

Hardening of Low-Alloyed Gold

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Abstract

The development of strengthened high carat Au alloys for jewellery applications is an interesting but challenging task, with significant potential for further development of new age-hardenable alloys. The paper first presents an overview on the possibilities and limitations to harden 22ct Au by conventional means, i.e. by alloying with conventional base metals (solid solution hardening) and in combination with heat treatment processes (age-hardening). The paper then refers to 22ct up to 24ct Au and reports on the enhancement of the age-hardening effect of the primary base metals by additions of selected secondary elements. It is suggested that the prevailing age-hardening mechanism in these types of alloys consists in precipitation of intermetallic phases formed by the primary and secondary additions.

Introduction

The increase of hardness, strength and wear resistance of low alloyed gold alloys for jewellery applications could be of particular interest for the growing markets in India, the Middle East and Asia, where high caratages (21/22-24ct) traditionally are preferred over the stronger but less precious counterparts with 18ct or lower caratages (1). Although soft gold alloys may be preferred due to tradition or culture, the overall trend towards miniaturisation of cross sections and diameters of jewellery pieces, in part related to a growing market for hollow jewellery, demands higher strength than currently available with conventional alloys. Furthermore, low-alloyed gold alloys are of considerable interest for technical applications, where a combination of high strength, ductility (forming operations) and electrical conductivity is required (2).

Pure gold is extremely soft in the as-cast and annealed states. Copper and silver, which are the main alloying elements in gold jewellery alloys, contribute some solid solution strengthening, with copper being more effective than silver due to the larger atomic size difference with gold. In 18ct jewellery alloys (75% Au*), a pronounced strengthening effect occurs during low temperature ageing, which is based on the formation of ordered AuCu-phases (3). This requires a minimum of 5% copper in 18ct alloys, but is becoming more pronounced for alloys with larger copper contents (4). As recently reviewed, the combination of order and precipitation hardening is the predominant strengthening mechanism in 18ct and lower carat jewellery alloys (5).

For high carat gold alloys, however, the possibilities to harden an alloy are limited due to the low amounts of alloying elements that can be added to the alloy, otherwise falling below the required caratage. This holds especially for 24ct jewellery alloys with a minimum of 99-99.5% Au depending on individual national legislation. Former studies (6,7,8) that are summarised in another source (1), have focused on microalloying additions of (light) metals with a promising potential for solid solution hardening due to a large difference in atomic size and weight to pure gold. Other studies focused on microalloying with rare-earth, refractory or light metals/elements. Additions of elements with a negligible solubility in gold at low temperatures introduce a potential for precipitation hardening by formation of gold-based ordered (so-called intermetallic) phases or eutectic structures.

In fact, most of this work initially was based on corresponding alloy development for electronic applications. Whereas the industrial exploitation of these types of strengthened alloys in electronics is successful (2), the suitability for jewellery applications seems to be limited. Possible reasons are: detrimental effects of the (micro-) alloying additions on melting, casting and working

* Compositions are referred to as wt% throughout the entire paper.

properties, as well as reduction in strength after remelting of material due to loss of alloying elements. Moreover, some of the alloying additions suggested are rare and expensive.

More recently, the development of 24ct gold alloys with increased hardness and good suitability for jewellery applications has been reported. The hardening effect, which is obtained by alloying with Co+ Sb and suitable heat treatment (9), is based on precipitation hardening and is most pronounced in combination with preceding cold-working.

Comparably little work on hardening 22ct Au alloys has been carried out (or published) so far (1). The development of alloys which can be hardened by heat treatment to hardness levels comparable to 18ct alloys has been reported recently, but corresponding details on alloy compositions were available only after finalisation of the present work (10,11,12) and will be referred to later in this publication.

The practical approach in development of age-hardenable alloys consists in alloying with a single element or base metal "Me", often far beyond the corresponding limits of solubility in the main metal matrix (here: Au), and identification of optimum subsequent age-hardening heat treatment parameters to precipitate finely distributed "Me"-rich particles. From the development of advanced age-hardenable high-conductivity high-strength copper alloys for connector applications (e.g. 13) it can be concluded, however, that the age-hardening process can be significantly altered or enhanced by further additions of suitable elements "A". These elements possess a large tendency to form finely dispersed Me_xA_y -phases in the Cu matrix with the primary base metal "Me". Phosphides and silicides of Co, Ni and Fe have been identified to give a high potential for age-hardening in Cu. In almost all cases, the most pronounced age-hardening effect is observed if the atomic ratio x:y of the additions "Me" and "A" correspond to the atomic stoichiometry of the expected reaction phase Me_xA_y . Figure 1 illustrates this for Ni- and Si-additions in copper: the maximum age-hardenability is obtained for compositions

with a Ni:Si-ratio of 2:1 (14); the formation of Ni_2Si -phases was confirmed later by transmission electron microscopy (TEM) investigations. An important side-effect for the electronic applications of copper alloys is, that the Cu-matrix is essentially free of alloying elements after the age-hardening treatment, which finally yields optimum electrical conductivity together with high strength.

From the results and experience available outlined above, it is obvious that the development of strengthened high carat Au alloys for jewellery applications, without detrimental effects on colour, melting and working properties, is still an interesting but challenging task, with a significant potential for further development of new age-hardenable alloys.

The main aim of the present study was to overview the possibilities and limitations to harden 22ct Au by conventional means, i.e. by alloying with conventional base metals (solid solution hardening) and in combination with heat treatment processes (age-hardening or precipitation hardening). With a view to the practical aspects, 'difficult' additions (e.g. highly reactive metals) were not considered, so the alloys discussed in this study should not require sophisticated alloying equipment or techniques and should be suitable for a 'normal' jewellery production environment. We have in a second step tried to enhance the hardening effect of the base metals by addition of selected further elements. This part of the work covered 22-24ct alloys, with the overall aim of studying if the hardening approach described above for copper base alloys can be successfully transferred to low alloyed gold alloys.

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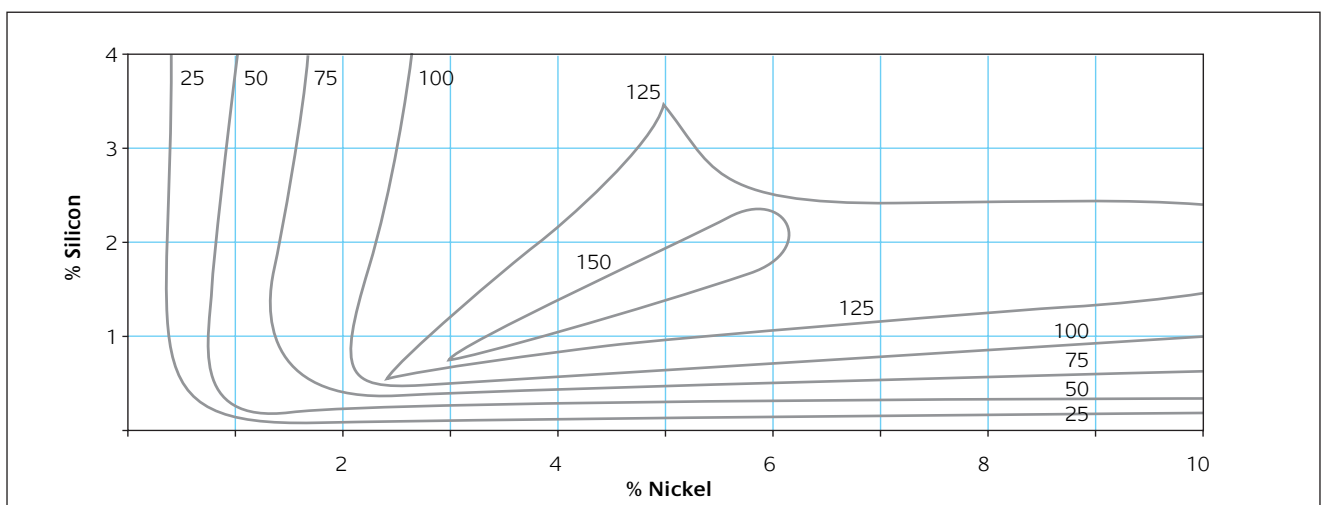


Figure 1
Age-hardening contribution in Copper by joint Ni- and Si- additions (14)*

Solid solution hardening of 22ct Au

A large share of jewellery is produced by investment casting without any subsequent heat treatment or mechanical working. The drawback for 22ct gold jewellery is a low as-cast hardness, which typically is around 60 HV1 depending on the silver:copper ratio. Therefore the objective of a first series of experiments has been to increase the hardness in the as-cast state without impairment of colour, investment casting properties etc. The hardness in an as-cast state is determined primarily by solid solution hardening, although some precipitation hardening may contribute depending on cooling rate or quenching schedule.

Experimental

For reference purposes the properties of three standard 22ct alloys were determined, containing either silver or copper as major alloying elements, leading to characteristic colour variations, or a balance of Ag/Cu leading to an intermediate colour (denoted 'medium' in Table 1). The silver-rich and copper-rich alloys throughout this paper are referred to as 'bright' and 'dark' yellow gold, respectively, although descriptions like 'pale', 'rich' or 'deep' may be more common in the jewellery industry.

An investigation of further alloying additions was based on the intermediate alloy composition and included conventional base metals known to affect the strength of jewellery alloys with lower caratage. Alloying additions were made in a range of 0.5% up to 2-3%: Cobalt (Co), Nickel (Ni), Iron (Fe), Zinc (Zn), Gallium (Ga), Antimony (Sb) and Barium (Ba). The investigation was carried out by melting/casting small button samples (20g) under protective gas atmosphere in an induction furnace using Au-based master alloys with 5-10% of base metal addition.

All samples were examined by standard metallographic procedures. Hardness HV1 was determined on the

metallographic cross sections of the as-cast button samples. In addition, the solution treated state was investigated, i.e. after annealing at 700-900°C for usually 1h. In order to evaluate the hardness in a 'realistic' as-cast state (i.e. after investment casting), test samples and some jewellery ring samples were cast for selected alloys, using a standard investment casting process (Indutherm vacuum equipment, graphite crucibles and stoppers, Argon protective gas, gypsum bonded investment). Further experiments for a preliminary evaluation of suitability for jewellery applications included cold-rolling (ductility) and colour measurements.

Results and Discussion

Additions of Zn, Ga, Fe, Sb and Ba showed only minor effects on hardness or no effect at all in 22ct Au. A summary of hardness data for the more relevant alloys tested is given in Table 1. The dependence of hardness on the amount of added base-metal is shown in Figure 2. From the data it is obvious, that the largest solid solution hardening effect is achieved by cobalt-additions of about 2-2.5%, with Ni being slightly less effective.

For some of the alloys with Co selected for investment casting trials, the as-cast hardness of samples taken from investment cast material turned out to be lower than for the corresponding small button samples. A corresponding drop in hardness was obtained upon solution annealing of the button samples, which indicates a small contribution of precipitation hardening to the hardness of the as-cast but slowly cooled button samples. The investment casting trees were quenched 15min after casting, however, and it is reasonable to assume that the hardness in an investment cast state will depend on the cooling conditions after casting.

These issues are also confirmed by the metallographic microstructure analysis. In an as-cast state, the microstructure of 22ct Au with Co is heavily segregated as

Table 1

Alloy composition in % and hardness of as-cast button samples for selected alloys

Alloy Nr	Colour/Type	Ag	Cu	Co	Fe	Ni	Sb	Au	Hardness HV1 as-cast state
AuH_01	bright yellow / Reference	5.5	2.8					bal.	55
AuH_02	dark yellow / Reference	2.8	5.5					bal.	70
AuH_03	medium / Reference	4.15	4.15					bal.	60
AuH_13	medium / Sb1	3.65	3.65				1.0	bal.	65
AuH_18	medium / Co2	3.15	3.15	2.0				bal.	105
AuH_19	medium / Ni2	3.15	3.15			2.0		bal.	90
AuH_25	medium / Fe2	3.15	3.15		2.0			bal.	75
AuH_47	bright yellow / Co2	4.0	2.3	2.0				bal.	115 / 90*
AuH_45	dark yellow / Co2	2.3	4.0	2.0				bal.	130 / 100*

* The second value corresponds to hardness of investment cast material as opposed the data for as-cast button samples (see text for further explanations).

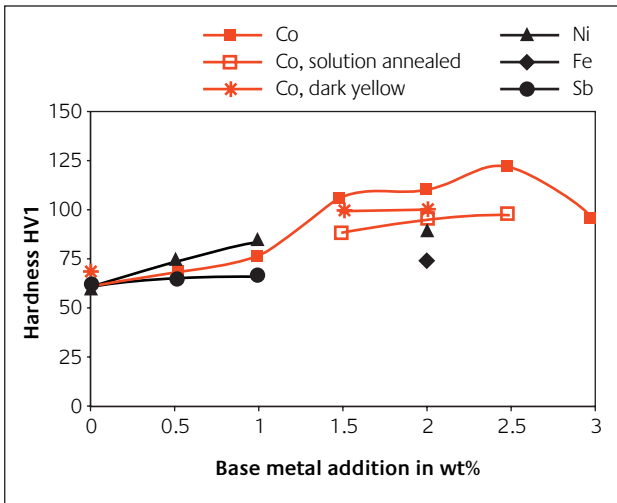


Figure 2

Dependence of hardness in as-cast 22ct Au button samples on amount of base metal.

* Data for the 'dark yellow' Co correspond to hardness of investment cast material, whereas all other data in this graph refer to as-cast button samples (see text for further explanations)

compared to conventional 22ct Au without Co (Figures 3a and b). Scanning electron microscopy (SEM) investigations also reveal coarse Co-rich precipitations at grain boundaries (Figure 3c). Segregations and precipitations dissolve readily during high temperature solution annealing treatment (Figures 3d).

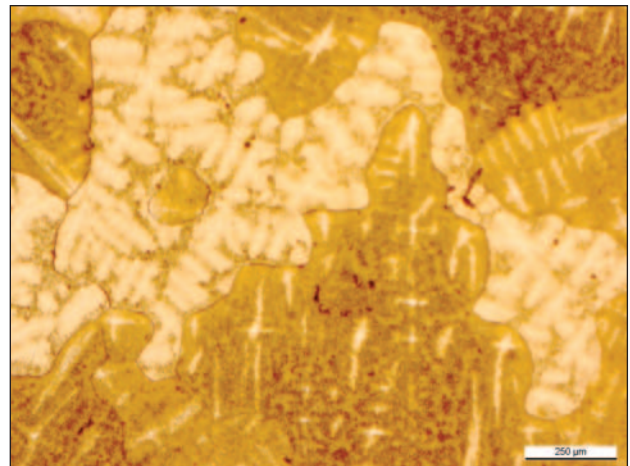
With regard to an optimum Co-content (criterion: the highest hardening effect achievable in the as-cast state) it turned out that Co-contents exceeding ~2-2,5% caused a drop in as-cast hardness. Note in Figure 2 that the hardness after solution annealing also levels off at ~2% Co.

These effects are attributed to the corresponding decrease of the copper content with increasing cobalt addition, since copper itself is a very effective hardener of gold. The latter is also the reason for the lower hardness levels in the Ag-rich bright yellow 22ct alloys. The overall increase of hardness by solid solution hardening with cobalt is independent of the Ag/Cu-ratio, however, namely ~30-35 points HV1 for ~2% Co.

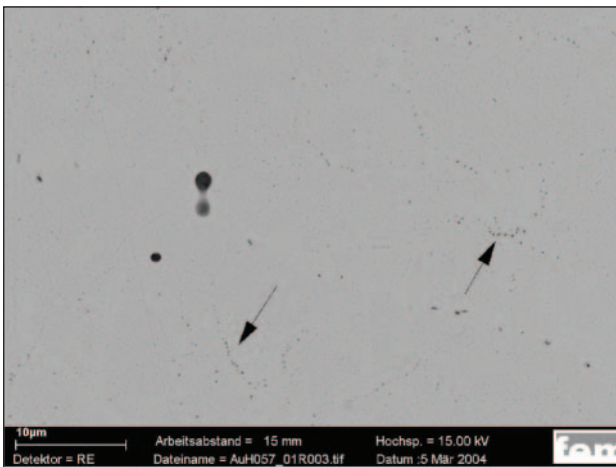
It is questionable, whether this hardness increase can be judged as relevant for jewellery applications or not, since there is still a large difference from standard 18ct alloys with



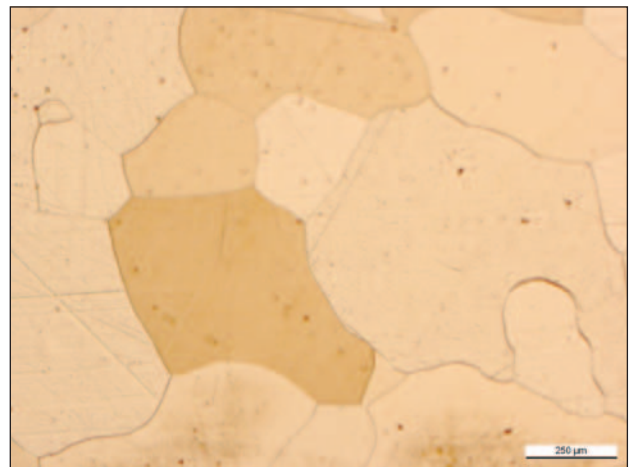
a) as-cast microstructure of 22ct Au without Co



b) investment cast state of 22ct Au with Co



c) investment cast state of 22ct with Co, backscatter electron image in SEM



d) investment cast 22ct Au with Co after solution annealing (850°C/1h/wq)

Figure 3

Microstructure of 22ctAu a) without Co-addition, b)-d) with Co-addition (1.5%) in different states

around 150 HV1 in an annealed state. Anyway, all alloys rolled well without crack formation (except for alloys containing 1% of Sb or Ba respectively) indicating good ductility. The colour differences from the reference alloys were acceptably low. The investment casting trials on the alloys with Co showed that slag formation during melting is low and does not impair the casting process. No reaction with crucible material and investment material was observed so the alloys can be cast successfully with a standard investment casting process. Details on the suitability for jewellery applications have been presented elsewhere (16, 17).

Age-hardening of 22ct Au (1st step)

Except for Zn and Ga, the base metals additions investigated in this study have a low solubility in pure Au at low temperatures, (e.g. the binary Au-Co- and AuSb-phase diagrams in Figure 4) which may allow precipitation hardening in 22ct gold alloys based on suitable heat treatment schedules. The theoretical precipitation hardening 'capacity' of Cobalt in pure Au is quite notable, although somewhat lower compared to most rare earth metals and significantly lower than for titanium and zirconium (6). Neither titanium, which is well-known for causing very

effective precipitation hardening in 990 Au (1, 19), nor Zr were included in the alloy screening process, mainly because of their notable reactivity with conventional casting and annealing atmospheres.

Experimental

In order to evaluate the age-hardening potential of the alloys, the study was extended to solution annealing of cold-rolled samples (70%) between 700°C and 900°C for 1 hour, followed by water quenching (= wq) and subsequent ageing between 200°C and 400°C from 20min to 2h. In addition, samples from the investment cast material with Co were heat treated in a similar way, but without cold-working before solution treatment. All annealing treatments were carried out in protective Argon atmosphere. After standard metallographic investigations the hardness HV1 was again determined on metallographic cross sections.

For potentially interesting alloys, basic properties and the influence of heat treatment parameters on mechanical properties, ductility and corrosion resistance were determined. After validation of properties by industrial partners, the study has been extended into the influence of further additions aiming at reduced grain size and improved oxidation resistance.

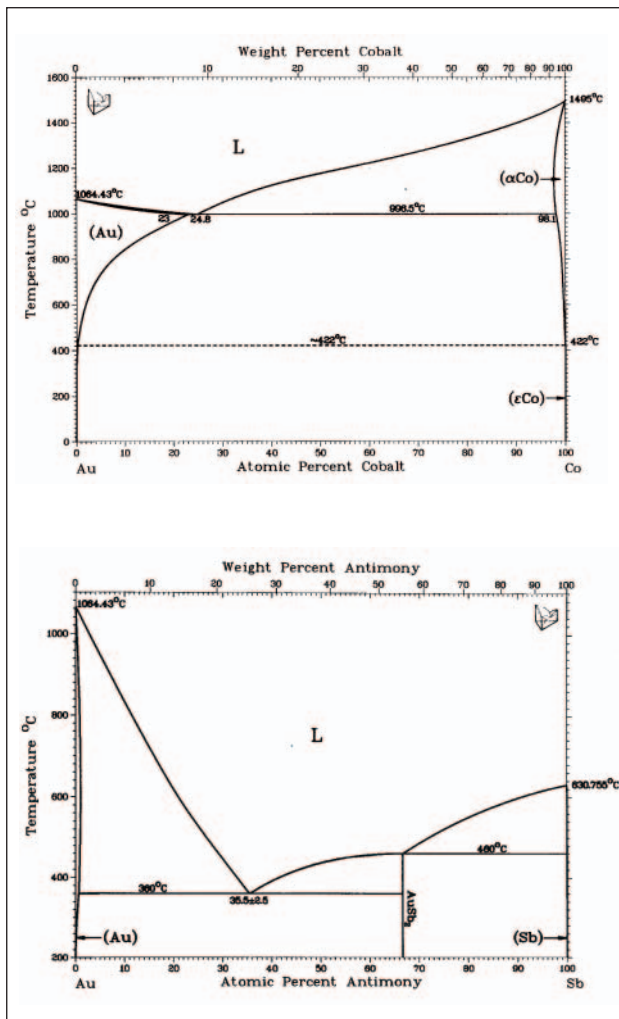


Figure 4
Binary phase diagrams Au-Co and Au-Sb (18)

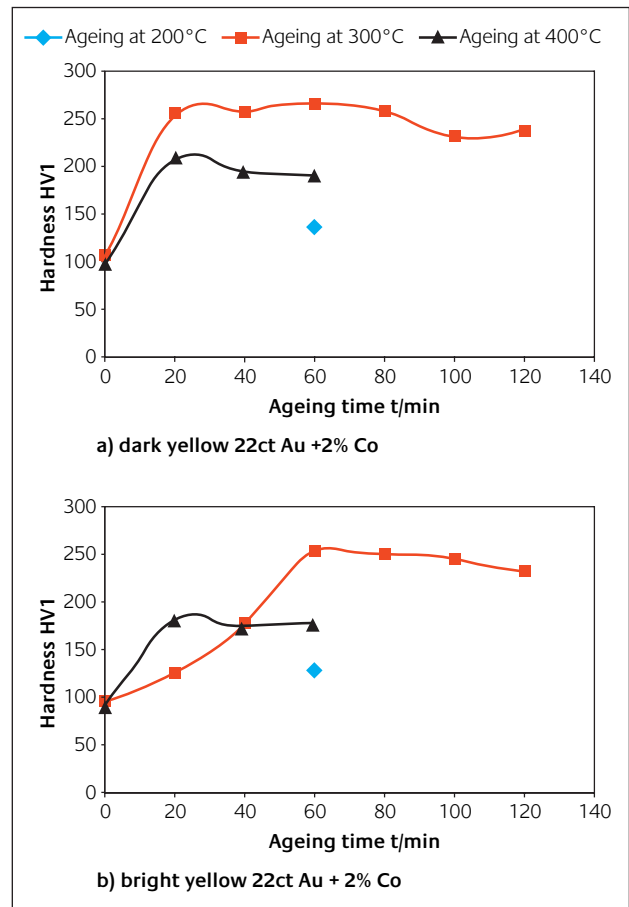


Figure 5
Age-hardening curves for 22ct Au alloyed with 2% Co after solution annealing treatment at 850°C / 1h, followed by water quenching

Results and Discussion

Within the screening procedure, the reference alloys without base metal addition as well as the alloys with Ni-, Fe-, Sb-, Zn-, Ga- or Ba- additions showed no age-hardening effect within the given range of heat treatment parameters. The alloys with Co-additions age-hardened after solution annealing at 850°C or higher, but showed no age-hardening after annealing at 700°C or 800°C.

Figures 5a and b show the age-hardening curves for the Cu-rich and Ag-rich 22ct alloys with 2% cobalt (referred to as alloys AuH_45 and AuH_47 in Table 1) after solution annealing at 850°C. The data shown correspond to investment cast material, but are similar to results obtained on rolled and homogenised material.

For both alloys, an optimum age-hardening effect occurs during ageing at 300°C, with a peak hardness of 260-270 HV1 after 1h. Ageing at 200°C is comparably sluggish and ageing at 400°C yields a lower peak hardness (although higher data for $t < 20$ min cannot be excluded). The data for 300°C suggest, that the age-hardening kinetics are retarded in the Ag-rich alloy compared to the Cu-rich alloy.

For both cases it is assumed that the age-hardening mechanism consists in the formation of finely dispersed Co-rich precipitates with their size being in the nanometer range. TEM analysis of the microstructures would be required for confirmation but are still in the preparation stage, however.

With a view to the high peak hardness obtained, the age-hardening potential of alloys with lower amounts of Co-addition were investigated. For 1% Co, and starting from an as-cast hardness of 75 HV1, the peak hardness does not exceed 125 HV1 for homogenisation at 850°C and ageing at 300°C.

For alloys with 1,5% Co, however, as-cast hardness and age-hardening properties are comparable to the alloys with 2% Co, as shown in Figure 6. The age-hardening kinetics are slower but the peak hardness obtained is only slightly lower

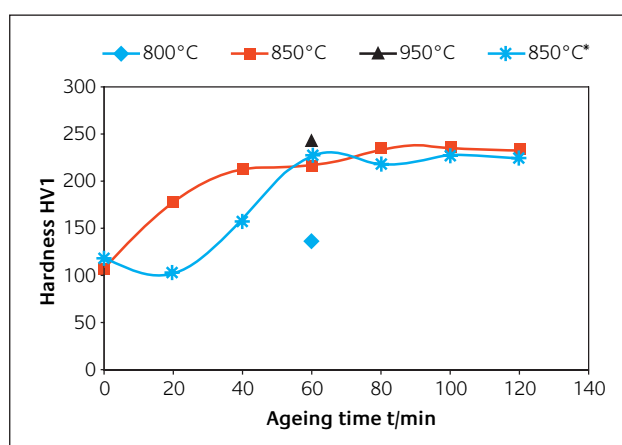


Figure 6
Age-hardening curves at 300°C after solution annealing treatment for 1h at different temperatures, followed by water quenching, for Cu-rich 22ct Au + 1,5% Co, and *Ag-rich material (data only for 850°C)

(~235 HV1) than for alloys with 2% Co. Again a slight retardation of age-hardening kinetics of the bright yellow Ag-rich alloy compared to the dark yellow Cu-rich alloy is observed.

Figure 6 also indicates the influence of homogenisation temperature on the age-hardening properties of the dark yellow 22ct Au alloyed with Co. Decreasing the temperature for solution annealing down to 800°C reduces the age-hardening potential drastically, whereas further increases of the temperature up to 950°C provides no significant benefit over annealing at 850°C with respect to the maximum hardness level obtained. For the bright yellow 22ct Au with cobalt, an increase of the homogenisation temperature to 900°C accelerated age-hardening for low ageing times. Higher solution annealing temperatures allowed for improved chemical homogenisation and are beneficial in terms of corrosion resistance (see below).

The scatter in hardness data within a sample can be quite significant. Experiments with different Au-Co-master alloys (from 2.5 – 10% Co) revealed that the scatter in hardness data was reduced after using lower Co-contents in the master alloy. Hence, the scatter finally was attributed to inhomogeneities in the Co-distribution that originate from the melting process. Higher homogenisation temperatures before ageing will also help in reducing scatter of hardness data.

Properties of age-hardenable 22ct Au + Co for jewellery applications

The age-hardening properties of the 22ct alloys with Co and the hardness level achievable, in combination with good mechanical working properties of these alloys, might be of high interest for 22ct jewellery applications. This is especially true with a view to the actual trend towards miniaturisation of cross sections and diameters of jewellery pieces that are manufactured either by investment casting or cold working. The alloy development presented in reference (10) reports comparable as-cast hardness and age-hardening properties as presented here, as well as good suitability for jewellery applications, and it has been disclosed finally, that the development is also based on the approach of alloying with Co (11). Whereas in that complementary study property testing focused on an alloy with 2.5% Co, further property testing in the present study focused on alloys with 1,5-2% Co. The investigation of the basic property spectrum for 22ct Au + Co including: colour, density and melting range, corrosion resistance, mechanical properties, melting process and investment casting as well as remelting of scrap, in general yielded promising results which were confirmed by preliminary trials of industrial partners. Details are reported elsewhere (16, 17).

Although the validation was positive in general, it was concluded by the author and the cooperating industrial partners, that the exploitation of the high strength obtainable by age-hardening may be limited by the fact that comparably high solution annealing temperatures (~ 900°C)

are required for good age-hardening and corrosion resistance properties, in combination with the need for annealing under protective gas atmosphere. Full exploitation of the maximum strength may also be limited by a corresponding drop in ductility down to very low values. In part, too high hardness was mentioned to be detrimental for surface polishing. For a particular application, a compromise would need to be found between the strength and ductility levels that are really required. It was shown, that this compromise can be achieved by variation of the Co-content, which determines the strength in the fully age-hardened state, but also very effectively by the variation in ageing temperature and ageing time.

The hardening properties in combination with excellent workability were judged by the industrial partners as interesting for particular applications, especially filigree items and hollow jewellery applications. With regard to general casting applications, the main targets for further improvement were seen in fluidity improvement, grain refinement, reduction of shrinkage porosity and oxidation of castings. It was shown that some corresponding improvements are achieved by additions of Ir for grain refinement or addition of Si for improved oxidation resistance and fluidity of the melt (16,17). These additions significantly affect the hardening properties, however, and limit the obtainable peak hardness to ~170 HV. While this is much less than for the same alloy without Ir or Si, it may well be sufficient for a good spectrum of applications and beneficial in terms of ductility.

Age-hardening of 22ct Au (2nd step)

The age-hardening process studied so far relates to the addition of a single primary base metal, cobalt, and the age-hardening mechanism presumably consists in precipitation of nanometer-sized Co-rich phases, with some Ag, Cu and/or Au dissolved in the Co-lattice.

As indicated in the introduction, the aim of the 2nd step of the present study has been to find out, if age-hardening of Au alloys can be successfully altered or enhanced if selected secondary additions are added in stoichiometric proportions, aiming at precipitation of (intermetallic) phases formed by a reaction of the primary and secondary addition.

Table 2:

Composition in % for 22ct alloys included in the 2nd screening of age-hardening properties

Alloy Nr	Total amount in wt% of expected phase	Ag	Cu	Co	Fe	Ni	Sb	Si	Au
AuH_27	1% Co ₂ Si	3.65	3.65	0.81				0.19	bal.
AuH_31	1% CoSb	3.65	3.65	0.33			0.67		bal.
AuH_32	0.5% CoSb	3.9	3.9	0.16			0.34		bal.
AuH_33	1% Ni ₂ Si	3.65	3.65			0.81		0.19	bal.
AuH_37	1% NiSb	3.65	3.65			0.33	0.67		bal.
AuH_38	0.5% NiSb	3.9	3.9			0.16	0.34		bal.
AuH_39	1% FeSi	3.65	3.65		0.67			0.33	bal.
AuH_43	1% FeSb	3.65	3.65		0.36		0.64		bal.

Experimental

Another screening of 22ct alloy compositions was carried out, see Table 2. The experimental schedule was identical to the one already described above. A AuSi-master alloy with 0.8% of Si was used in addition to the ones already mentioned before. It is notable, that the total amount of

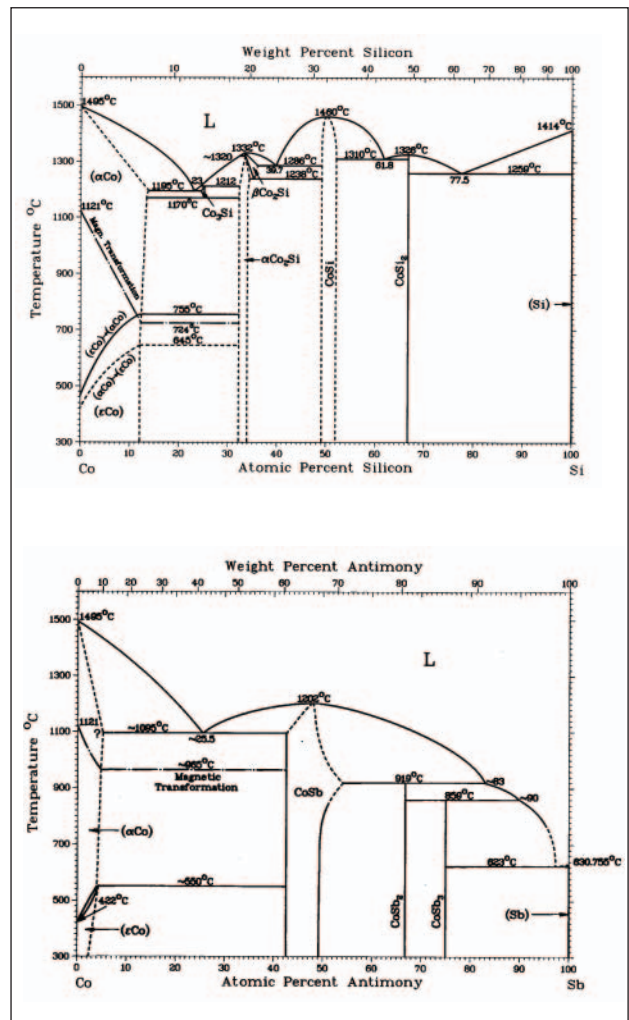


Figure 7
a) Co-Si-phase diagram; b) Co-Sb-phase diagram (18)

additions was limited to either 0,5 or 1%. In the following the alloy composition is referred to as the total of primary and secondary addition; e.g. 1% Co+Sb, which equals 0,33% Co + 0,67% Sb (compare with Table 2).

The compositions of alloys with Si additions were designed in accordance with the stoichiometry of possible reaction phases Co_2Si , Ni_2Si and FeSi , which all have melting points around 1300-1400°C, indicating high thermodynamic stability (see e.g. CoSi-diagram, Figure 7a). Although precipitation hardening by Phosphides is known for Cu-alloys, Au alloys with P-additions have not been studied yet due to difficulties with master alloy preparation. Instead, and obviously motivated by the results reported in (9), alloys with Sb-additions were included in the screening. Intermetallic CoSb-, NiSb- and FeSb-phases of approximately 1:1 atomic stoichiometry occur in the corresponding binary systems (see e.g. CoSb-diagram, Figure 7b) and the alloy compositions in Table 2 (in weight %) were chosen accordingly.

Results and Discussion

The alloys with Co+Si and Ni+Si-additions displayed no age-hardening potential at all, irrespect of solution treatment temperature (700-850°C) and ageing temperature (300-400°C). In contrast, the alloys with Fe+Si - additions showed an age-hardening effect up to 160 HV1 during ageing for 1h at 400°C and after a solution annealing treatment at 850°C (1h / water quenching). However, all Si-containing alloy samples started cracking during rolling from ~40% rolling reduction on. The microstructures of as-cast samples are very heterogeneous, with Si-rich grey/blue phases in interdendritic spaces or at grain boundaries, which do not dissolve in the matrix during homogenisation at high temperatures (Figure 8). Instead partial melting of grain boundary areas occurred for high homogenisation temperatures. Obviously the thermodynamic driving force for formation of the base metal-silicides is too high in the quaternary Au-based system,

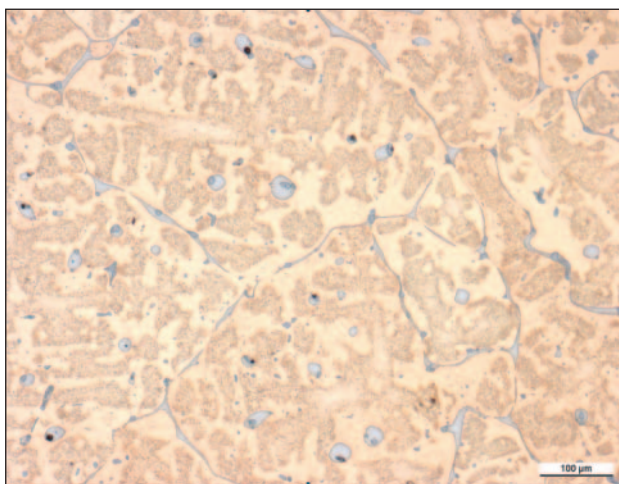


Figure 8
Microstructure of 22ct Au with 1% Fe+Si -addition after casting and homogenisation at 700°C / 1h

so that (low-melting) silicides mainly form by primary crystallisation directly from the melt and belong to the phase equilibria at homogenisation temperature.

For alloys with Sb-additions instead of Si, the situation is different. The alloys with Fe+Sb-additions did not indicate any age-hardening potential within the range of heat treatment parameters studied. In contrast the alloys with Co+Sb- and Ni+Sb-additions age-hardened during ageing at 300°C and 400°C after solution annealing at 700°C as well as 850°C. The corresponding age-hardening curves obtained after solution treatment at 700°C are shown in Figure 9; no benefit was obvious for solution treatment at higher temperatures in terms of hardening properties.

The age-hardening behaviour of the Co+Sb- and Ni+Sb-alloyed material is comparable, with a broad hardness peak at 400°C / 20-60min at 145-155 HV1 for alloys with a total amount of 1% of Co+Sb or Ni+Sb, respectively. For the lower total amount of 0,5% a maximum hardness level of ~120 HV 1 is obtained. Age-hardening kinetics at 300°C are retarded for the Co+Sb-alloyed material, which was not observed for the Ni+Sb-material.

The peak hardness, that is obtained for these alloys is far below the peak hardness obtained by alloying with 1,5 – 2 % Co. Nevertheless the results are judged as very interesting,

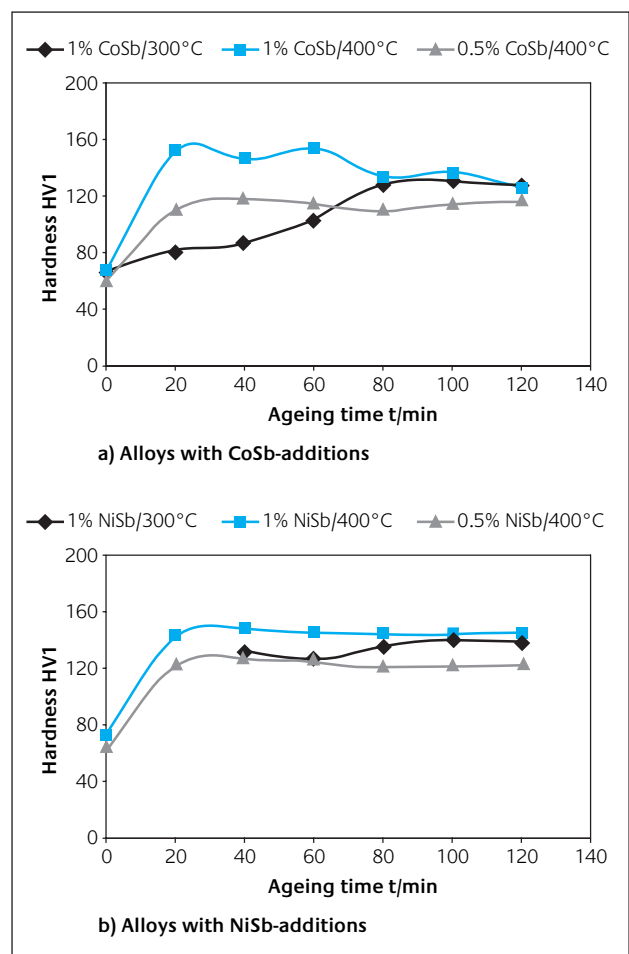
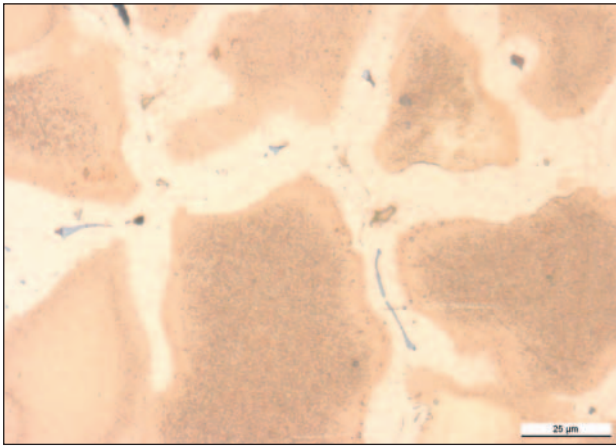
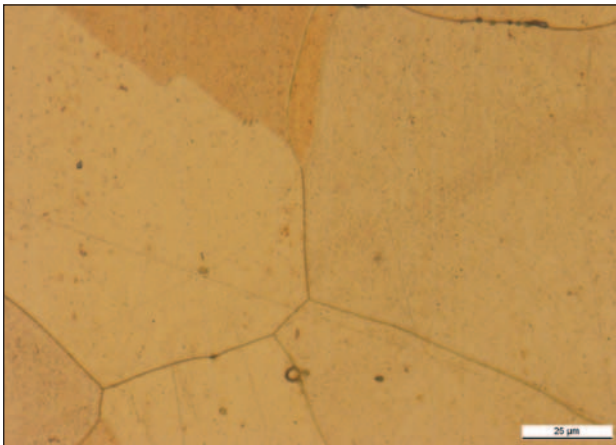


Figure 9
Age-hardening curves of 22ct alloys with 0.5 and 1% of a) Co+Sb and b) Ni+Sb - additions, after solution annealing at 700°C / 1h / wq



a) As-cast microstructure



b) microstructure of the same sample as in a) after cold-rolling (70%) and annealing at 700°C/1h/wq

Figure 10
Microstructure of 22ct Au with 1% addition of Co+Sb

since no age-hardening effect at all was observed by single alloying with Ni or Sb (see above). Furthermore only a comparably slight age-hardening effect was observed for an alloy with 1% Co, whereas pronounced age-hardening is observed in an alloy with only 0,33% Co if only 0,67% Sb was added. This suggests, that the age-hardening mechanism prevailing in these samples differs from the one assumed for alloys with single Co-additions (see discussion at the end).

Properties of age-hardenable 22ct Au + CoSb / NiSb for jewellery applications

With regard to 22ct jewellery applications, the results could be of some interest, because the temperature for solution annealing treatment can be down to 700°C compared to 850°C in case of single Co-additions.

As observed for the samples with Si-additions, the alloys with Sb-additions of 0,67% showed a tendency to cracking, starting at a rolling reduction of ~40%. The microstructure analysis revealed, that a grey Sb-rich phase segregates at grain boundaries during solidification, which dissolves completely during annealing at 700°C / 1h after cold-rolling (Figure 10). The same observations were made for the Ni+Sb-

alloyed material. Interestingly, the Sb-rich grain boundary phases do not dissolve during annealing at 850°C, indicating complex phase equilibria in these quaternary systems.

The reduced ductility in the as-cast state may well restrict the exploitation of these types of alloys for jewellery applications, especially investment casting.

Age-hardening of 990/995 Au

In a last step, it has been of interest to enlarge the screening of age-hardening behaviour based on Co+Sb- and Ni+Sb-additions to the higher finesses of 990 and 995 Au, and to compare the results with those obtained for 22ct Au.

Experimental

Similarly to the approach for 22ct Au, stoichiometric ratios of Co+Sb or Ni+Sb, using the same total amounts (see Table 2), were used now for alloying pure Au (4N-purity). Also, some further reference alloys were included, containing either 1% of Co or Sb, respectively, as well as another alloy containing Co+Sb, but in an off-stoichiometric ratio. The general testing schedule followed the scheme already described earlier.

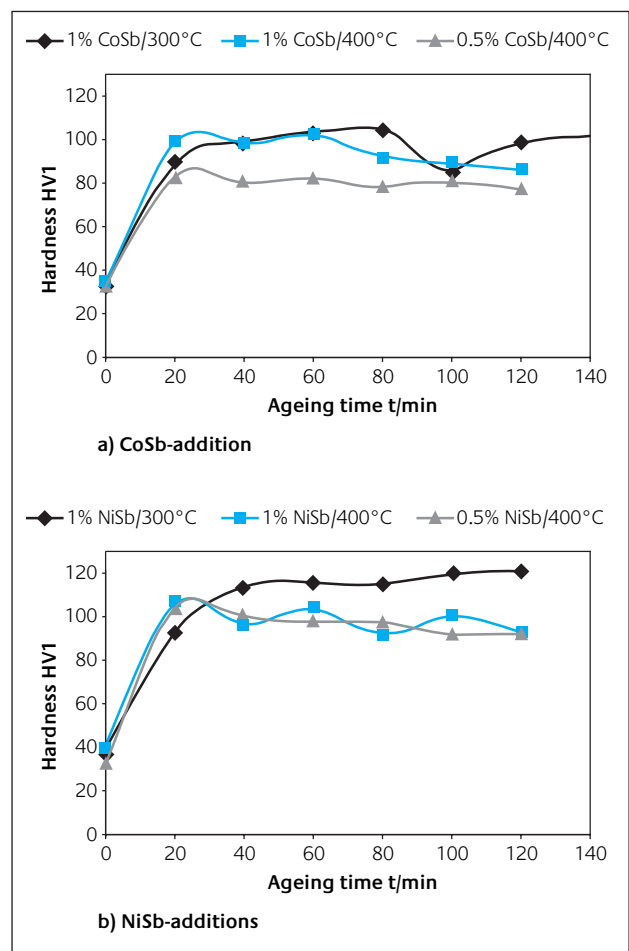


Figure 11
Age-hardening curves for 990/995 Au alloyed with 0.5 and 1% of a) Co+Sb- and b) Ni+Sb-additions, after solution annealing at 700°C / 1h/wq

Results and Discussion

Similarly to the observations for 22ct Au, the samples containing Co+Sb and Ni+Sb in stoichiometric proportions age-hardened after solution annealing at 700°C and during ageing treatments at 300°C and 400°C, with no obvious benefit of solution annealing at higher temperatures. The corresponding age-hardening curves that were obtained after solution annealing treatment at 700°C are shown in Figure 11.

In contrast to the behaviour of the 22ct alloys, the Ni+Sb-additions turned out to be slightly more effective when added to pure Au compared to the Co+Sb-additions, with maximum hardness levels of 120 and 100 HV1 for the material alloyed with 1% Ni+Sb and Co+Sb, respectively. Apart from that, similar characteristics are observed for age-hardening of 990/995 Au and 22ct Au by Co+Sb- and Ni+Sb-additions: quick increase to the maximum hardness level within 20min, little tendency to over-ageing within 2h of ageing treatment at these temperatures; and overall hardness increase between 60-80 points HV1 for total additions of 1% Ni+Sb or Co+Sb. This similarity suggests that identical age-hardening mechanisms prevail in 22ct and 990/995 Au if alloyed with Ni+Sb and Co+Sb.

As a further basis for discussion, it is important to compare the age-hardening behaviour of pure Au containing only a single base metal, i.e. either Co, Ni or Sb. Whereas for alloys with either 1% Sb or Ni, no age-hardening is observed within the present range of heat treatment parameters (ageing 20min-2h at 300° - 400°C), an alloy with 1% Co age-hardens quickly at 300°C up to a peak hardness of ~70 HV1. Direct comparison with the ageing characteristics of Co+Sb-alloyed material at 300°C (Figure 12), reveals that hardening is less pronounced if compared to alloying with Co+Sb in stoichiometric ratio, even for the low total amount of only 0,5% of Co+Sb. Furthermore a strong overageing effect is observed for Au + 1% Co leading to a drop down to 40 HV1 after 2h.

The third ageing curve in Figure 12 refers to an alloy

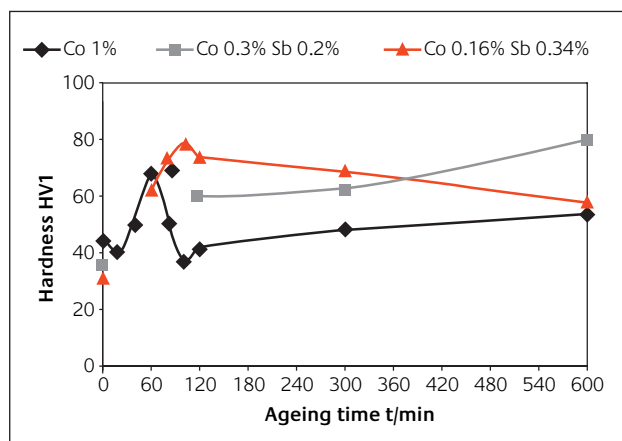


Figure 12

Comparison of age-hardening curves at 300°C for 990/995 Au alloyed with Co and Co+Sb additions, respectively, after solution annealing at 700°C/1h/wq

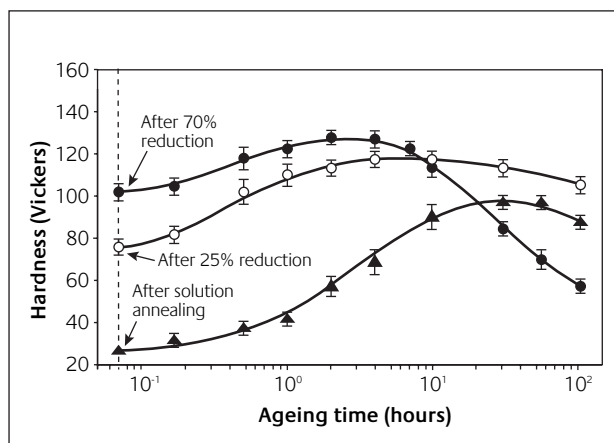


Figure 13

Age-hardening curves at 300°C for 995 Au alloyed with 0.2% Co + 0.3% Sb additions, without and with preceding cold-working (9)

containing 0,3% Co + 0,2% Sb, hence also a total amount of 0.5% Co+Sb but in an off-stoichiometric ratio (compare with Table 2). The age-hardening kinetics are significantly retarded if compared to the alloy with Co+Sb in stoichiometric ratio, but the same hardness level of 80 HV1 eventually is obtained for very long ageing times (~10h).

Comparably slow age-hardening kinetics with a peak hardness of ~100 HV1 after ~30h at nominally the same ageing temperature of 300°C has been reported for another 995 Au alloy containing Co+Sb in a slightly off-stoichiometric ratio (0.2% Co and 0.3% Sb), as shown in Figure 13 taken from reference (9). Although the small deviation from the exact stoichiometric ratio Co:Sb (0.16% Co and 0.34% Sb) may well be the determining factor (see discussion below), the large difference in age-hardening kinetics is striking and may also be caused by unrevealed differences in experimental conditions.

Properties of age-hardenable 990/995 Au + CoSb/ NiSb for jewellery applications

Within this study, no further work was devoted to the assessment of further properties of 990/995 Au alloyed with Co+Sb or Ni+Sb. The solidification microstructures of the 990/995 Au alloyed with Co+Sb- and Ni+Sb-additions are comparable to the ones reported for 22ct Au. They showed Sb-rich grain boundary segregations leading to reduced ductility in the as-cast state. While this may restrict exploitation for jewellery investment casting applications, the overall property spectrum as presented in reference (9) for 995 Au with 0.5% Co+Sb in slightly off-stoichiometric ratio seems to be promising.

The study in reference (9) aimed at optimising the strength of 995 Au alloyed with Co+Sb by a combination of cold-working and subsequent age-hardening, as obvious from Figure 13. The acceleration and enhancement of age-hardening by preceding cold-working, as well as the preservation of the cold-work strength during the subsequent ageing process, are important aspects for applications involving deformation, they have not been the focus of the present study.

Discussion of age-hardening mechanisms in low alloyed gold

Age-hardening in low-alloyed gold alloys can be obtained by single additions of Cobalt, but additions in excess of 1% are required to obtain a significant hardening effect as shown for 22ct Au alloys. The age-hardening characteristics of alloys with Co are significantly altered if Sb is added: Remarkable age-hardening is observed for as little total amounts of 0,5% Co+Sb and is most pronounced if the ratio Co:Sb corresponds to the atomic stoichiometry of the intermetallic CoSb-phase observed in the binary Co-Sb-system (see Figure 7). Furthermore, age-hardening is obtained with joint Ni+Sb-additions, even for low total amounts of 0.5% of Ni+Sb in a stoichiometric ratio corresponding to an intermetallic NiSb-phase, whereas no age-hardening is observed for single additions of either Ni or Sb.

Therefore it may be reasonable to assume that the prevailing age-hardening mechanism in these types of alloys consists in precipitation of intermetallic CoSb- and NiSb-phases. No evidence about the structure and stoichiometry of the precipitations in these samples is available yet. It should be mentioned, that another intermetallic phase (Ni_5Sb_2) exists in the binary NiSb-system, with its stability being comparable to the NiSb-phase.

The TEM-results reported in reference (9) for Co+Sb in 995 Au suggest age-hardening by disc-shaped Sb-rich precipitates, which according to the AuSb-phase diagram (Figure 4) could consist of intermetallic AuSb-phases. However, no precipitation-hardening by single Sb-additions was observed in the present study. In principle, a co-precipitation of both, Co-rich and Sb-rich-precipitations, as opposed to intermetallic CoSb-precipitations, cannot be ruled out.

More recently in another complementary study on hardening of Cu-rich 22ct Au alloys (12), it has been shown that significant precipitation hardening is observed by joint addition of either Ni+Sn or Ni+Ga. Similarly to the observations in the present study, most pronounced age-hardening is observed for stoichiometric Ni:Sn or Ni:Ga-ratios, which are near to stable intermetallic phases occurring in the specific binary systems (NiGa , Ni_3Sn_2), whereas less pronounced or no age-hardening has been observed for off-stoichiometric alloying additions. Since no age-hardening in 22ct Au is observed for single additions of either Ni, Sn or Ga, it is again reasonable to assume that precipitation of the corresponding intermetallic phases, or ternary intermetallic phases like Cu_2NiSn (12), is the prevailing age-hardening mechanism in these alloys.

Summarising the discussion above, it is obvious that enhancement of the hardening effect of conventional base metals in Au is possible by addition of selected further elements, suggesting that the hardening approach identified a long time ago for Copper base alloys (13, 14) can be successfully transferred to low alloyed gold alloys.

These issues and assumptions require further detailed investigation and confirmation, preferably by high resolution transmission electron microscopy (TEM), although modelling

of the phase equilibria in the ternary and quaternary systems should be very helpful in addition. Furthermore, more information about the properties of these types of alloys for jewellery manufacturing are required.

Ongoing or future work will show if the alternative approaches to age-hardening will lead to new alternatives for strengthened 22ct –24ct Au jewellery alloys with a satisfying property spectrum. Whether or not the described approach for hardening low-alloyed gold alloys is of interest also for industrial applications, especially electronic applications, was beyond the scope of this study.

Some preliminary investigations confirmed, that the electrical conductivity of an alloy with 0.5% Ni+Sb in the solution annealed state is about 38% of pure Au, but recovers to ~72% in the age-hardened state.

Conclusions

From the list of conventional base metals, Cobalt produced the most pronounced solid solution hardening (~100 HV1) and age-hardening (260 HV1) in 22ct Au alloys. Extended property testing of corresponding 22ct Au alloys with ~1.5-2% Co yielded promising results. Further work showed, that the age-hardening behaviour of 22ct and 990/995 Au alloyed with Co or Ni can be remarkably influenced by additions of Sb. A total of only 1% of Co+Sb- or Ni+Sb-additions lead to a peak hardness of ~150 HV1 for 22ct Au and 100-120 HV1 for 990 Au. Possible benefits of the second approach are

- lower overall amounts of alloying additions
- lower solution annealing temperature (700°C compared to 850°C)
- very quick age-hardening kinetics, in combination with
- very little tendency to overage.

It is suggested that the age-hardening mechanism in these alloys consists in precipitation of intermetallic CoSb- and NiSb-phases. Considering also complementary results from other sources, which hint at age-hardening by intermetallic NiSn- or NiGa-phases in 22ct Au, it is obvious, that an enhancement of the age-hardening effect of conventional base metals in Au is possible by addition of selected further elements. The results suggest, that the hardening approach identified long time ago for high-strength high-conductivity Copper base alloys, can be successfully transferred to low alloyed gold alloys.

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