Original Article

Metallurgical processes for hardening of 22Karat Gold for light weight and high strength jewelry manufacturing

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\begin{abstract}
The present work reports about the process developed for hardening 22Karat gold (Au-5.8 wt.%Cu-2.5 wt.%Ag). The present hardness of 22Karat gold is 85–90HV (Vickers scale). The target hardness aimed is 150HV in the final jewelry product, similar to the hardness of 18Karat gold, however without compromising luster and purity (91.7 wt.%). Titanium is added as the quaternary element in micro concentrations that grain refines the as-cast structure of 22Karat gold and improves the strength of the cast jewelry products. On other hand the narrow solid solubility of Ti in Au is used to convert the 22Karat gold into age hardenable gold alloy suitable for making hand-made jewelry products. This paper reports the optimization of various process parameters in industrial scale, required for producing hard 22Karat gold containing Ti through age hardening process. In lab scale the titanium concentration required was optimized to 0.5 wt.%, to obtain effective age hardenability in 22Karat gold was studied. In industry the melting and casting trials of 22Karat gold with the addition of 0.5 wt.% of Ti to obtain maximum yield was performed. The annealing and cold-working operations were conducted to the Ti-22Karat gold that lead to production of hand-made bangles were studied. The age hardening treatments (Solutionizing and Artificial Aging (AA)) were conducted to the Ti-22Karat gold bangles to obtain hardness >150HV.
\end{abstract}

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1. Introduction

The high Karat gold mainly, 22Karat is highly preferable for jewelry manufacturing in Indian subcontinent. The purity of gold in 22Karat is 91.7 wt.% and rest of the composition is majorly occupied by Cu and Ag. Due to the drastic increase in the price of gold in recent years, customers willingness to buy gold for jewelry purpose has reduced significantly. This left lot of scope on producing light weight jewellery. However with the present strength and hardness of 22Karat gold, manufacturing light weight jewellery is difficult. Increasing the hardness and
strength of the 22Karat gold similar to 18Karat gold without losing its purity, luster and brilliance and workability will lead to weight saving and improves the buckling and sagging resistance of load bearing parts of the jewelry. The high hardness also improves the scratch and wear resistance of the jewelry parts. Currently for the studded jewelries (holds precious and semi-precious stones using prongs) only 18Karat gold are used for high strength. High strength in 22Karat has potential to replace the 18Karat gold in the studded jewelry manufacturing sector.

Very less work on hardening and strengthening of 22Karat gold was reported in the literature. The review article on microalloying 24 Karat gold with various transition, alkaline, alkaline earth, refractory and rare earth metals to improve hardness has suggested that such microalloying technique can be adopted to 22Karat gold and 18Karat gold [1,2]. Taylor [3] added elements like cobalt and boron to the 22Karat gold and converted it into an age hardenable alloy. Several elements [4] namely Sb, Ga, Ba, Ni, Fe have been tried for grain refinement and age hardening of 22Karat gold, However, resulted no improvement in the strengthening effect. Fischer-Bühner [4] have tried adding 2 wt.% cobalt to 22Karat gold which showed improved hardness in both cast and wrought stage of 22Karat. The hardness obtained here is 260 HV after age hardening treatment. The hardenability of 22Karat gold has been improved by addition of various elements such as Zn,Co, Ir, Re, Ni, Sn, Ga, In, Ge by compensation the concentration of Cu and Ag [5]. However alloying with these elements resulted in poor workability, perceptible colour change. Alloying 22Karat gold with Nickel and Cobalt have proven to causes allergic problems to skin like contact dermatitis and therefore not suitable for making jewellery [6]. Cretu et al. [7] have reported that Mintek, South Africa, a gold jewelry manufacturer invented an age hardenable 22Karat gold with good workability. The maximum hardness obtained of that 22Karat gold was 274 HV after cold working and age hardening. However, no evidence on the composition, workability and product development was available in the literature. Gafner [8] has measured the hardness factor of different elements such Co, Rh, Ru, Ti, U, Zr, Tb, Dy, Ho, Er, Ti in gold. Among all elements, Ti has highest hardness factor of 12.5 and proved to be an efficient grain refiner. Titanium of concentration about 1 wt.% showed good age hardenability in 990 gold [8]. However, Ti is highly reactive to oxygen at high temperature and therefore needs vacuum/inert atmosphere melting furnaces for alloying with gold. The age hardenable 990 gold containing Ti found potential as soldering wires in electronics application [9]. The Au-1.6 wt.% Ti alloy which has high modulus of elasticity and hardness and good corrosion resistance are used to produce dental crowns [10,11]. Incidentally the present authors have not come across any work on Ti alloyed in 22Karat gold.

The present authors have attempted to increases the hardness of 22Karat gold (90 HV) (Vickers scale) similar to 18 Karat gold (150 HV) by grain refinement and age hardening using Titanium. To overcome the high reactive nature of Ti at high temperature it is added to molten 22Karat gold through Au-Ti master alloy, which does not need any vacuum or inert atmosphere. The work has been done in two different phases.

In lab scale the optimization of the Ti concentration for efficient grain refinement and age hardening was performed with in-depth microstructural and phase investigation of the Ti containing 22Karat gold. At industry the focus is much on the melting and casting, annealing & cold-working operations of Ti containing 22Karat gold in larger volume (500–1000 g) to obtain good yield similar to the existing 22Karat gold. The jewelery products (hand-made bangles) using the Ti containing 22Karat gold has been manufactured and subjected to age hardening treatment to obtain the desired hardness (>150 HV) in the product. During the trials proof of concepts on the purity, colour and workability of Ti containing 22Karat gold in line with the existing 22Karat gold has been established.

Titanium (Ti) is a light weight element with a density of 4.5 g/cc [12] and possesses high strength due to its HCP crystal structure. The melting point of Ti is 1668 °C and it is reactive with oxygen at high temperatures. When FCC metals like gold was alloyed with titanium, it has good growth restriction factor (GRF) due to its high segregation power. Therefore, they are efficient grain refiners for gold even in solute form [8]. The Au-Ti equilibrium diagram shows that at 1125 °C, Au4Ti and molten Au undergoes peritectic reaction, which possibly nucleates a-Au upon freezing [13]. On other hand, the narrow solid solution of Ti in Au can very well suitable for age hardening. The Au4Ti intermetallic that forms while alloying Ti with gold can dissolve and re-precipitate at nano-scale in the Au matrix via age hardening treatment (solutionizing and artificial ageing). Ti is also having added advantage that it has zero toxicity and therefore does not cause any skin allergies or dermatitis when used in jewelries.

2. Materials & methods

Gold in the form of coins (99.99 wt.% pure) was supplied by Titan Company Ltd. (jewelry division), India. Copper and Silver (99.99 wt.% Pure) in used in granular form were supplied by Titan company Ltd. Elemental Titanium (99.7 wt.% pure) in the rod form purchased from Sigma-Aldrich, USA was used.

The Au-6 wt.% Ti master alloy was prepared using vacuum arc melting furnace (AM-133 Vacuum System Technologies and Services Ltd) with a vacuum of below 1 × 10⁻⁶ bar and melting started at 0.39 bar argon atmosphere. The Ti concentration were chosen with the help of Au-Ti phase diagram to obtain complete intermetallic phase, Au₄Ti in the alloy. As the intermetallic phase is brittle and enables easier pulverization of the master alloy into granules which can be easily added to the molten 22Karat gold. As we see in the section 3.4 the adding method of the master alloy into the 22Karat gold largely influences the quality of the 22Karat gold melt, its fluidity, Ti loss during melting and the slag formation and final yield in the casting. The chemical composition of the Au-6 wt.% Ti master alloy produced were analyzed using ICP-OES. The phases present in the master alloy were analyzed using X-Ray diffraction (PANalytical X’pert Pro) with nickel-filtered Cu-Kα radiation as the X-ray source (λ = 1.5406 Å). The microstructure of the Au-6 wt.% Ti master alloy was studied using Scanning electron microscopy and EDX elemental analysis (FEI Quanta FEG-200).

Titanium is added into 22Karat gold through Au-6 wt.% Ti master alloy for grain refinement of the as cast structure. On other hand Ti is added to convert the 22Karat gold into age
hardenable alloy for the production of hand-made jewelry. The flow chart (Fig. 1) shows the processes carried out for Ti-22Karat gold at both lab and industry. The process steps for hardening was included in the regular process line in order to obtain the desired hardness in the final product.

A detailed and systematic studies of grain refinement and age hardening was carried out for the 22Karat gold in lab scale which is discussed in section 3.2. In this study the Au-6 wt.%Ti master alloy addition level (i.e., the Ti concentration in wt.%) required for effective grain refinement and age hardening of the 22Karat gold was studied. The microstructure of grain refined samples was studied using metallurgical optical microscope (Leica DM2700 M) and the grain sizes are measured using linear intercept method. The nano scale precipitates formed in the peak aged Ti-22Karat samples were analyzed using Transmission electron microscope (JEOL, JEM2100, Japan). The hardness of the grain refinement and age hardened samples are measured using Vickers hardness testing machine at 500 g load with 10 s dwelling time. The master alloy addition level for grain refinement and age hardening has been optimized and that was followed as the standard operating procedure (SOP) during the industrial trials.

However newer challenges were faced when performing the process trials in industry. For the 22Karat gold with Ti addition through Au-6 wt.% master alloy, the optimization of the melting temperature, melt cleanliness to obtain quality castings with maximum yield similar to the regular 22Karat gold was essential. Since alloying was done in an open induction melting furnace the titanium loss (since Ti is highly reactive metal) during alloying that leads to increased purity of gold has been the serious issue during the industrial trials. The parameters for effective annealing, cold working (rolling-wire drawing) of the Ti-22Karat gold was also optimized during the industrial trials.

For industrial trails the 22Karat (Au-5.8 wt.%Cu-2.5 wt.%Ag) gold alloy about 500 g was prepared by melting the gold coins with copper and silver granules of desired concentration. The melting was done at medium frequency open induction melting furnace at temperature ranges from 1200 °C to 1400 °C. The Au-6 wt.%Ti master alloy at desired Ti concentration was added into the melt, followed by manual stirring with graphite rod. The melt is then isothermally held for 5 min. before casting. Cast jewelry products are produced through investment casting method. Casting is done in a specialized furnace and poured in an investment flask containing ceramic slurries [14]. The grain refinement studies were matched with the cooling rate obtained in investment casting mould.

For hand-made jewelries the molten Ti-22Karat gold is poured into a preheated graphite mould to obtain rectangular or cylindrical castings of desired size (discussed in the section 3.5). The castings obtained were annealed followed by cold-rolling and wire drawing to obtain desired size rods and sheets as per the requirement for the manufacturing of jewelries (discussed in section 3.6 and 3.7). Later the jewelries produced using Ti-22Karat gold were subjected to age hardening treatments (solutionizing and artificial aging) (discussed in section 3.8). Solutionizing treatment will provide a super-saturated solid solution of Ti in gold and artificial aging treatment aid in precipitation of nano scale Au$_4$Ti precipitates in the Ti-22Karat gold alloy which contributes to the increased hardness. The purity of gold in the 22Karat gold is measured after casting by fire assay method and the purity 91.7 wt.% is maintained. The colour and luster of the jewelries produced were tested using CIELAB spectrometer which is discussed in section 3.9. In all our trials of hardening the Ti addition is compensated by decreasing the Ag concentration in 22Karat gold both during grain refinement and age hardening processes.

3. Result and discussion

3.1. Synthesizing Au-6 wt.%Ti master alloy

The Au-Ti phase diagram [13] shows the presence of Au$_4$Ti intermetallic particles along with the α-Au phase in the gold rich side. The density of Au$_4$Ti intermetallic is 16.73 g/cc [ICSD No. 98-009-9947]. The density of molten Au (17.4 g/cc) [15], which is found to be matching with the density of Au$_4$Ti intermetallic. This allows the Au$_4$Ti particles to be easily admixed and distributed in molten Au. Three different master alloys of various Ti concentrations (3, 4 and 6 wt.%) was prepared using Vacuum Arc Melting method. Among all the alloy prepared the Au-6 wt.%Ti showed larger volume of Au$_4$Ti intermetallic particles with smaller amount of Au$_4$Ti and α-Au in the matrix. The alloy also allowed easier pulverization due to its brittle nature.
3.2. Optimization of Ti concentration for the Grain refinement & age hardening of Ti-22Karat gold in lab trials

3.2.1. Grain refinement
The grain refinement of 22Karat gold (91.7 wt.% pure) was done by heterogeneous nucleation. The Au-6 wt.%Ti master alloy in mm sized granules was added into the molten 22 Karat gold at temperature (1250 °C). The addition of master alloy was varied from 0.1 to 0.3 wt.% of Ti (Table 1) to study the grain refining efficiency. Fig. 2(a) and (b) compares the microstructure of cast 22Karat gold and grain refined 22Karat gold with 1.67 wt.% of Au-6 wt.%Ti master alloy (0.1 wt.%Ti) addition. A drastic change from coarse grain structure (450 µm) to finer grain structure (21 µm) is evident from the microstructure. Increasing the addition level of the master alloy (0.2 and 0.3 wt.% Ti) does not show any significant improvement in the grain refinement. But there is little increase in the grain sizes (Table 1) while increasing the grain refiner addition due to recalescence [16,17]. The hardness measured in 22Karat gold after grain refinement showed a drastic improvement in comparison to as-cast 22Karat gold (Table 1). The higher hardness achieved in 22Karat gold is 128 HV after grain refining with 0.1 wt.%Ti addition.

3.2.2. Age hardening
The grain refinement of the as-cast structure of 22Karat gold by the addition of Ti can improve the hardness of the cast gold jewelry, but not suitable for the hand-made jewelry. During wrought processing of the regular 22Karat gold, the castings obtained was annealed in a box type furnace at 650–800 °C for 1h followed by rapid cooling in water for homogenization. The annealing process breaks the as-cast coarse grains into equiaxed grains and enables the secondary process like cold working, wire drawing and other operations that are essential for making the wrought products of the 22Karat gold [8]. Further, while making the hand-made products, the 22Karat gold alloy undergoes several heating and cooling cycles to maintain soft. Such practices to the grain refined 22Karat gold will lead to grain coarsening and causes softening to the alloy.

Applying age hardening process once the product is made will be the right choice to retain the workability in the 22Karat gold. The solid solubility limit of Ti in Au at 800 °C is 1.2 wt.% and at 400 °C is 0.4 wt.% [8]. Beyond the solid solubility limit, it forms Au₄Ti intermetallic along with α-Au. The narrow solid solubility of Ti in Au aids age hardening of Au by forming controlled precipitation of the Au₄Ti precipitates in the matrix through artificial aging.

The lab studies for age hardening was performed by varying the Ti addition from (0.1–1 wt.%) in the 22Karat gold. The Ti was added through Au-6 wt.%Ti master alloy in molten 22Karat gold and manually stirred for 30 s, which is then isothermally held for 5 min. for homogenization before casting in billet or rod form. The annealing and age hardening temperature of 24K gold containing 1 wt.% Ti at 800 °C for 60 min and 600 °C for 30 min respectively [8]. Same procedure is followed for the Ti-22Karat gold castings, which was annealed at 800 °C for 60 min in a box type muffle furnace, followed by water quenching for homogenization. Further it is cold-rolled or wire drawn to 90% reduction. The samples of dimension (20 × 5 × 2 mm) have been sliced from the cold worked Ti-22Karat alloy and were solutionized at 800 °C for 60 min. in a box type muffle furnace under inert atmosphere followed by rapid quenching in cold water which gives a super saturated solid solution of Ti in Au. The hardness obtained for the solutionized sample is less, in comparison to as-cast Ti-22Karat alloy (Fig. 3).

The solutionized Ti-22Karat gold samples were artificially aged at 600 °C for 30 min. in a muffle furnace followed by air cooling. Artificial aging forms fine nano scale precipitates of Au₄Ti in the Au matrix which gives the higher hardness to the gold. The addition of titanium to the gold increases, the
Table 1 – Details of the grain refinement and age hardening studied conducted to 22Karat gold with various Ti concentration.

<table>
<thead>
<tr>
<th>Sl no.</th>
<th>Ti-22Karat Alloy composition in wt.%</th>
<th>Processes</th>
<th>Other operations</th>
<th>Average grain size, μm</th>
<th>Hardness of Ti-22Karat gold</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Cu</td>
<td>Ag</td>
<td>Ti</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>91.7</td>
<td>5.8</td>
<td>2.5</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>2.</td>
<td>91.7</td>
<td>5.8</td>
<td>2.4</td>
<td>0.1</td>
<td>Grain refinement</td>
</tr>
<tr>
<td>3.</td>
<td>91.7</td>
<td>5.8</td>
<td>2.3</td>
<td>0.2</td>
<td>Grain refinement</td>
</tr>
<tr>
<td>4.</td>
<td>91.7</td>
<td>5.8</td>
<td>2.2</td>
<td>0.3</td>
<td>Grain refinement</td>
</tr>
<tr>
<td>5.</td>
<td>91.7</td>
<td>5.8</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6.</td>
<td>91.7</td>
<td>5.8</td>
<td>2.0</td>
<td>0.5</td>
<td>Age hardening</td>
</tr>
<tr>
<td>7.</td>
<td>91.7</td>
<td>5.8</td>
<td>1.75</td>
<td>0.75</td>
<td>Age hardening</td>
</tr>
<tr>
<td>8.</td>
<td>91.7</td>
<td>5.8</td>
<td>1.5</td>
<td>1.0</td>
<td>Age hardening</td>
</tr>
</tbody>
</table>
formation of secondary phase particle (Au₄Ti) also increases with enhanced hardness values of the samples [9]. After age hardening treatment, the hardness values of the 990-gold alloy is increased to (>150 HV) due to the formation of Au₄Ti precipitates in the gold matrix. The Ti-22Karat gold did not showed any aging response for the lower Ti concentrations below 0.3 wt.%. According to the Au-Ti phase diagram [13] the maximum solid solubility of Ti at 400 °C is 0.4 wt.%. For precipitation of 0.4 wt.%Ti or below, it needs lower aging temperature i.e., <400 °C. At such low temperature activation of Ti in Au is poor and Ti gets oxidized and caused the formation of TiO₂ in gold [18]. The minimum concentration for age hardening is 0.5 wt.% of Ti which showed effective aging response at 600 °C for 30 min. Increasing the addition level of Ti showed improvement in aging at 600 °C for 30 min which can be seen from the hardness bar chart shown in Fig. 3. There is an increase in the peak hardness with the increase in the addition level of Ti. In the present work, the Ti concentration is optimized to 0.5 wt.%, since higher Ti concentration in 22Karat gold increases the work hardening rate, which seems to be difficult in any cold-working operation. And the concerns about retaining the bright yellow colour and luster of regular 22Karat gold in the present alloy also restricted the Ti concentration to 0.5 wt.%.

The industrial trials were carried out to scale-up the hardening process to the large volume of 22Karat gold for a pilot scale jewelry production. The lab studies have shown that Ti can effectively age hardens 22Karat gold even at the lowest addition level (0.5 wt.%). The optimization of parameters of various process steps during industrial trials are as follows.

### 3.3. Overview of the process

1. **Alloying the 22Karat with Ti**
   (a) Melting: Varying the melting temperature, way of adding the Au-6 wt.%Ti master alloy, stirring and homogenization, melting atmosphere, melt cleanliness (slag formation, gold loss, Ti loss and final yield)
   (b) Casting: Various type of moulds have been tried to minimize the casting defects (piping, porosity, slag inclusion)

2. **Annealing treatment**: The pre-annealing and intermittent annealing treatments to obtain the softness in Ti-22Karat gold that enables the cold-rolling/wire drawing operations

3. **Cold rolling and wire drawing**: These two methods to obtain maximum yield in the Ti-22Karat gold alloy for the product making. The surface defects formed during cold-working operation, which is also connected to the quality of the casting has been studied during the trials.

4. **Hand-made products**: Bangles (of dia 60 mm and of weight ~7.3 g) are produced from the Ti-22Karat gold

5. **Solutionizing & Artificial Aging**: The bangles produced are solutionized and artificially aged to obtain the final hardness in the product. Following, the products are undergone Quality Assurance (QA) testing for purity and colour. The results were matched with the regular 22Karat gold.

### 3.4. Allo^

Optimization the melting and casting parameters for alloying the Ti into 22Karat gold is essential, since Ti is the only reactive elements among other elements (Au, Cu and Ag) in gold alloy. The regular melting process of 22Karat gold will be not suitable for the present 22Karat gold alloying with 0.5 wt.% of Ti. The melting point of gold (1064 °C) increases when alloyed with Ti. At 0.5 wt.% Ti the melting point increases beyond 1100 °C as per the Au-Ti phase diagram [13]. The lab trials have proven that, setting higher melting temperature >1250 °C is essential to dissolve completely the Au-6 wt.% Ti master alloy in the molten gold. In industrials trials the optimization of the melting temperature for large volume melts is found to be essential, not only to dissolve the master alloy, but for homogenous mixing of Ti, to obtain good fluidity in the melt, minimizing slag formation and increasing the yield.

The melting and casting trials conducted in the industry by varying the process parameters are shown in the Table 2. The elements required for 22Karat gold (Au, Cu and Ag of desired concentration) about 500–1000 g was melted in an open induction melting furnace with or without argon cover gas, the melting temperature was varied from 1250 °C to 1450 °C. The melt temperature was continuously monitored by laser pyrometer (Raytek - Ranger 3i plus).

The Au-6 wt.%Ti master alloy of 8.35–16.7 wt.% (0.5 wt.% Ti) was added into molten 22Karat gold (500–1000 g) in the granular form (1–2 mm), followed by manual stirring of the melt with graphite rod for 30 s to obtain homogeneity and to enable faster dissolution of master alloy pieces. The melt is then held isothermally for 5 min. before pouring into a graphite mould for casting. Our trials have shown that adding the master alloy in the form of bulk pieces (5–10 mm) slows the dissolution of the master alloy and delays the Ti release into the molten gold. Adding the master alloy in powder form (<100 μm) does not mix well in the melt too. In both the case there was a huge Ti loss in the alloy, which caused an increase in the purity of gold > 91.7 wt.% in the castings obtained.

At temperatures 1250–1350 °C, melting the 22Karat gold and adding Au-6 wt.%Ti master alloy increases the amount of slag formation due to the poor dissolution of master alloy. It should be noted that only temperature range is presented in this paper, since the furnace used for melting and alloying in Industry was an open induction melting furnace, which exhibited a 100 °C temperature fluctuation. The slower dissolution of master alloy causes oxidation and that create slag in the surface of the melt. While pouring the melt into a mould this slag separates and pulls out some clean melt with it, which decreases the casting yield. In addition, it was also observed a decrease in the melt fluidity and as the result, the pourability gets affected and the casting obtained has lot of defects such as cracks, porosity and slag inclusion. These defects in the casting affects the cold-working of the alloy in the later stage of the jewelry manufacturing. Increasing the melting temperature to 1350–1450 °C decreases the % slag formation in comparison to the low temperature, (Table 2) however not completely and hence it is decided to deploy argon purging facility to the induction melting furnace. The argon purging set up comprises of heavy stainless steel (SS) lid to graphite crucible of the induction furnace. This SS lid is connected to high pure argon cylinder, equipped with a flow controller. During melting operation, the charge is kept in the crucible along with the granules of Au-6 wt.% Ti master alloy and argon is passed
Table 2 – Details of study performed to optimized various parameters of alloying and melting Ti-22Karat gold to obtain minimum slag% and zero Ti loss.

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Melting Atmosphere</th>
<th>Temperature °C</th>
<th>Time (min.)</th>
<th>Average Slag %</th>
<th>Average Ti loss (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ambient</td>
<td>1200 to 1250</td>
<td>5</td>
<td>4.5</td>
<td>0.3</td>
</tr>
<tr>
<td>2.</td>
<td>Ambient</td>
<td>1350 to 1450</td>
<td>5</td>
<td>2.8</td>
<td>0</td>
</tr>
<tr>
<td>3.</td>
<td>Argon purging</td>
<td>1350 to 1450</td>
<td>5</td>
<td>1.5</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 4 – Scatter plot shows the % slag obtained during the melting trials of 22Karat gold with the addition of 0.5 wt.%Ti at various temperature. The melting was done in an open induction melting furnace with and without argon purging.

at rate of 1.5 bar to flush the oxygen present in the crucible. While heating and during the melting operation the argon continuous to flow at the same rate and enable cleanliness in the melt. The combination of higher melting temperature (1350–1450 °C) and argon purging have drastically decreased the slag % obtained (Table 2).

Fig. 4 shows the percentage of slag formation plotted as the function of the number of melting and alloying trials conducted by varying the temperature and melting atmosphere. It clearly shows that at melting at 1250–1350 °C under ambient atmosphere, the average slag % (among 30 melting trials) obtained is 4.5% indicating poor dissolution of master alloy and Ti loss due to oxidation. The Ti loss is measured indirectly by measuring the purity of Au in the casting through fire assay method. To ensure further the retained Ti is also measured via ICP-OES method. While increasing the melting temperature from 1350–1450 °C the % slag formation reduced and consistency in all 5 trials performed and the average slag % measured is 2.8 indicating a clear improvement in the dissolution of the master alloy. Further the average slag obtained was reduced to 1.5% which is attributed to the argon purging in combination with the higher melting temperature.

3.5. Casting of the Ti-22Karat gold

During melting the 22Karat gold with 0.5 wt.%Ti, enough care has been taken to reduce the viscosity of the melt, decrease the slag formation and increasing the quality of melt by various melt treatments. Even care was taken to avoid the slag inclusion in the melt during pouring. But it was observed that the fluidity of the molten 22Karat gold alloy after the addition of Au-6 wt.%Ti master alloy was quite less compared to the regular 22Karat gold, which does clearly affect the pourability and the quality of the casting. The trials were conducted (Table 3) to optimize the right casting condition and mould required for pouring in combination with the optimized melting parameter (discussed in section 3.4) of the Ti-22Karat gold. This is to obtain high yield in the castings with minimum defects that enables smoother and easier cold-working. Once the molten Ti-22Karat gold is casted, drilled chips were taken from different parts of the casting about 1 g for measuring the purity of gold by fire assay method. For 22Karat the purity 91.7–91.75 wt.% will be maintained.

The billet casting was initially tried for the Ti-22Karat gold melt. Billet casting serves as the precursor for cold-rolling to produce gold alloy sheets for hand-made jewelry products. Two different type of billet castings were carried out using rectangular graphite mould with short or large openings for pouring. The dimension of the moulds are 90 × 45 × 25 mm and 50 × 40 × 15 mm respectively. Fig. 5 shows the side view and top view of the Ti-22Karat gold casting obtained from rectangular mould with short opening. The dimension of the casting is 53.79 × 44.80 × 24.89 mm and the quantity of the melt was 972.10 g. The slag obtained during melting is 25.95 g. Large piping was observed on the top of the casting and found deeper through the cross section. The surface of the casting exhibit layered like structure formed due to the poor pourability of the melt caused by increased viscosity. Before subjecting the castings for the cold-rolling operation the piping was removed mechanically from the casting, which decrease the yield significantly. The yield is 88% (subtracting the slag which was removed from the melt before pouring) for the casting obtained from rectangular mould with large opening and 92% for the casting obtained from rectangular mould with short opening (Table 3). Adopting argon purging and higher melting temperature for the Ti-22Karat gold, has helped to overcome the fluidity and the slag problem in the melt and yielded quality casting. However, the formation of piping in the castings cannot be avoided, which decreased the yield and found detrimental to the cold-working operations. (discussed in the section 3.6)

Casting trials have been carried out for Ti-22Karat gold of about 500 g, using cylindrical taper mould. The casting obtained is of size, 20 mm in the top and 14 mm in the bottom and 150 mm height. The castings have exhibited smoother surface (Fig. 6) and showed significant decreases in the defects like cracks and layered structure, due to the increase in the melt fluidity, pourability and decreased slag%. The weight of casting is 480.74 g and the slag is 18.81 g. The yield obtained in this cylindrical casting is 97% (Table 3) which is similar to the regular 22Karat gold. In addition, the piping formed was smaller and shallow in comparison to the rectan-
Table 3 – Details of studies performed to cast Ti-22Karat gold in various types of moulds to obtain minimum casting defects and maximum yield.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Mould shape</th>
<th>Mould dimension, mm</th>
<th>Casting dimension, mm</th>
<th>Casting Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rectangular mould with Long opening</td>
<td>50 × 40 × 15 mm,</td>
<td>49.27 × 39.27 × 14.59</td>
<td>88</td>
</tr>
<tr>
<td>2.</td>
<td>Rectangular mould with short opening</td>
<td>90 × 45 × 25 mm,</td>
<td>53.79 × 44.80 × 24.89</td>
<td>92</td>
</tr>
<tr>
<td>3.</td>
<td>Tapered cylindrical mould</td>
<td>24 mm² top, 14mmφ bottom × 150 mm height</td>
<td>24 mm² top, 14mmφ bottom × 150 mm height</td>
<td>97</td>
</tr>
</tbody>
</table>

Fig. 5 – The casting of Ti-22Karat gold, casted using a rectangular mould (short face is open to atmosphere) of quantity 1000 g. (a) The front view shows the cracks marks in red arrows, (b) Top view of casting shows piping in the casting marks in red arrow.

Fig. 6 – Cylindrical tapered casting of Ti-22Karat gold of quantity 500 g. (a) The front view shows smoother and defect free surface and (b) top view shows the piping.

gular mould and could be easily sheared off. The final weight of the casting (suitable for wire drawing operation) is 440.50 g which is 25% higher than the castings obtained through the rectangular moulds

3.6 Cold rolling and wire drawing of Ti-22Karat gold

Cold-working like cold-rolling and wire drawing was carried out for the Ti-22Karat gold into square rod shaped of dimension 6 mm × 6 mm to meet gold smiths requirement to produce jewelries. Both the rectangular shaped casting and cylindrical casting were subjected to cold-rolling and wire drawing operation respectively to obtain the square rods. The detail of the studies performed is shown in Table 4.

Before subjecting the Ti-22Karat gold for cold-working operation, annealing was carried out in a box type furnace under nitrogen atmosphere at 800 °C for 60 min. followed by water quenching. In this process the undissolved Au₄Ti particles added through the Au-6 wt.%Ti master alloy would dissolve completely. At the same time the annealing operation can also break down the as-cast microstructure of the gold alloy and enables smoother cold-working operations.

The rectangular casting of Ti-22Karat gold was cold-rolled in order to the thickness to 6 mm and convert it into a plate form. At each pass of cold-rolling ~0.5 mm thickness of the casting was reduced. The alloy was intermittently annealed after every three passes at 650 °C for 45 min in a box type furnace under nitrogen atmosphere followed by water quenching for softening. This 6 mm plates were sheared into square rods of 6 mm × 6 mm (Fig. 7a) of varying length. The gold smith joins the square rods together by brazing, which is further cold-rolled into longer thin sheets (90% reduction) as shown in
Fig. 7 – Cold-rolled and sheared Ti-22Karat gold rectangular casting (a) square rod of 6 mm x 6 mm size (b) rejected square rod pieces due to cracks, and slag entrapment. (The red arrows shows the visible cracks in the square rods.)

Fig. 8 – Thin sheets cold-rolled from square rods of Ti-22Karat gold (a) sheet alloy shows rough surface and sides. (b) peel off on the surface (marked by red arrow).

Fig. 8 (a) and (b). The surface of the rods was appeared rough with peeled off edges. Larger cracks were visible beneath the surface. This could be attributed the poor quality of rectangular castings and the increase in the work hardening rate of Ti-22Karat gold in the presence of Ti. Some cracks also show visible slag entrapment inside the rod. It was witnessed that nearly 40% of the square rods are sheared and rejected due to cracks and slag entrapment (Fig. 7(b)). The yield (material suitable for jewelry making) obtained in both type of rectangular casting is 53–74% (Table 4).

While cold rolling the square rods into thin sheets (about 90% reduction) surface peel off was visible (Fig. 8 (a) and (b)). The surface peel off could be formed due to the presence of voids or slag entrapped in the castings, which expanded over the surface while rolling. These defects lead to larger rejection of Ti-22Karat alloy for jewelry manufacturing.

The cylindrical casting of Ti-22Karat gold were wire drawn into square rod of dimension 6 mm x 6 mm. The maximum reduction obtained is 70% reduction with an average reduction rate 0.9 mm per pass. Square rod about 750 mm length was achieved in one casting as per the requirement of the goldsmith and no joining of rods were required. Intermittent annealing to soften the alloy was carried out at 650 °C for 45 min under nitrogen atmosphere followed by waster quenching in water while wire drawing the casting. Fig. 9 (a) and (b) shows the square rod of Ti-22Karat gold obtained after wire drawing the cylindrical tapered casting. It is visible that the surface peel off and rough sides are largely minimized because of the better quality of casting obtained (Fig. 6) quality casting. The yield obtained is 88% with a minimum wastage as shown in Fig. 9(b).

3.7. Manufacturing hand-made bangles with Ti-22Karat gold

The square rods obtained from the cylindrical tapered castings of Ti-22Karat gold is further used for jewelry making particularly hand-made bangles. The rods are cold rolled further into thin sheets and wound in a mandrel as shown in Fig. 10. It is must be understood that the workability of Ti-22Karat gold is not as easy as a regular 22Karat gold, since the presence Ti increases the work hardening rate drastically. On other hand the continual heating of the alloy by flames while making the jewelry at temperatures 400–600 °C can allow precipitation in the Au4Ti intermetallic particles in the alloy which increases the hardness exceptionally. The undesired hardness in the alloy formed during working, resulted in burr formation at the edges (red arrow marks of Fig. 10) of the cold-rolled sheets which comes out on further processing and causes loss in the alloy. Hence intermittent annealing at 650 °C in nitrogen atmosphere followed by water quenching is adopted even during jewelry manufacture for improving the softness in the alloy.

3.8. Age hardening treatment of the hand-made bangles (solutionizing and artificial aging)

The bangles once produced were subjected to solutionizing treatment using a box type furnace for 800 °C for 60 min. under nitrogen atmosphere followed by water quenching. Then the bangles are artificially aged in a box type muffle furnace at 550 °C for 30 min. under ambient atmosphere followed by air cooling. Fig. 11(a) shows the bangles obtained after artificial aging with blackened surface due to oxidation. The blackened surface was removed by polishing as shown in Fig. 11(b). The hardness of the bangles was measured in the sides of the rim using Vickers hardness testing machine with 500 g load and 10s dwelling time. The average hardness obtained is 160HV. Similarly, the flexural strength of the hard bangles was measured by applying compressive load up to 25 kgf and observed no deformation in the bangles, which was not possible in the
regular 22Karat gold. With Ti-22Karat gold (Au-5.8%Cu-2.0%Ag-0.5 wt.%Ti) bangles are made in 7–8 g of diameter 60.3mmφ and thickness 1.0 mm. The weight reduction was possible only because of the higher hardness (160 HV) obtained in bangles after age hardening treatments.

3.9. Colour and Luster of the hand-made bangles made by Ti-22Karat gold

The one of the objectives of the present work is to retain the colour (bright yellow) of regular 22Karat gold in the novel hardened 22Karat gold. However, the age hardening treatment (solutionizing and artificial aging) of the bangles produced with Ti-22Karat gold exhibited a perceptible change in the colour in comparison to the regular 22Karat gold. Instead of bright yellow colour, the jewelry made with Ti-22Karat gold showed a pale-yellow colour after polishing (Fig. 11(b)). This could be attributed to presence of nano scale Au₄Ti precipitates in the surface of the bangles, that modified the visible light reflection. Trials have been carried out starting from melting to age hardening treatments by changing only the Cu and Ag concentration (listed in Fig. 12). Some trials have been performed by only changing the Cu and Ag concentration in 22Karat gold have 0 wt.% Ti. Cretu et al. [19] have demonstrated the method of measuring the colour gold using CIELAB spectrophotometer in a highly polished surface. The method in CIELAB spectrophotometer expresses the colour as three-dimensional co-ordinates: L*, a*, and b*, where L* is the luminance (brightness). The a* co-ordinate measures the intensity of the green (negative) or red (positive) component of the spectrum, while the b* co-ordinate measures the intensity of the blue (negative) or yellow (positive) component. In the present study the colour of the samples was defined by plotting a* and b* co-ordinates as a point in the 2D space. The L* obtained for the 22Karat gold with 0.5 wt.%Ti was same as the regular 22Karat gold.
The scatter plot (Fig. 12) shows the $a'$ and $b'$ values of various 22Karat gold containing 0.5 wt.% Ti with varying Cu and Ag concentrations. For comparison the $a'$ and $b'$ values of regular 22Karat is also shown in the scatter plot. The black colour points represent the composition of 22Karat gold containing 0.5 wt.%Ti, where only the Cu concentration has been varied. Similarly, the red colour points represent the composition, where both Cu and Ag concentrations was varied without the addition of Ti. The green colour points represent the composition where only the Ag concentration was varied in the 22Karat gold containing 0.5 wt.% Ti. The blue point represents the composition of regular 22Karat gold (Au-5.8 wt.%Cu-2.5 wt.%Ag). It can be seen from the scatter plot that no composition matches exactly with the regular 22Karat gold. However, the composition no.12 with 0.5 wt.%Ti (green) is observed closer to the colour of regular 22Karat.

The lab trials and industrials trials have shown that Titanium addition can effectively grain refines and age hardens 22Karat gold at lower concentrations of Ti added through Au-6 wt.%Ti master alloy. Industrial trials were successful in optimizing the parameters required to establish better melting and casting practice of Ti-22Karat gold. The industrials scale studies performed to established the cold-working operation of the Ti-22Karat gold that has led to jewelry production (Hand-made Bangles) has given us a better understanding on the process. With the age hardening treatment (solutionizing and artificial aging) of the hand-made bangles made using Ti-22Karat gold, higher hardness (160 HV) was achieved similar to 18Karat gold. The industrial trials have showed that producing light weight jewelries with high strength was possible in 22Karat gold with smaller addition of Ti, without compromising on the workability, colour and purity. similar to regular 22Karat gold.

5. Outlook

Other processes which are also essential but not focused in this present work are

1. Brazing and welding of Ti-22Karat gold: Since it was understood from the present trials that the Ti in the alloy oxidizes on repeating heating that forms TiO₂ on the surface of Ti-22Karat gold which may affect joining.

2. Retaining Ti concentration in Ti-22Karat gold after several melting and casting operation: In the customer side, the jewelries made using Ti-22Karat may be remelted for a change of design for several time. So it is must to understand the retainment of Ti after in the Ti-22Karat gold after several melting and casting operation

3. Refining of the Ti-22Karat gold: It is important to know that Ti can be removed completely from the gold with the existing refining processs adopted used for regular 22Karat gold.

4. Trying out various other jewelry products using Ti-22Karat gold: In the present work only hand-made bangles are made using Ti-22Karat. Other jewelry products where more working and strength is required like chains and links used for chains will be tried by re-visited the cold-working trials if necessary.

Conflicts of interest

The authors declare no conflicts of interest.

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