TEN HOT METALLURGY QUESTIONS!

A hitlist of the questions most frequently asked by our customers

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Why is silver useful in gold alloys?
Aka: Why do I have to pay an alloy so much?
Why is silver useful in gold alloys?

In yellow gold:

Perfectly miscible, no loss, highly deformable....

Extremely high shininess, intensifies color hue

International standards based on ternary formulas Au-Ag-Cu

Age-hardenable in 585‰
Why is silver useful in gold alloys?

In white gold:

Improves fluidity in Ni-based formulations, in all titles

Protects stones thanks to a lower shrinkage during cooling
Why is silver useful in gold alloys?

Cheaper alternatives:

Zinc, with limits on color, risk of loss, low chemical resistance

Gallium, Indium, tin, but only in small quantities
What burnout cycle and why?
First, what is an investment? 

Powdery mixture of:

- 70-75% Silica (refractory) \([\text{SiO}_2]\)
- 25-30% emi-hydrate calcium sulphate (binder) \((\text{CaSO}_4^{\circ\frac{1}{2}}\text{H}_2\text{O})\)
- Additives, impurities (borax...)

Reaction with water brings to hydrate calcium sulphate, then reduced to anhydrous calcium sulphate by heating

\[
\text{CaSO}_4^{\circ\frac{1}{2}}\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CaSO}_4^{\circ2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \\
(@25^\circ\text{C}) \hspace{1cm} (@104^\circ\text{C}, @246^\circ\text{C})
\]
What burnout cycle and why?

Low temperature part: long and steady
- Evaporates water without overpressures
- Melts and evaporates wax without burning

High temperature part: high temps can be reached because the water is already eliminated
Lower risk of breaking or defects
- Gives maximum mechanical resistance
- Eliminates wax residues
What burnout cycle and why?

<table>
<thead>
<tr>
<th>Step</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>hours</td>
<td>100</td>
<td>250</td>
<td>270</td>
<td>350</td>
<td>750</td>
<td>750</td>
<td>600</td>
</tr>
<tr>
<td>hours</td>
<td>250</td>
<td>270</td>
<td>350</td>
<td>750</td>
<td>750</td>
<td>600</td>
<td>600</td>
</tr>
</tbody>
</table>

Burnout cycle for investment flasks
Optimizing preparation

Must be used before expiry date!

Remixable to improve homogeneity of components

Water powder ratio: 36 – 40%

- Changes the hardening time
- Depends on the room temperature
- Impacts the investment mechanical resistance
Do you have an alloy at title 375 with 24K color?
Reflectivity

1 – Pure gold
2 – 50% Au – 50% Ag (At.)
3 – 90% Ag – 10% Au (At.)
4 – 95% Ag – 5% Au (At.)
5 – Pure silver
Distance from pure color

Legend:
- 22k
- 21k
- 18k White
- 18k Yellow
- 18k Red
- 14k Yellow
- 14k Red
- 9k Yellow
- 9k Red
- Other Metals
Why is everything cracked?
Coarse crystal grains

Crystal grain boundary = Crack development barrier

Fine crystal grains

Crack development is restrained
Why do pieces crack?

Excessively high process temperatures:

- Excessive overheating (metal or investment) leading to grain growth

- Alloys oxidation, leaving, on the solidification front, unwanted compounds
Why do pieces crack?

Excessively low temperature

- Voids, internal porosities
- If the item is incomplete, it is also less resistant from the mechanical point of view
Why do pieces crack?

Wrong processing times:

Too long a quenching

E.g.: 3 hours before quenching

(→ grain growth!)
Why do pieces crack?

Too quick quenching

Excessive stress:

Hardness + low thermal conductivity (Ni-based alloys)
Stress during cooling

Excessive thermal gradient, So much that it generates a stress between skin (cold, small specific volume) and core (still hot, high specific volume)
Position six

How to improve stone-in-place casting?
Common issues

Stone breakage

Color shift

Stones falling from the item
Fundamental:

Prongs with adequate size and tolerances

Well made mounting

Constant quality stones
Thoughts on the alloy

Thermal expansion varies with the formulation:

Silver/copper ratio (yellow gold):

More silver means:
- Higher shrinkage
- More strength on the stone

If I lose the stones, I need an alloy with more silver
If my stones break, I choose a formula with more copper
Thoughts on the alloy

For Ni-based alloys, hardness is the largest risk factor
Less nickel means:

- Less strength on the stone

Silver addition in a white alloy (from practical experience):

- Lower shrinkage
- Increasing thermal exchange
- Better heat sink
Thoughts on time

Thermal shock on stones must be avoided...

...and this goes opposite from metal protection

Risk of grain growth
(metal cracks, Lacking strength on stones)

Example on an 18K yellow

2h: 20% loose stones
1 h: 7% loose stones
30’: 0% loose stones
10’: stones crack
Thoughts on cooling

Useful on white gold:

To have a gentler cooling curve the flask can be re-put in the furnace after pouring (10-15 minutes)

In this way the metal can be left to settle at an intermediate temperature
Position five

How to avoid cracks in 750‰ red gold?
Red: equilibrium cooling
Blue: immediate cooling
Intermetallic compounds

Order-disorder transformation possible with Cu/Au 1:1 atomic ratio, leading to a face-centered tetrahedric super-lattice, with high hardness deriving from atom size difference.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition at.% Cu</th>
<th>Pearson symbol prototype</th>
<th>Strukturbericht designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au–Cu hT solid solution</td>
<td>0–100</td>
<td>cF4-Cu</td>
<td>A1</td>
</tr>
<tr>
<td>Au₃Cu</td>
<td>10–38.5</td>
<td>cP₄-AuCu₃</td>
<td></td>
</tr>
<tr>
<td>AuCu (I)</td>
<td>42–57</td>
<td>tP₄-AuCu</td>
<td>L₁₂</td>
</tr>
<tr>
<td>AuCu (II)</td>
<td>38.5–63</td>
<td>cI₄₀-AuCu (II)</td>
<td></td>
</tr>
<tr>
<td>AuCu₃ (I)</td>
<td>67–81</td>
<td>cP₄-AuCu₃</td>
<td>L₁₂</td>
</tr>
<tr>
<td>AuCu₃ (II)</td>
<td>66–?</td>
<td>tP₂₈-PdCu₃</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.26. Section sequence parallel to the base plane of the tP2-AuCu (I) type structure. A tP4 pseudo-cell is outlined by dotted lines.
How to reduce this problem?

In the alloy:
Elements that modify the Au-Cu ratio
(Silver, zinc)

Elements that reduce the risk for cracks
(grain refiners)
In case of stone-in-place casting:

- Put bottom of tree in contact with running cold water
- Cool the flask with a fan
- Wait 10-15 minutes
- Quench in warm water (60-80°C)
Annealing: one more or one less?
Area reduction calculation

**Riduzione lastra**

- Dim. iniziale = 100
- Dim. finale = 30

Area iniziale 100x100.
Area finale 100x30.
Rapporto di riduzione = 70%

**Riduzione filo quadro**

- Dim. iniziale = 100
- Dim. finale = 55

Area iniziale 100x100.
Area finale 55x55.
Rapporto di riduzione = 70%

**Riduzione filo circolare**

- Dia. iniziale = 100
- Dia. finale = 55

Area iniziale 50x50 XTR.
Area finale 28x28 XTR.
Rapporto di riduzione = 70%
Too heavy plastic deformation:
- excessive number of dislocations, damaged microstructure

Lacking deformation:
- Lacking or non-homogeneous dislocations: after annealing some zones are having grain growth, others are still in recrystallization
Hollow chain with iron core
# Sheet deformation

<table>
<thead>
<tr>
<th><strong>Initial process (sheet)</strong></th>
<th><strong>Modified process (sheet)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong> Melting</td>
<td>1 Melting</td>
</tr>
<tr>
<td><strong>2</strong> Rolling</td>
<td>2 Rolling</td>
</tr>
<tr>
<td><strong>3</strong> Annealing</td>
<td>3 Annealing</td>
</tr>
<tr>
<td><strong>4</strong> Rolling</td>
<td>4 Rolling</td>
</tr>
<tr>
<td><strong>5</strong> Annealing</td>
<td>5 Annealing</td>
</tr>
<tr>
<td><strong>6</strong> Rolling</td>
<td>6 Hollow chain shaping (iron)</td>
</tr>
<tr>
<td><strong>7</strong> Annealing</td>
<td>7 Annealing</td>
</tr>
<tr>
<td><strong>8</strong> Rolling</td>
<td>8 Rolling</td>
</tr>
<tr>
<td><strong>9</strong> Annealing</td>
<td>9 Annealing</td>
</tr>
<tr>
<td><strong>10</strong> Hollow chain shaping (iron)</td>
<td>10 Hollow chain shaping (iron)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Initial</strong></th>
<th><strong>Modified</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting</td>
<td>Sheet 22,0x5,2 mm</td>
</tr>
<tr>
<td>Red. 50% → 2,5 mm</td>
<td>Sheet 22,0x5,2 mm</td>
</tr>
<tr>
<td>660°C, 45 minutes, stat.</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td>Red. 70% → 0,8 mm</td>
<td>Red. 70% → 0,8 mm</td>
</tr>
<tr>
<td>Red. 37% → 0,5 mm</td>
<td>Red. 37% → 0,5 mm</td>
</tr>
<tr>
<td>660°C, 45 minutes, stat.</td>
<td>Ø = 5,80 mm</td>
</tr>
<tr>
<td>Red. 24% → 0,38 mm</td>
<td>Ø = 5,80 mm</td>
</tr>
<tr>
<td>660°C, 45 minutes, stat.</td>
<td>Ø = 5,80 mm</td>
</tr>
</tbody>
</table>
## Hollow wire deformation

<table>
<thead>
<tr>
<th>Second part (drawing)</th>
<th>Modified process (drawing)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong> Drawing</td>
<td>Ø 5,80 mm → Ø 4,70 mm</td>
</tr>
<tr>
<td><strong>2</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td><strong>3</strong> Drawing</td>
<td>Ø 5,00 mm → Ø 4,40 mm</td>
</tr>
<tr>
<td><strong>4</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td><strong>5</strong> Drawing</td>
<td>Ø 4,40 mm → Ø 3,60 mm</td>
</tr>
<tr>
<td><strong>6</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td><strong>7</strong> Drawing</td>
<td>Ø 3,60 mm → Ø 2,80 mm</td>
</tr>
<tr>
<td><strong>8</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td><strong>9</strong> Drawing</td>
<td>Ø 2,80 mm → Ø 2,10 mm</td>
</tr>
<tr>
<td><strong>10</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td><strong>11</strong> Drawing</td>
<td>Ø 2,10 mm → Ø 1,40 mm</td>
</tr>
<tr>
<td><strong>12</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td><strong>13</strong> Drawing</td>
<td>Ø 1,40 mm → Ø 0,90 mm</td>
</tr>
<tr>
<td><strong>14</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
<tr>
<td><strong>15</strong> Drawing</td>
<td>Ø 0,90 mm → Ø 0,55 mm</td>
</tr>
<tr>
<td><strong>16</strong> Annealing</td>
<td>660°C, 45 minutes, stat.</td>
</tr>
</tbody>
</table>
I got hardspots on an item surface: why?
Which causes for hardspots?

- Very common examples: Contaminations from metals

Spectrum 1:
Ruthenium 17.96%
Iridium 82.04%

Spectrum 2:
Ruthenium 22.23%
Iridium 77.77%
Which causes for hardspots?

- Very common examples: Contaminations from metals

Spectrum 5:
- Copper 2.14%
- Osmium 97.86%

Spectrum 6:
- Copper 2.55%
- Osmium 97.45%
Very common examples: Contaminations from non-metallic compounds

Spectrum 5:
- Oxygen 48%
- Aluminum 52%

Spectrum 8:
- Iron 72.5%
- Chromium 9.6%
- Carbon 7%
As cast silver is too soft! How to harden it?
Hardening elements...?

Limited as cast hardness, miscibility problems

- Nickel (release)
- Manganese (high tarnishing, slag)
- Tin (porosity, quality issues)

From internal characterization:
- Ni 95 HV
- Mn 75 HV
- Sn 80 HV
- In 45 HV
AgCu alloys are suitable for age-hardening!

![Phase diagram of Ag-Cu alloys with key points labeled: L, 961.93°C, 760°C, 1084.87°C.](image-url)
Age-hardening: principle of functioning

$T_0 = 700-740^\circ C$, 40 minuti

$T_2 = 300^\circ C$, 60 minuti
Inert atmosphere or vacuum in the hardening furnace?

Both work well, but not to harden the item...

There are other metallurgies in which the atmosphere can harden the surface (nitridization, carbo cementing)

Advantage: protection from oxydation and thermal stability
Can I add the plastic deformation hardness to that from age-hardening?

Unfortunately no, hardening is obtained by a limitation to the dislocation mobility, and it’s not an additive property.
Position one

How many times can I re-use an alloy?
It depends....

- Production process
- What does the alloy come in contact with
- Investment reaction
- Alloy overheating
- Refractory residues
- Oxydation / Oxygen intake
- Lubricant residues
Consumption of functional elements in the alloy

Deoxidizers getting lower need to be replenished

Silicon content of a yellow alloy at title 750 after several casting and recasting cycles
In casting it is recommended to use at least 50% of new alloy with each casting.

Clean scraps with pickling and magnetic tumbler.

Do not exceed with reuse!
- 6 times at max for yellow/red gold
- 4 times for white gold

Aim: a stable process
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