Characterization of new Cd free yellow gold brazing alloys.

M. Dabalà, M. Magrini, M. Poliero*

D. I. M. E. G., University of Padova, Italy * Leg. Or., Bressanvido, Vicenza, Italy

Introduction

Production of a full range of handmade jewelry is obtained using gold brazing alloys at the same karats of materials that must be joined. Generally a brazing alloy facilitates a permanent bonding of two metallic pieces by heating at a temperature higher than T liquidus of brazing alloys, but lower than T solids of assembling materials. Thanks to a capillary action, brazing material flows into the joint cavity. Historically jewelry brazing alloys were obtained through a chemical alloying of Au, Ag and Cu with adding elements such Zn and Cd in various proportions. Lowmelting elements such Cd are employed to decrease the melting range and to impart desiderable wetting and flow characteristics. Moreover Cd is very toxic for human organism and can be assumed through inhalation of CdO fumes. In order to substitute Cd for brazing alloys the most applicable elements are Sn, In and Ga $\binom{1,2}{2}$. The aim of this work is the characterization of yellow gold brazing alloys containing Indium and Gallium in order to verify if Cadmium substitution with these elements increases or decreases materials performance.

Experimental Design

Yellow gold brazing alloys at different composition and karats (18, 14 and 9 Kt) were prepared in form of 1 mm and 0,5 mm diameters wires and in form of foils. Chemical compositions of alloys are summarized in table 1. Three different chemical compositions of 18 and 14 Kt alloys and two chemical compositions of 9 Kt alloy were prepared

	Ag%	Cu%	Zn%	In%	Ga%
18 Kt/1	6.25	8.50	5.50	4.75	-
18 Kt/2	5.75	9.50	6.00	3.75	-
18 Kt/3	5.25	12.25	6.50	1.00	-
14 Kt/1	13.33	15.00	8.75	4.58	-
14 Kt/2	14.16	14.58	9.17	3.75	-
14 Kt/3	14.16	14.58	10.00	2.92	-
9 Kt/1	31.88	18.13	8.12	3.12	1.25
9 Kt/2	29.38	10.63	10.62	2.50	0.62

Table 1: Chemical composition of brazing alloys

Later samples of wire underwent 20 minutes annealing at 550° C in air. Alloys characterization was lead through metallographic analyses of wire, microhardness measures with microhardness tester LEITZ-Wertzlar, tensile tests with Instrom 1121, differential thermal analyses with

Differential Scansion Calorimeter NETSCHE with heating rate of 2,5 K/min.

Differential thermal analysis determines the physical-chemical variations (e.g. temperature), recording these effects in correspondence of endothermic or exothermic behaviour. Thus this is a powerful thermoanalytical instrument in order to determine fusion ranges, because

436

of its skill to record process enthalpy variations.

Fluidity and wetting tests were performed according to Normandeau (), using brazing alloy foils with dimension 14 x 3 x 0,25 mm previously polished and deoxidized. These foils were positioned on two foils of conventional alloys at the same karats. The cavity was 0,25 mm. The samples were heated in oven at 35°C higher than solidus temperature of conventional alloys for 5 minutes. Surface of joints, cooled in air, were examinated to determine fluidity of brazing alloys. Then metallographic analysis on brazed joints was made to emphatize erosion behaviour, presence of microporosity or fractures. Indeed microhardness profiles were made to evaluate coupling resistance.

Results

Metallographic analysis of alloys shows a substantial work hardening by drawing of wires, deformation and shredding of crystalline grains, that tend to lean in stress direction and to increase microstructural disorder (Fig. 1). Annealed alloys (Fig. 2) exhibit an increase in grain size with a partial rearrangement. $\binom{3}{1}$



Fig. 1: 18 Kt alloy hardening (500 X)



Fig. 2: 18 Kt alloy annealed (500 X)

440

Alloys	Microhardness	Alloys	Microhardness
	(HV)		(HV)
18 Kt-1 hardening	244	14 Kt-2 hardening	295
18 Kt-1 annealed	150.3	14 Kt-2 annealed	177.3
18 Kt-2 hardening	254	14 Kt-3 hardening	227.5
18 Kt-2 annealed	144.8	14 Kt-3 annealed	189.5
18 Kt-3 hardening	234	9 Kt-1 annealed	167
18 Kt-3 annealed	160	9 Kt-2 hardening	170
14 Kt-1 hardening	274.3	9 Kt-2 annealed	168.7
14 Kt-1 annealed	182.2		

Results of microhardness analyses are summarized in table 2:

Table 2: Microhardness values of wire brazing alloys

The results confirm the substantial work hardening by drawing of wires in agreement with metallographic analyses.

The analyses point out that critical deformation degree (cr) alloys show hardness values higher than 200 HV (theoretical limit for malleable alloys); moreover annealing at 550° C for 20 minutes produces a severe decrease in hardness.

In table 3 are summarized the yielding strength and Young modulus of examined alloys.

Alloys	Yield	Young	Alloys	Yield	Young
	strength	modulus		strength	modulus
	(Kg/mm ²)	(Kg/mm ²)		(Kg/mm^2)	(Kg/mm ²)
18 Kt-1 hardening	16	636	14 Kt-2 hardening	21	221
18 Kt-1 annealed	15.4	50.1	14 Kt-2 annealed	17.4	55.7
18 Kt-2 hardening	20	415	14 Kt-3 hardening	22.7	1274
18 Kt-2 annealed	14.1	42.3	14 Kt-3 annealed	12.5	385
18 Kt-3 hardening	13.8	431	9 Kt-1 annealed	21.8	99.5
18 Kt-3 annealed	13.6	50.2	9 Kt-2 hardening	17.3	85.5
14 Kt-1 hardening	16.2	450	9 Kt- 2 annealed	16.4	79
14 Kt-1 annealed	13.6	150			

Table 3: Yield strength and Youngmodulus of alloys

Yield strength of hardened alloys is lower than the annealed ones, obviously. Cadmium containing alloys $\binom{1}{}$ show yield strength slightly greater than Cadmium free ones, but these show a greater ductility that makes them more suitable to precious working. Moreover an increase in In and Ga contents decreases yielding strength, as shown in fig. 3.





In table 4 are summarized the results of differential thermal analyses. All the samples present an endothermic peak at temperature included between 273 and 349 °C. This peak denotes some recovery of the material with disappearance of internal tensions.

(°C) (°C) 18 Kt/1 291.4 730 765 35 18 Kt/2 298.9 682 767 85	Alloys	T recovery	T solidus (°C)	T liquidus	Tl – Ts (°C)
18 Kt/1 291.4 730 765 35 18 Kt/2 298.9 682 767 85		(°C)		(°C)	
18 Kt/2 298.9 682 767 85	18 Kt/1	291.4	730	765	35
	18 Kt/2	298.9	682	767	85
18 Kt/3 322.4 792 829 37	18 Kt/3	322.4	792	829	37
14 Kt/1 348.3 669 741 72	14 Kt/1	348.3	669	741	72
14 Kt/2 335 660 745 85	14 Kt/2	335	660	745	85
14 Kt/3 323.6 668 748 80	14 Kt/3	323.6	668	748	80
9 Kt/1 637 702 65	9 Kt/1		637	702	65
9 Kt/2 273.9 658 721 63	9 Kt/2	273.9	658	721	63

Table 4: Thermal characteristic of brazing alloys

Cadmium free brazing alloys show liquidus and solidus temperatures values close to brazing alloys containing Cd reported by Normandeau (¹). Some samples show increased thermal characteristics since liquidus temperatures are lower than Cd brazing samples.

Results of wetting and fluidity test are summarized in table 5

Alloys	Si (mm ²)	Se (mm ²)	Si/Se
18 Kt	3.5	14.14	4.04
14 Kt	3.5	17.30	4.94
9 Kt	3.5	13.32	3.80

 Table 5: Fluidity test of alloys

442

The tests above point out that the brazing materials during fusion process exhibit a good fluidity, and the covered surface is 4 times greater than the original. Moreover, all the joints show a good color agreement between the base metal and the brazing coupling. The metallographic analyses of brazing joints emphasize a good bonding between the base and the brazing metals, too. There is no evidence of erosion behaviour and porosity, though in some samples localized fractures are recorded. We can confirm that alloys Cd free show a fair wetting.

The microhardness profiles are summarized in fig. 4, 5, and 6.

The low microhardness values recorded in the conventional alloys around the joint could be caused by heating close to solidus temperatures, during oven brazing operations, especially for 18 Kt alloys coupling. This heating drives to secondary recrystallization, to increase in size of crystalline grains, with a decrease in resistance characteristics of the materials (4).

Into the coupling the microhardness values are the same of the conventional and brazing metals before the fusion process, thus this shows a good resistance characteristic of joints.

Conclusion

Gold brazing alloys Cd free exhibit better thermal characteristics than the Cd containing ones, neverthless an increase of fusion range for 18 Kt alloys is also showen. Furthermore this behaviour does not affect the alloys' fluidity, which is excellent in many samples. This good characteristic enables a satisfactory filling of joint cavity. Besides,



Fig 4: Microhardness profile of 18 Kt brazing alloy



Fig 5: Microhardness profile of 14 Kt brazing alloy



Fig. 6: Microhardness profile of 9 Kt brazing alloy

metallographic analysis shows good bonding between the alloys, absence of erosion behaviour and porosity, and the presence of localized fractures. Mechanical resistance of brazing coupling is also satisfying.

Brazing alloys Cd free show hardness greater than 200 HV, but annealing process at 550 °C for 20 minutes enables the ductility recovery. A lower yielding strength and a greater ductility are also recorded, which makes these materials more suitable for working operations than Cd containing alloys.

Our aim is to demonstrate that Cd can be completely and surely substituted in brazing alloys with In and Ga, while not affecting any of the materials' characteristics.

References

1) G. Normandeau "Cadmium free gold brazing alloys", <u>Proceeding of the</u> <u>Santa Fe 1989</u>, Met-Chem Research Inc 1990, pg. 179-209

2) G. Normandeau "Cadmium free brazing gold alloys", <u>Gold</u> <u>Technology</u>, 18, 1996, pg. 20-24

3) A. Langford "Cold work and annealing of karat gold jewelry alloys" <u>Proceeding of the Santa Fe 1989</u>, Met-Chem Research Inc 1990, pg. 358-360.

4) M. F. Grimwade, Gold Technology, 2, 1986, pg. 17-19

446