are the processing of metals in the plastic state, physical metallurgy, materials testing and metallurgical thermodynamics.



Milorad Zrilić is a Research Assistant at the University of Belgrade, Faculty of Technology and Metallurgy, Department of Graphic Engineering. He received his MSc degree in 1993. His subjects of interest are experimental techniques, fracture mechanics, composite materials and residual stresses.



Tatjana Volkov-Husović is a Professor at the University of Belgrade, Faculty of Technology and Metallurgy, Department of Metallurgical Engineering. She received her PhD degree from the University of Belgrade, Faculty of Technology and Metallurgy in 1999. Her subjects of interest are transport phenomena in metallurgy, heat transfer in metallurgy, rational design, thermal stability of refractories, characterisation and testing of refractories and mathematical modelling.



Branka Petković is an Assistant Professor at the University of Pristina, Faculty of Natural Science and Mathematics, Department of Chemistry, Serbia. She received her PhD degree from the University of Belgrade, Faculty of Chemistry, in 2013. Her subjects of interest are the development of electrochemical and optical analytical methods, electrochemistry and coordination chemistry.

