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Differences in the mode of thermomechanical processing between white gold alloys to produce semi-finished products

M. B. Miric[1*], R. S. Peric[2], S. P. Dimitrijevic[3], S. A. Mladenovic[4], S. R. Marjanovic[5]

[1]*Directorate of Measures and Precious Metals, Beograd, Department of the control subjects in precious metals, Nis, Serbia*
[2]*PERIC & PERIC & Co. d.o.o., Pozarevac, Serbia*
[3]*Innovation center of the Faculty of Technology and Metallurgy, Belgrade, Serbia*
[4]*Techical Faculty in Bor, University of Belgrade, Bor, Serbia*
[5]*Techical Faculty in Bor, University of Belgrade, Bor, Serbia*

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The results of the investigation of the reduction degree on the hardness of a gold sample with chemical composition Au58,5Ag15Cu9,5Ni9Zn5Pd3 for old white gold alloy and Au58,5Ag18Cu10,5Ga8Zn5 (wt %) for new white gold alloy, are shown. The obtained results show that hardness of samples is higher when total reduction is higher, and that it decreases after process annealing. Also, the mechanical properties of the investigated alloys were compared. Alloy without Ni has lower hardness and higher elongation values.

Keywords: white gold; rolling; drawing; hardness; total elongation; nickel; gallium.

INTRODUCTION

With the beginning of the human race evolved an aspiration of the people for beautification and wearing jewelry. The rich and beautiful yellow color, good mechanical properties and relatively easy way of processing, have made gold a major element to use for this purpose [1, 2, 3].

Almost all metals in pure elemental state are very soft, malleable and difficult for mechanical processing [4,5]. This feature happens to be an advantage in the production of contemporary jewelry because it allows mixing pure gold with other appropriate elements to a higher or smaller degree, depending on the production technology and the grade of jewelry you want to get [6]. However, its disadvantages are ductility, wear and susceptibility to mechanical injuries during processing of jewelry [7]. Gold alloys are widely used in jewelry, mostly in the form of wires and thin strips.

White gold alloys were developed as substitutes for platinum and are mainly used for jewellery. The whitening or bleaching of gold is a process of creating a material that is cheaper and easier to alloy and fabricate than platinum. There are two groups of commercial white gold alloys, in one of which the bleaching element is nickel and in the other - palladium. Because of the strong hardening effect of nickel, white gold alloys containing large amounts of nickel do not have the deformation characteristics desired for jewelry manufacture It is possible to obtain a better combination of colour and mechanical properties in white golds by bleaching with palladium, but since the price of palladium is about 1 000 times that of nickel, these better alloys are more costly [8,9].

Also, nickel has long been known as a major skin allergen. In an attempt to reduce the occurrence of allergic contact dermatitis caused by nickel, the European Parliament and EU Council passed the Nickel Directive. For products designed for direct and long-term contact with the skin (earrings, necklaces, bracelets, etc.) the rate of release of Ni should not exceed 0.5 $\mu g \cdot cm^2$ per week. A more recent measure passed by the Commission, Directive 2004/96/EC, in an attempt at more effective protection of EU citizens and taking into consideration new findings on the toxic properties of nickel, sets a migration limit of 0.2 $\mu g \cdot cm^2$ per week. This new limit also applies for earring posts inserted into the pierced ear or into other pierced parts of the human body [10].

The new line of total nickel-free white alloy was created to provide maximum protection for sensitive skin. The Italian company Legor produced new alloy Proderma [11,12]. Proderma was created as a practical response to the growing attention towards phenomena of allergy and skin intolerance in contact with some commonly used metals in the gold industry, including nickel. This brand contains NPF alloys (nickel/palladium free), which do not contain the two most common whitening elements, that for several reasons may not be acceptable or not compatible. Instead, they contain gallium as a

* To whom all correspondence should be sent:
E-mail: mladenmiric@dmdm.rs

whitening component and a slightly higher percentage of Ag and Cu (REF).

In this study, we performed a comparative analysis of old and new white gold alloy strips obtained from molten pieces of rectangular cross-section. We investigated the influence of rolling, drawing and annealing on the mechanical properties of those two types of white gold strips.

EXPERIMENTAL PROCEDURE

Preparation of the sample

Mixing of gold with purity of 999,9 ‰ and the corresponding master and finished pre-alloys was used to obtain the needed mixtures of white gold for jewelry making. From those two mixtures castings with composition (determined by the FISHERSCOPE X-RAY XAN-DPP unit located at the Directorate of Measures and Precious Metals, Belgrade) 58,5% Au, 15% Ag, 9,5% Cu, 9% Ni, 5% Zn and 3% Pd for old white gold and 58,5% Au, 18% Ag, 10,5% Cu, 8% Ga, 5% Zn (wt %) for new NPF white gold, with dimensions of 92 mm × 28,6 mm × 4,7 mm were effused using a melting procedure at a temperature of 1064ºC and fixed periods of mixing.

Rolling process

Prepared castings were passed through working rolls to obtain a thickness of 0.38 mm, which was appropriate for cutting on circled cutting scissors. After each reduction, samples were taken for mechanical investigations. After each fifth reduction the samples were heated in a furnace at a temperature of 650ºC for 10 min. Aforementioned samples were cut to the width of 18.5 mm and passed through 4 cylinder plates rolling machine where tubes were obtained. Subsequently, we performed gas brazing of the tubes with tungsten electrodes in argon atmosphere at a current of 10V and 12A.

Drawing process

The obtained tubes were passed through a drawing bench with diamond dies to obtain the diameter most commonly used for making necklaces and bracelets (tables 2 and 4). After each fifth reduction the samples were heated in a furnace at temperature of 650ºC for 10 min. Along with the cast samples, samples obtained in rolling and drawing processes were taken for mechanical examination.

RESULTS AND DISCUSSION

The parameters of rolling and drawing for old white gold with Ni alloy are given in Table 1 for rectangular samples, and table 2 for tube samples. Figures 2 and 3 demonstrate the results of hardness investigation for the same old white gold with Ni alloy.

Table 1. Rolling parameters for the tested old white gold with Ni alloy samples

b, mm	h, mm	Total height reduction, %	Single height reduction,%	F_0/F	HV 10
28.6	4.7				153
28.7	4.5	4.25	4.25	1.0444	160
28.8	4.2	10.64	6.67	1.1190	176
28.9	3.6	23.40	14.29	1.3056	206
29.0	3.1	34.04	13.89	1.5161	250
29.1	2.8	40.43	9.68	1.6786	263
29.3	2.2	53.19	21.43	2.1364	275
29.5	1.8	61.70	18.18	2.6111	296
29.7	1.3	72.34/0	27.78	3.6154	**314**/182*
29.9	0.87	81.49/33.77	33.08	5.4023	245
30.1	0.58	87.66/55.38	33.33	8.1034	279
30.3	0.38	91.91/70.77	34.48	12.3684	311/157*

b‑Sample width, HV 10 - Vickers hardness,h ‑ Sample height,
* Hardness after annealing,, F – Cross section area

Table 2. Drawing parameters for the tested white gold alloy

l, mm	Ø, mm	Single elongation,%	Total elongation,%	HV 10
150	6.0			173
153	5.8	2.0	2.0	186
158	5.5	3.27	5.33	207
164	5.0	3.80	9.33	231
169	4.8	3.05	12.67	248/182*
182	4.6	7.69	21.33	200
196	4.3	7.70	30.67	210
214	3.9	9.18	42,67	242

l‑Tube length, Ø‑Tube diameter, HV 10 - Vickers hardness
* Hardness after annealing

We show that for higher total height reduction the hardness values increase (Figure 1).

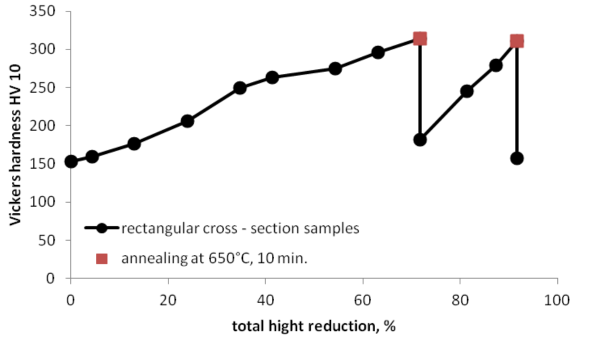

Fig. 1. Dependence of white gold alloy strips hardness on total height reduction

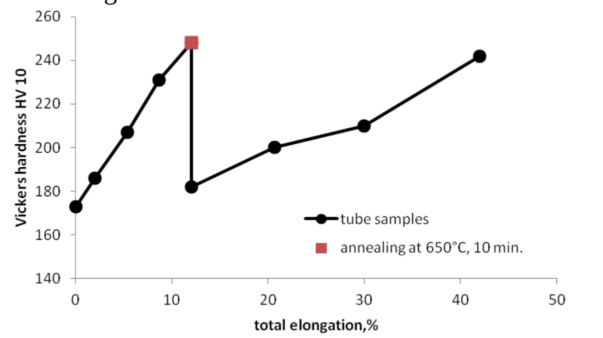

Fig. 2. Dependence of white gold alloy tubes hardness on the total elongation.

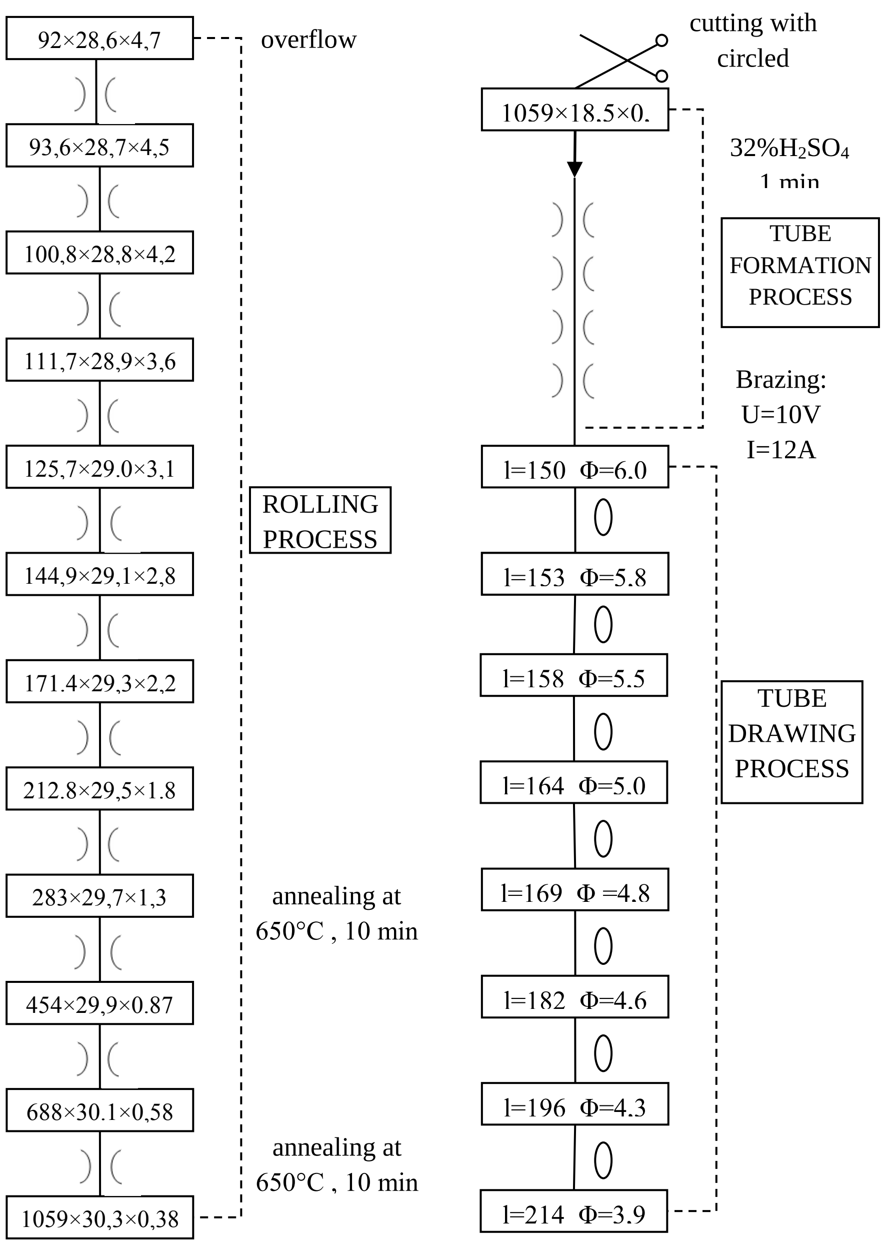

Fig. 3. Schematic view of the study of old white gold alloy with Ni.

After process annealing, the hardness values decrease, and for further total height reduction, hardness increases again.

Our results demonstrate that as total elongation increases, hardness values also increase (Figure 2). After process annealing, values for hardness decrease, and with subsequent increase of percentage of elongation, hardness increases again.

Figure 3 presents a schematic view of the study of old white gold alloy with Ni.

The parameters of rolling and drawing for new white gold NPF alloy are given in tables 3 and 4, for rectangular and tube samples, respectively. Diagrams in figures 2 and 3 represent results of NPF alloy hardness investigation.

Table 3. The parameters of rolling for tested new white gold NPF alloy samples

b mm	h mm	Total hight reduction, εhuk	Single hight reduction, %	F_0/F	HV 10
28,6	4,7				146
28,7	4,5	4,25	4,25	1,0444	154
28,9	4,1	12,77	8,88	1,1463	170
29,0	3,5	25,53	14,63	1,3429	201
29,2	2,9	38,30	17,14	1,6207	247
29,4	2,6	44,68	10,34	1,8077	260
29,6	2,1	55,32	19,23	2,2381	270
29,8	1,6	65,96	23,80	2,9375	292
29,9	1,2	74,47/0	25,00	3,9167	**310**/180*
30,1	0,8	82,98/33,33	33,33	5,8750	240
30,3	0,5	89,36/58,33	37,50	9,4000	275
30,5	0,38	91,91/68,33	24,00	12,3684	305/150*

b-Sample width, h-Sample height, HV 10-Vickers hardness, * Hardness after annealing,, F–Cross section area

Table 4. Drawing parameters for the tested new white gold NPF alloy

l, mm	Ø, mm	Single elongation %	Total elongation, %	HV 10
150	6.0			170
154	5.7	2.66	2.66	182
159	5.4	3.25	6.00	203
165	5.0	3.77	10.00	230
173	4.7	4.85	15.33	**242**/180*
184	4.5	5.20	22.67	199
197	4.2	7.06	31.33	209
216	3.9	8.80	44.00	240

l-Tube length, Ø-Tube diameter, HV 10 - Vickers hardness
* Hardness after annealing

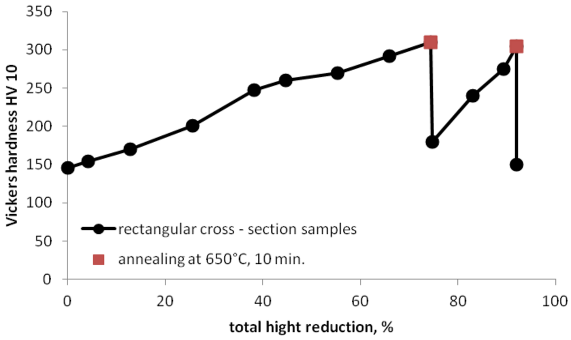

Fig. 4. Dependence of the hardness of white gold alloy strips on total height reduction

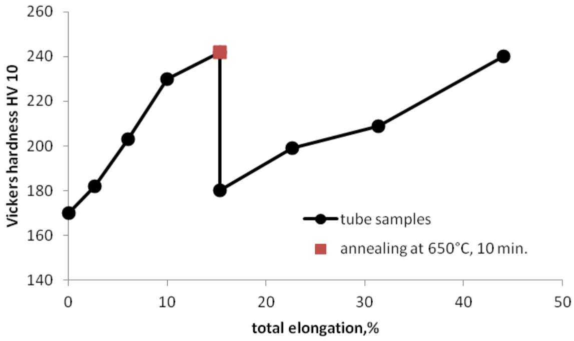

Fig. 5. Dependence of the hardness of white gold alloy tubes on total elongation

Based on the results presented in Tables 1 – 4 the following comparison between the two white gold alloys can be made: regarding the total reduction, the new white gold alloy has a higher value (74.47) than the old white gold alloy (72.34). At the same time, total elongation is higher for the new alloy (15.33) than for old alloy (12.67). These differences in the degree of reduction and elongation are the result of the presence of very dispersive liquid Ga over the macro and micro grain boundaries, since the liquid phase lays over almost each grain with definite nm or µm dimension.

Vickers hardness for the new alloy with Ga, after annealing process, is almost the same as for the old alloy with Ni (180 *vs.* 182). For both alloys, permanent hardness increase is consequent to grain fragmentation of solid solutions or intermetalloids, under the influence of strains caused by dislocations accumulation on grains boundaries. Such accumulation with short, (only 10 min), annealing process at 650°C, enables dislocations to move drastically lowers Vickers hardness.

CONCLUSION

Based on the experimental research performed and the results obtained, we can conclude the following:

During cold rolling, for higher total height reduction, the hardness values increase for both old and new white gold alloys (slightly more for old white gold alloys, tables 1 and 3). After the annealing process, the hardness values rapidly decrease. Subsequent increase in total height reduction causes an increase in hardness again.

The relative elongation data obtained are in good correlation with literature values [2].

During the drawing process, with an increase in total elongation, the hardness values increase for both old and new white gold alloys (more for old white gold alloys, tables 2 and 4). After the annealing process, the hardness values rapidly decrease. Subsequent increase in reduction results in an increase in hardness again.

These investigations show that using the new alloy NPF, strips and tubes of mechanical properties appropriate for jewelry making, can be obtained by rolling and drawing processes.

Moreover, new alloy NPF showed slightly better thermomechanical properties in comparison to old alloy. Gallium, used instead of nickel, proved to be a good replacement. The only flaw is that its use is not providing the desired white color component of the funds used for the development of modern jewelry. However, this can easily be overcome by coating with a layer of semi-finished rhodium, in order to obtain the desired jewelry white as shown in Picture 1.

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Picture 1. Products before and after coating with a layer of semi-finished rhodium

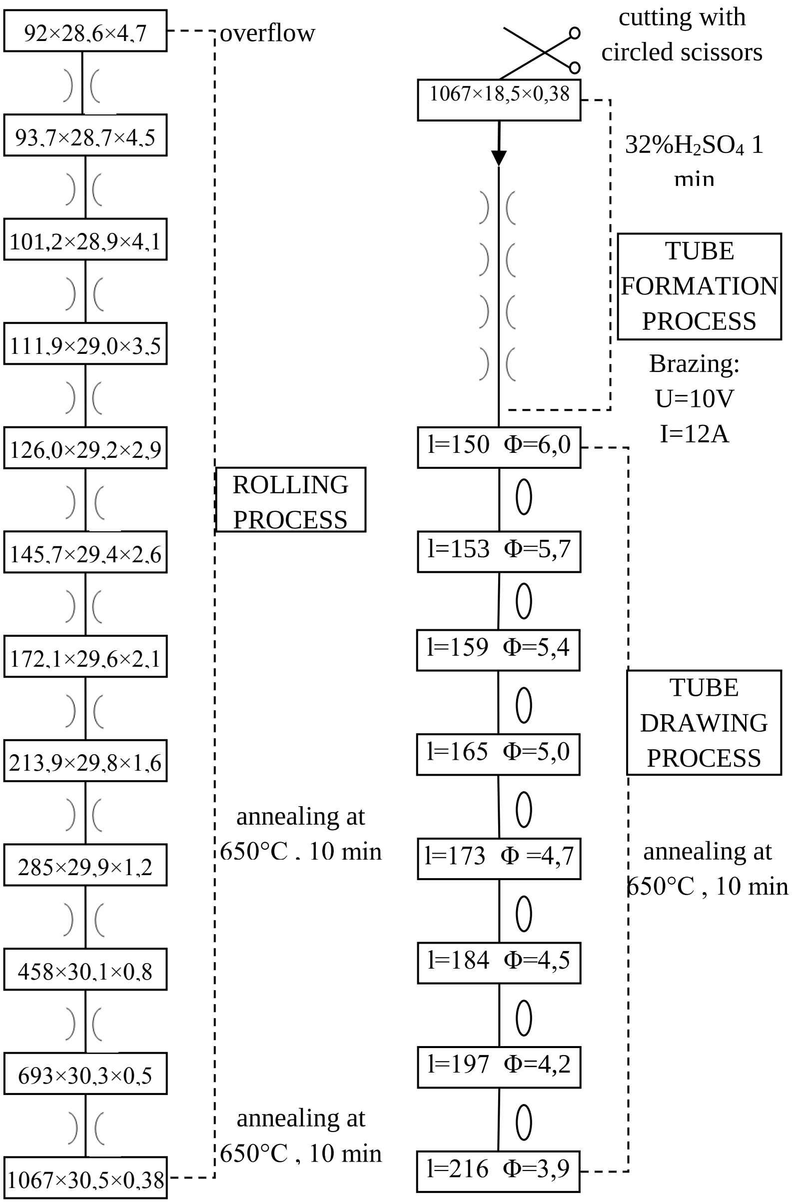

Fig. 6. Schematic presentation of the study of the new white gold NPF alloy

REFERENCES

1. S.Mozgovoy, J.Heinrich, U.E.Klotz, R.Busch, Establishing the process Mineralogy of gold ores, *Intermetallics*, **18**, 2289, (2010).
2. S.Watanabe, L.S.Benner, T.Suzuki, K.Meguero, S.Tanaka, Precious Metals Science and Tecnology, International Precious Metals Institute, Allentown, 1991.
3. P.K.Liaw, G.Wang, J.Schneider, *Advances in bulk metallic glasses*, *JOM*, **62**, 9 (2010)
4. J.Schroers, B.Lohwongwatana, W.L.Johnson, A.Peker, *Materials Science and Engineering:A*, **449**, 235 (2007).
5. C.Cretu, E.Lingen, Colored Gold Alloys, *Gold Bulletin*, **32** , 115 (1999).
6. Corti, Dr. Christopher W., The Role of Hardness in Jewelry Alloys, Santa Fe Symposium on Jewelry Manufacturing Technology, Albuquerque, New Mexico, USA, May 2008.
7. D.Maggian, S.Bortolamei, M. di Siro, A. Carlotto, D.Bruttomesso, C. Girardi , Characterization of 14-Karat Gold Alloys, 25th Santa Fe Symposium on Jewelry Manufacturing Technology, Albuquerque, New Mexico, USA, May 2011.
8. G. Normandeau, White golds: a review of commercial material characteristics & alloy design alternatives, *Gold Bull.*, **25**, 94 (1992).
9. B. MacCormack, John E. Bowers, New white gold alloys, *Gold Bull*., 14, 19 (1981).
10. M. Pouzar, M. Schmidt, A. Krejcova, T. Cernohorsky, Nickel Release from Piercing Jewellery, *SRX Chemistry*, **1-6**, (2010).
11. A.Basso, M.Poliero, A.Frisco, R.Bertoncello, Legor group S.p.A. , White-Gold Alloys for Gold Jewelry and the new EN1811:2011 Standard on Nickel: Limitations and Possibilities, 27th Santa Fe Symposium on Jewelry Manufacturing Technology, Albuquerque, New Mexico, USA, May 2013.
12. S.Bezzone, Nickel Release Tests on Current Production Jewelry, 27th Santa Fe Symposium on Jewelry Manufacturing Technology, , Albuquerque, New Mexico, USA, May 2013.

РАЗЛИКИ В НАЧИНА НА ТЕРМОМЕХАНИЧЕСКА ПРЕРАБОТКА МЕЖДУ СПЛАВИ НА БЯЛО ЗЛАТО ЗА ПРОИЗВОДСТВО НА ПОЛУГОТОВИ ПРОДУКТИ

М. В. Мирич[1], Р. С. Перич[2], С. П. Димитриевич[3], С. А. Младенович[4], С. Р. Марджанович[5]

[1]*Дирекция за измерания и благородни метали, Белград, катедра законтролни субекти от благородни метали, Ниш, Сърбия*

[2]*Перич & Перич & Съд. ООД, Пожаревац, Сърбия*

[3]*Иновационен център към технологичен и металургичен факултет, Белград, Сърбия*

[4]*Технически факултет в Бор, Белградски университет, Бор, Сърбия*

[5]*Технически факултет в Бор, Белградски университет, Бор, Сърбия*

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(Резюме)

Показани са резултатите от изследването на степента на намаляване на твърдостта на проба злато с химически състав Au58,5Ag15Cu9,5Ni9Zn5Pd3 за стара сплав на бяло злато и Au58,5Ag18Cu10,5Ga8Zn5 (тегловни%) за нова сплав на бяло злато. Получените резултати показват, че твърдостта на пробите е по-висока, когато общото намаление е по-високо, и че тя намалява след процеса отгряване. Също така, са сравнени механичните свойства на изследваните сплавите. Сплав без Ni има малка твърдост и по-високи стойности на удължение