

Characterization of new yellow cadmium-free gold brazing alloys

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Introduction

Production of a full range of jewellery is usually obtained using gold brazing alloys ('solders') of the same gold content (caratage) as the materials that must be joined. Generally, a brazing alloy (often called 'solder' in the jewellery industry) facilitates a permanent bonding of two metallic pieces by heating at a temperature higher than the Liquidus temperature of the brazing alloys, but lower than the Solidus temperature of the parent materials to be joined. A high liquidus temperature of the brazing material can cause some problems because any high temperature treatment decreases the mechanical properties of the parent alloy by annealing and can fade the surface of the jewellery.

Historically, jewellery brazing alloys (solders) have been obtained by alloying gold-silver-copper alloys with additions of metals such as zinc (Zn) and cadmium (Cd). Low-melting metals such as Cd are employed to decrease the melting range and to impart desirable wetting and flow characteristics.

However, cadmium is very toxic to human organs. The fumes generated during the melting process contain CdO that is very irritant to the respiratory system and can be

absorbed through inhalation. Several studies have implicated exposure to CdO fumes as an industrial health hazard that must be controlled, and the International Agency for Research on Cancer has classified Cd as a carcinogen. The temperatures involved in brazing often exceed the Cd boiling point (797°C) and the vapor pressure of Cd is very high under these conditions. Thus, there is a requirement by the industry for cadmium-free brazing alloys.

Substitution of Cd in jewellery brazing alloys can be done by use of other low melting point metals; the most applicable are tin (Sn), indium (In) and gallium (Ga) as well as zinc (1,2). In and Ga have very low melting points (156°C and 30°C respectively) and high boiling points (2080°C and 2403°C). Additions of a few percent of these elements depress the melting range of Au-Ag-Cu alloys, but the solubility of In and Ga is limited and in multicomponent systems, especially in silver-rich alloys, these elements do not significantly affect the liquidus temperatures but depress the solidus temperatures, resulting in a widening of the melting range.

Whilst a number of cadmium-free brazing alloys are commercially

available at all caratages, there is little published on the performance of such solders. This paper reports on work carried out to characterise the properties of yellow gold jewellery cadmium-free brazing alloys containing indium and gallium in order to determine whether cadmium substitution by these elements adversely affects performance.

Experimental procedures

Yellow gold brazing alloys of different composition and gold content (18, 14 and 9 ct) were prepared in the form of 1 mm and 0.5 mm diameters wires and as foils. The chemical composition of the alloys are given in Table 1. Three different compositions of 18 and 14 ct gold alloys and two compositions of 9 ct gold alloys were prepared. Samples of wire were annealed at 550°C for 20 mins in air.

The alloys were characterised by metallography of the wire, by microhardness measurements on a Leitz-Wertlar microhardness tester, tensile tests on an Instron 1121 machine and differential thermal analysis using a Netsche Differential Scanning Calorimeter with a heating rate of 2.5 K/min.

Differential thermal analysis is a powerful technique for evaluating changes in physical-chemical properties as a function of temperature because it records exothermic or endothermic behaviour.

Fluidity and wetting tests were performed according to Normandeu (1), using brazing alloy foils of dimension 14 x 3 x 0.25 mm, pre-polished and deoxidized. These foils were positioned between two foils of conventional jewellery alloys of the same caratage with a spacing of 0.25 mm. The samples were heated in a furnace in a nitrogen atmosphere at a temperature 35°C higher than the solidus temperature of the jewellery

Table 1. Composition of brazing alloys

	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	55.25	12.25	6.50	1.00	-
14 Kt /1	13.33	15.00	8.75	4.58	-
14 Kt /2	14.16	14.25	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	19.38	10.62	2.50	0.62

alloys for 5 minutes. After cooling in air, the brazed joints were examined to determine the fluidity of the brazing alloys. Serious errors can occur if the surfaces of the assembled foils are not the same in all tests. For this reason, we prepared a mirror-like surface for all samples by the usual metallographic polishing methods. Metallographic analysis was carried

out on sections of brazed joints to determine erosion behaviour, the presence of any microporosity or fractures. Microhardness profiles were made to evaluate coupling resistance.

work hardening necessary for recrystallization.

Among the more important mechanical properties that are of interest to goldsmiths are the yield strength, the strain and the ductility characteristics. In Table 3, the yield strength and Youngs modulus results are summarised. The 9 ct alloys do

Results

Metallographic analysis of the alloys shows a substantial work hardening resulting from the drawing of the wires, Figure 1. Annealed alloys exhibit an increase in grain size with a partial rearrangement of the structure, Figure 2 (3).

The results of microhardness analyses, summarized in Table 2, confirm the substantial work hardening of the drawn wires. These measurements show that the alloys with a critical degree of deformation (ϵ_{cr}) show hardness values higher than 200 HV (theoretical limit for malleable alloys); moreover, annealing at 550°C for 20 minutes results in a severe decrease in hardness, due to lowering of the internal strain by recrystallisation. The critical amount of deformation is the minimum amount of

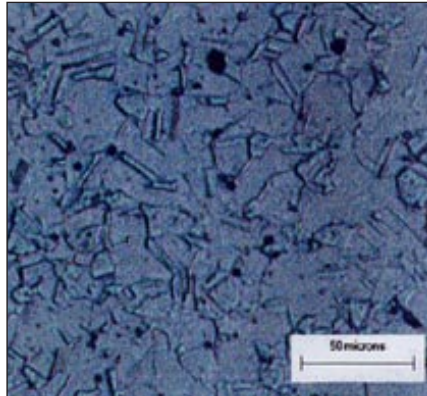


Figure 1 - 18 Kt alloy work hardened

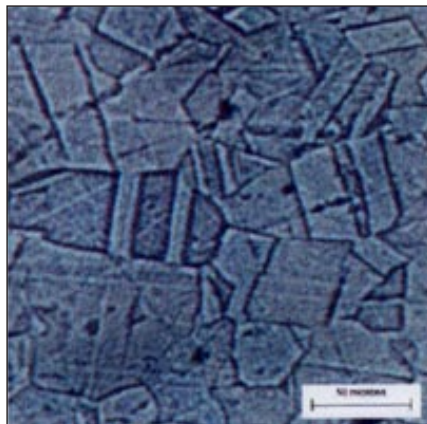


Figure 2 - 18 Kt alloy annealed

Table 2. Microhardness values of brazing alloy wires

Alloys	Microhardness (HV)	Alloys	Microhardness (HV)
18 Kt-1 hardened	244	14 Kt-2 hardened	295
18 Kt-1 annealed	150.3	14 Kt-2 annealed	177.3
18 Kt-2 hardened	254	14 Kt-3 hardened	227.5
18 Kt-2 annealed	144.8	14 Kt-3 annealed	189.5
18 Kt-3 hardened	234	9 Kt-1 annealed	167
18 Kt-3 annealed	160	9 Kt-2 hardened	170.5
14 Kt-1 hardened	274.3	9 Kt-2 annealed	168.7
14 Kt-1 annealed	182.2		

Table 3. Yield strength and Youngs modulus values of brazing alloys

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

Table 4. Thermal characteristics of brazing alloys

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

not show much reduction in properties after annealing as the annealing temperature is insufficient or cooling not sufficiently rapid. The preferential grain orientation obtained by drawing increases the elastic modulus when it is measured in stress direction. The yield strength of the work hardened alloys is lower than in the annealed condition, suggesting some hardening due to phase changes on cooling after

annealing. Cadmium-containing alloys (1) show yield strengths slightly greater than the cadmium-free ones, but the latter show a greater ductility that makes them more suitable for jewellery fabrication. Moreover, an increase in In and Ga contents decreases the yield strength, as shown in Figure 3.

The results of the differential thermal analyses are given in Table 4. All the samples show a broad

endothermic peak at temperatures between 273 and 349°C. This peak denotes some recovery of the material with disappearance of internal stress, as seen in Figure 4.

Cadmium-free brazing alloys show liquidus and solidus temperatures values close to those of brazing alloys containing Cd as reported by Normandeau (1). Some samples show increased thermal characteristics since liquidus temperatures are lower than Cd brazing samples. In alloys with In and Ga contents greater than 1%, a decrease of the melting temperatures is evident. The samples 18 Kt/2 and 14 Kt/2, with high percent of Cu and Zn shows a broad melting range.

The wetting and fluidity test results are summarized in Table 5 and show that the brazing alloys exhibit a good fluidity when molten, the surface area after flow being 4 times greater than that of the original. Also, all the joints show a good colour match between the base metal and the brazing joint. We evaluated the difference in colour by subjective comparison only as the colour spectrophotometers are not able to measure such small areas. Metallographic examination of the brazed joints showed a good metallurgical bonding between the parent and the brazing metals too. There was no evidence of any erosion of the parent metal by the brazing alloys or of porosity, though in some

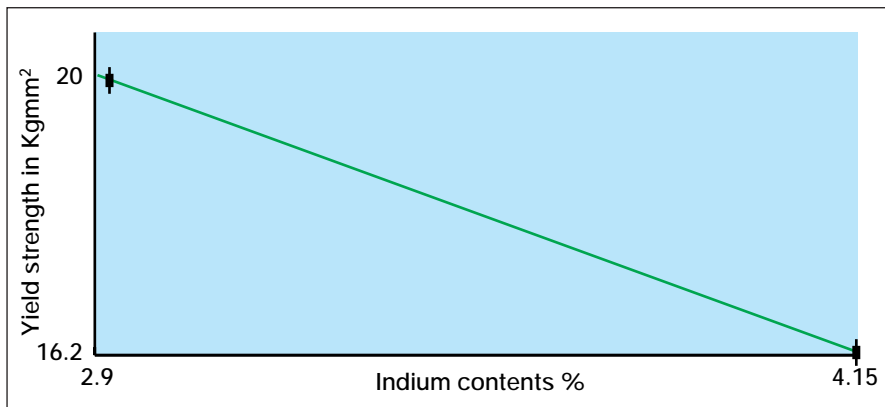


Figure 3 - Yield strength of alloys versus Indium contents in 14 Kt alloys

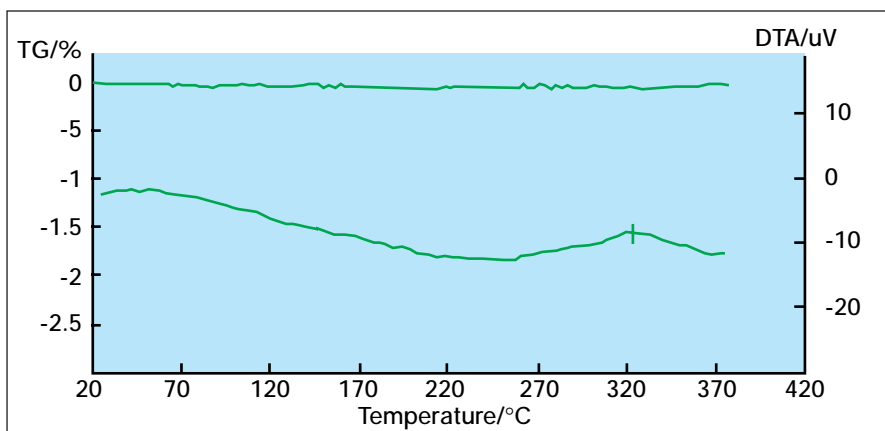


Figure 4 - DTA and TG curve of the 14 Kt/3 samples

Table 5. Fluidity test of alloys

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

samples localized fractures were recorded. We can confirm that cadmium-free brazing alloys show good wetting.

The microhardness profiles are given in Figures 5-7. The low microhardness values recorded in the conventional parent alloys around the joint could be caused by heating close to their solidus temperatures during

furnace brazing operations, especially for 18 ct alloy assemblies. This heating can allow secondary recrystallization, increasing the grain size, with a decrease in hardness of the materials (4). In the joint areas, the microhardness values are the same as those of the parent and brazing metals before the fusion process, a good characteristic of the joint.

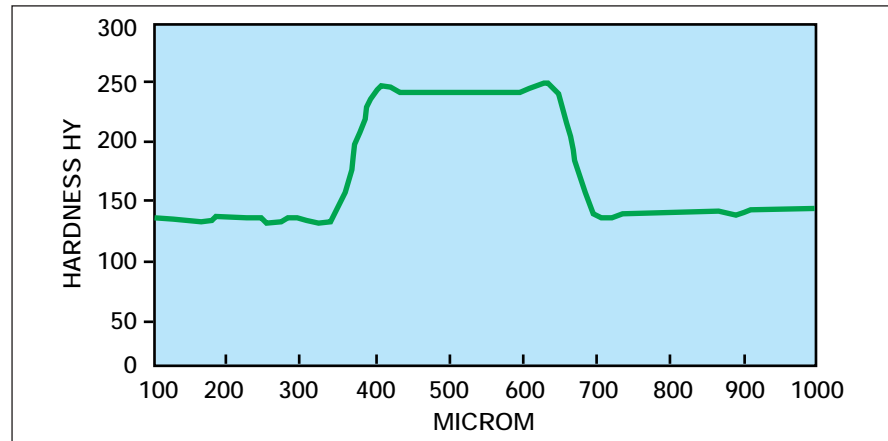


Figure 5 - Microhardness profile of 18 Kt brazing alloy

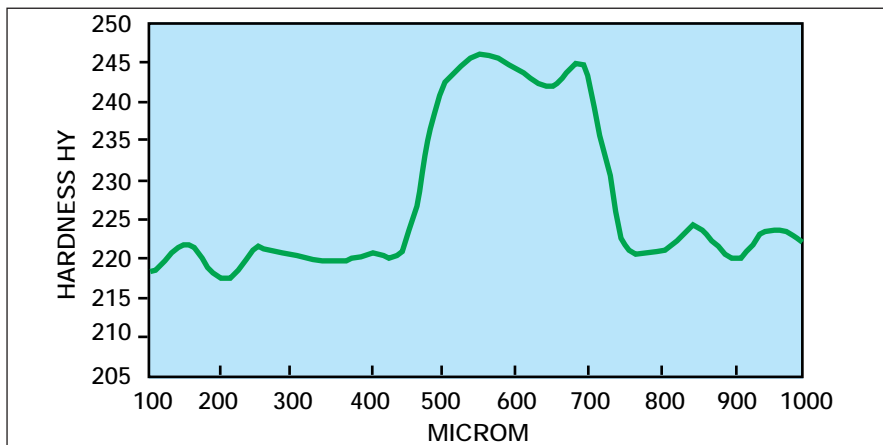


Figure 6 - Microhardness profile of 14 Kt brazing alloy

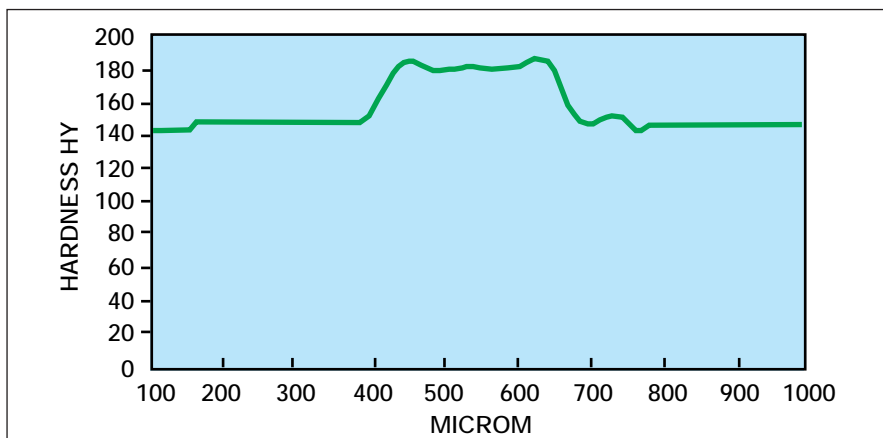


Figure 7 - Microhardness profile of 9 Kt brazing alloy

Conclusion

Cadmium-free gold brazing alloys exhibit better thermal characteristics than the cadmium-containing alloys, although an increase in the melting range of 18 ct alloys is seen. Furthermore, this behaviour does not affect the alloy fluidity which is excellent in many samples. This good characteristic enables a satisfactory filling of the joint cavity. In addition, metallographic analysis shows good bonding between the alloys, an absence of any erosion or porosity, but the presence of localized fractures in some instances. Mechanical behaviour of brazed joints is also satisfactory.

Cadmium-free brazing alloys show hardnesses greater than 200 HV after wire drawing, but annealing at 550°C for 20 minutes enables recovery of ductility. A lower yield strength and a greater ductility are also recorded, making these materials more suitable for further working operations than the cadmium-containing alloys.

These results demonstrate that cadmium in gold jewellery brazing alloys can be completely substituted in brazing alloys by indium and gallium, with little detrimental affect on any of the important materials characteristics.

References

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