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THERMODYNAMIC PROPERTIES OF ENVIRONMENTAL GOLD SOLDERS FOR USE IN GOLDSMITHING

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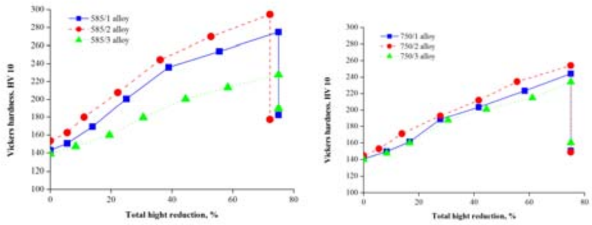
In this paper, we focused on the study of properties of cadmium free solders for jewelry with the corresponding percentage of indium. Indium is used as the best substitute of cadmium.[1,2] So far, solders with cadmium have given the best results in goldsmithing.[3] However, EU Directive of 2003 prohibited the use of cadmium in all technical, chemical and metallurgical processes, due to its carcinogenic properties as confirmed by the International Agency for Cancer Research.[4] Since the jewelry production has already begun the implementation of some new environmental solders, this paper aims to explain the technological and metallurgical characteristics of these solders.[5,6] We also observed a difference in the use and characteristics of these new environmental solders, compared with solders containing cadmium in its chemical composition.[3,4]



INTRODUCTION

In jewelry, two or more surfaces made of gold alloy with the same percentage of gold connect to each other using the gold alloy solders with the same percentage of gold, but different chemical composition.[6,7] Solders facilitate permanently bonding two or more metal works made from gold alloy with same percentage of gold, by heating to a temperature higher than the liquids temperature of solders, but lower than the solidus temperature of the material-alloys of the same origin to connect. High liquids temperature solders can change the mechanical properties of alloys of the same origin and can cause the surface of the piece of jewelry to fade.[7,8]

Historically solders were won by melting and mixing pure Au with the addition of appropriate amounts of Ag, Cu, Zn and Cd. Solders with a certain percentage of Cd have exceptional metallurgical properties (binding, sagging, durability, brittleness, hardness, ductility). Solders with Cd reduce the melting point alloys with same percentage of gold as a solder that binds them. Metals with low melting point such as Cd 594 K (321 °C) are used to reduce the melting point and to allow the desirable characteristics of humidity. Still Cd is very harmful to the human body. Several studies have shown that smoke generated as the melting process contains CdO which irritates the respiratory system which can be absorbed through the inhalation. CdO in industrial processes must be controlled, because the vapor pressure at temperatures of melting Cd 594 K (321 °C) is very large.

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CdO (formed by heating Cd in O_2, and varying in color from green to black) adopts an NaCl structure.

$$2\ Cd_{(s)} + O_{2(g)} \rightarrow 2\ CdO_{(s)}$$

It is insoluble in H_2O and alkalis, but dissolves in acids. Addition of dilute alkali to aqueous solutions of Cd^{2+} precipitates white $Cd(OH)_2$ and this dissolves only in concentrated alkali to give $[Cd(OH)_4]^{2-}$.

In aqueous solutions, $[Cd(OH_2)_6]^{2+}$ is present but it is only weakly acidic. Aquated $[Cd(OH)_4]^{3+}$ is present in concentrated solutions.

$$[Cd(OH)_6]^{2+} + H_2O \rightarrow [Cd(OH_2)_5OH\,]^{+} + H^{+};\ pK_a = 9$$

Cadmium enters in composition of a large number of complex compounds, such as $[CdCl_4]^{2-}$, $[Cd(NH_3)_4]^{2+}$, $[Cd(en)_3]^{2+}$, $[CdCl_6]^{4-}$ etc.[2]

Cd also damages the kidneys, causing anemia and bone disease.[2-4]

Cd can be replaced with a less soluble metals approximate characteristics such as Sn, In, Ga and Zn.[3] Adding a few percent of these elements reduces the melting temperature of environmental solders. Also, the solubility of Ga and In is limited in multicomponent systems, especially rich with Ag. These elements do not significantly affect on the liquids temperature, but have influence on the solidus temperature in the wide field of point. Therefore, we base in this paper on testing the characteristics Cd free solders for goldsmith with the corresponding percentage of In, that is used as the best Cd substitute.[6-8]

EXPERIMENTAL

1. Preparation of the sample

We investigated in these paper six different multicomponent alloys of gold (3 alloy fineness of 585 and 3 alloy fineness of 750).[8,9] Mixing of gold with pureness of 999,9 ‰ and the corresponding master and finished pre-alloys was used to obtain the needed mixtures. Warming, melting and production of alloys is performed in an induction furnace, in the pot for casting, under a nitrogen atmosphere (without the presence of oxygen), and then is poured directly from the graphite pot in cold water, in order to obtain small granules, maximum diameters up to ≈ Ø5-7 mm, which are later used for casting ingots into steel molds, of whom by rolling on the rolling flats receive sheets and strips. From these mixtures with correct melting procedure at temperature of 1064 °C and fixed periods of mixing (temperature slightly above the melting point of gold), obtained mixture discharged in wax coated gravity die-casting and obtained castings with same dimensions: 88 mm x 28.5 mm x 3.6 mm.

Composition of that alloy is determined by the FISHERSCOPE X-RAY XAN-DPP unit located in the Directorate of Measures and Precious Metals, in Belgrade, which is determined by their chemical composition and as shown in Table 1.

2. The rolling process

Prepared castings (see *Preparation of the samples*) were passed through working rolls to obtain the thickness of 0.9-1 mm, which was appropriate for cutting on circled cutting scissors. After each reduction, samples were taken for mechanical investigations (hardness, expansion, elongation).[10,11] After sixth reduction, when the hardness of the samples reached a high critical level, a rolling became labored, the samples were heated in a furnace at temperature of 652 ºC for 18 minutes. Here are samples taken before and after annealing. On these samples were carried out except mechanical investigation and determination of border flow and elastic modulus.

RESULTS AND DISCUSSION

The parameters of rolling for 3 Au alloy with fineness of 585 are given in Tables 2-4.

The parameters of rolling for 3 Au alloy with fineness of 750 are given in Tables 5-7.

Results of the analysis Vickers hardness HV 10 shows that the alloy with the critical degree of deformation show hardness values above 200 HV for solders with fineness 585 (close to the theoretical limit). When soldering fineness 750 hardness values are lower due to higher mass fraction of gold Au that is softer than a basic form of other metals that are composed of environmental solders. Annealing at 652 ºC for 18 minutes results in a strong reduction of the hardness (at least in an alloy with the lowest content of indium In), reducing the internal spurt and leads to recrystallization of samples. General, homogeneous multicomponent alloys environmental solders are cold-rolling and annealing at 652 ºC for 18 minutes obtain the appropriate plastic properties that enable them to good qualities on soldering. The solders with the highest percentage of zinc Zn and with minimum percentage of indium In show the lowest hardness in the solid state. This is explained by the emergence of resistance in his union, because after annealing, hardness values do not decrease too much.

Table 1

Qualitative and quantitative composition of the gold alloy solders

	Au‰	Ag‰	Cu‰	Zn‰	In‰
Alloy 585/1	585	133	150	87	45
Alloy 585/2	585	141	142	91	41
Alloy 585/3	585	141	145	100	29
Alloy 750/1	750	62	85	55	48
Alloy 750/2	750	57	95	60	38
Alloy 750/3	750	52	122	65	11

Table 2

The parameters of rolling for tested 585/1 alloy samples

b mm	h mm	Total height reduction, %	Single height reduction,%	HV 10
28.5	3.6			142.9
28.7	3.4	5.56	5.56	150.6
28.9	3.1	13.89	8.82	169.2
29.1	2.7	25.00	12.90	200.5
29.3	2.2	38.89	18.52	235.9
29.5	1.6	55.56	27.27	253.8
29.8	0.9	75.00/0	43.75	274.9/182.2*

b – sample width; h – sample height; HV 10 Vickers hardness; *hardness after annealing

Table 3

The parameters of rolling for tested 585/2 alloy samples

b mm	h mm	Total height reduction, %	Single height reduction,%	HV 10
28.5	3.6			153.4
28.6	3.4	5.56	5.56	162.6
28.8	3.2	11.11	5.88	179.7
29.0	2.8	22.22	12.50	207.5
29.2	2.3	36.11	17.86	244.4
29.4	1.7	52.78	26.09	269.8
29.7	1.0	72.22/0	41.17	294.7/177.3*

b – sample width; h – sample height; HV 10 Vickers hardness; *hardness after annealing

Table 4

The parameters of rolling for tested 585/3 alloy samples

b mm	h mm	Total height reduction, %	Single height reduction,%	HV 10
28.5	3.6			138.9
28.7	3.3	8.33	8.33	147.2
28.9	2.9	19.44	12.12	159.9
29.2	2.5	30.56	13.79	179.5
29.4	2.0	44.44	20.00	200.4
29.6	1.5	58.33	25.00	213.4
29.9	0.9	75.00/0	40.00	227.5/189.5*

b – sample width; h – sample height; HV 10 Vickers hardness; *hardness after annealing

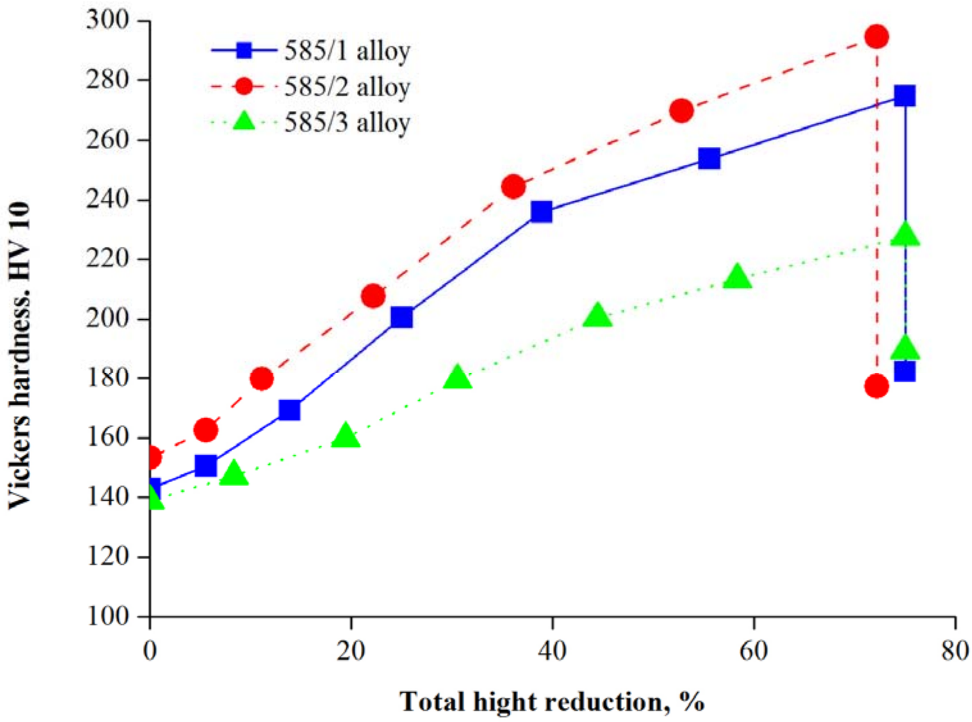

Fig. 1 – Dependence of hardness alloy fineness of 585 on total height reduction.

Table 5

The parameters of rolling for tested 750/1 alloy samples

b mm	h mm	Total height reduction, %	Single height reduction,%	HV 10
28.5	3.6			140.7
28.7	3.3	8.33	8.33	149.6
28.9	3.0	16.67	9.09	161.3
29.1	2.6	27.78	13.33	188.4
29.3	2.1	41.67	19.23	203.5
29.6	1.5	58.33	28.57	223.2
29.8	0.9	75/0	40.00	244.1/150.3*

b – sample width; h – sample height; HV 10 Vickers hardness; *hardness after annealing

Table 6

The parameters of rolling for tested 750/2 alloy samples

b mm	h mm	Total height reduction, %	Single height reduction,%	HV 10
28.5	3.6			144.6
28.7	3.4	5.56	5.56	152.8
28.9	3.1	13.89	8.82	171.0
29.1	2.6	27.78	16.13	192.9
29.3	2.1	41.67	19.23	211.8
29.5	1.6	55.56	23.81	234.4
29.8	0.9	75.00/0	43.75	253.9/148.8*

b – sample width; h – sample height; HV 10 Vickers hardness; *hardness after annealing

Table 7

The parameters of rolling for tested 750/3 alloy samples

b mm	h mm	Total height reduction, %	Single height reduction,%	HV 10
28.5	3.6			139.9
28.7	3.3	8.33	8.33	147.7
28.9	3.0	16.67	9.09	160.0
29.1	2.5	30.56	16.67	187.5
29.3	2.0	44.44	20.00	201.0
29.5	1.4	61.11	30.00	214.8
29.9	0.9	75.00/0	35.71	234.1/160.3*

b – sample width; h – sample height; HV 10 Vickers hardness; *hardness after annealing

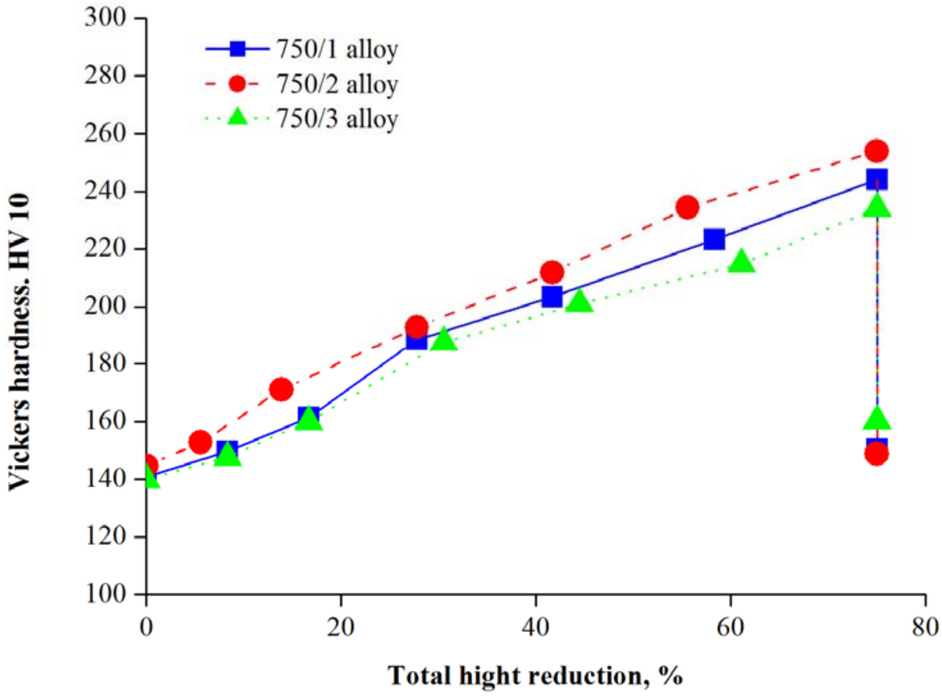

Fig. 2 – Dependence of hardness alloy fineness of 750 on total height reduction.

Samples taken after 6 passes to stand rolls were sampled before and after annealing at a temperature of 652 °C for 18 minutes and were examined by tightening where over determining tensile strength and relative elongation, determined and their modulus of elasticity and border flow. The results of this investigation are shown in Table 8.

Table 8

The values of border flow and elastic modulus of the examined environmental solders in hard and annealed state

Fineness of solder	Border flow kg/mm^2	Modulus of elasticity kg/mm^2	Fineness of solder	Border flow kg/mm^2	Modulus of elasticity kg/mm^2
585/1 annealed	16.2	450	750/1 annealed	16	636
585/1 hard	13.6	150	750/1 hard	15.4	50.1
585/2 annealed	21.0	221	750/2 annealed	20	415
585/2 hard	17.4	55.7	750/2 hard	14.1	42.3
585/3 annealed	22.7	1274	750/3 annealed	13.8	431
585/3 hard	12.5	385	750/3 hard	13.6	50.2

Table 9

The values of the melting temperature of enviromental gold solders in annealed state

Fineness of solder	585/1	585/2	585/3	750/1	750/2	750/3
Melting temperature°C	762	771	782	765	783	809

Environmental solders show the value of the border flow slightly lower than solders with cadmium Cd, but enviromental solders show greater ductility which makes them more suitable for goldsmith. Increasing amounts of indium In reduces the yield strength except for the alloy 750/3 where the share of indium In is 1%. Also, flow limit values are slightly reduced after annealing at solders same chemical composition fineness of 750, a little more with the solders of the same chemical composition fineness of 585, and that show stability of the present multicomponent system alloys. But, modulus of elasticity also show a large decrease after annealing. The highest modulus of elasticity shows solder 585/3 with a large percentage of zinc Zn and with a small percentage of indium In (1%), which indicates that indium In have a very good modulus of elasticity – is very similar to cadmium Cd (which was previously used for the preparation of commercial solders).

Different thermal analyses are important for monitoring changes in the physical-chemical characteristics in function of temperature for explaining exothermically and endothermally behavior. Melting point of samples taken after annealing was determined in the Laboratory for Geochemistry, Cosmochemistry and Astrochemistry (Faculty of Sciences, University of Niš). The results are shown in Table 9.

Enviromental solders show the value of the melting temperatures similar to cadmium alloys. Some samples showed increased thermal performance since the melting temperature lower than that of cadmium solders. It is evident the reduce of the melting temperature, when the percentage of indium In, in alloys is greater than 1%. Solders with more percentage of indium In are more diffused and used for soldering of thinner and smaller items of gold jewelry, while those with a lower percentage of indium In used for soldering of larger and heavier pieces of gold jewelry.

Samples of solders 585/2 and 750/2 with a higher proportion of copper Cu and Zn have a wide range of melting.

Our further metallographic analysis suggests that there is some evidence of microporosity and erosion. In structures with more noticeable indium In content is good after recrystallization annealing, while somewhat less pronounced in alloys 585/3 and 750/3 with lower indium content In.

CONCLUSIONS

Alloys with a small percentage of indium show a least hardness values. These alloys exhibit large differences elastic modulus, as well as small differences in the yield strength testing of samples before and after annealing. This indicates some instability in these systems. The alloys (585/3 and 750/3) showed worse results (sagging, castability, ductility, brittleness) than alloys with higher indium content and therefore can't find their full implementation in goldsmithing and there are in accordance with the practice facts. Therefore, the results and recommendations of this study the use of alloys 585/1, 585/2, 750/1 and 750/2 in goldsmithing.

Color of environmental solders is very similar to cadmium solders, even after soldering solder does not change color, but that you need to protect sites in which the solder is applied by.[3] This is confirmed by all the world recognized method for detecting color in jewelry such as Munsell system, Cieleb and DIN.[11,12] There are no obstacles to the implementation of these researched and recommended environmental solders in goldsmithing, especially if one takes into account the detrimental effect of carcinogenic cadmium Cd.[4]

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