OXYGEN AND SILVER

Relevance to Good Delivery Bars

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LBMA Assaying and Refining Conference
PREAMBLE

What is the Oxygen problem for Silver?

- It is not (mainly) the financial one, that oxygen counts as silver (even at a high level of 100 ppm the loss would be only ~£1 per bar)
- Instead it is that Oxygen is readily soluble in molten silver...
Starter Question

Gay-Lussac discovered in 1830 how much oxygen a bath of molten silver could contain in solution.

Question:

For a 30 kg bath of molten silver (enough for one GD Bar) how much oxygen at 1 atmosphere pressure could it hold?
PREAMBLE

What is the Oxygen problem for Silver?

- It is not (mainly) that oxygen counts as silver (even at a high level of 100 ppm the loss would be only ~£1 per bar)
- Oxygen is very soluble in molten silver ......
- but not in solid silver
- It can therefore spoil physical appearance of GD bars
PREAMBLE

What is the Oxygen problem for Silver?

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• Oxygen is very soluble in molten silver ...... but not in solid silver
• It can therefore spoil physical appearance of GD bars

The Challenge
Preventing absorption by or removal of oxygen from molten silver

Lessons for Silver from Poling of Copper?
COPPER POLING

What is (was) poling and can it be used for silver?

Wood + Heat = CO + H₂

Oxygen (soln. or Cu₂O) + CO + H₂ = CO₂ + H₂O
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Preventing absorption or removal of oxygen from silver

Lessons for Silver from Poling of Copper?

Attempts to find a speaker from a GD Copper Refiner

Similarities and differences between copper and silver etc
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Preventing absorption or removal of oxygen from silver

Lessons for Silver from Poling of Copper?
Attempts to find a speaker from a GD Copper Refiner
Similarities and differences between copper and silver etc
Failed attempts! That is why I am here.
SURVEY OF GD REFINERS

Managing Oxygen in Silver

Questions

• Raw material for melting?
• Melting method (ie furnace type and capacity)?
• Methods of minimisation of oxygen absorption?
• Use of flame polishing during casting?
• Need for physical treatment of cast bars?
• Analysis of oxygen in molten and solid silver?

Results

• Many similarities to obviating problems
• Some unique solutions
SCOPE

Cosmological Digression - Oxygen and Metals
Physical Chemistry of the Silver-Oxygen System

- Molten silver
- Solid silver

Good Delivery Issues

- Why oxygen counts as silver
- Analysis is not easy (or necessary?)
- Possible impact on bar quality

GD Refiner Strategies to avoid Oxygen Problems

- Oxygen absorption – sources and prevention
- Removal of oxygen from molten silver
- Casting Methods

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Let’s talk about OXYGEN
From the stellar forge to the Earthly anvil
Oxygen Occurrence

- Milky Way

Excluding Dark Matter, the Milky Way consists of:
- 75% Hydrogen
- 23% Helium
- 1% Oxygen
- 1% Everything else
Oxygen’s Nuclear and Chemical Stability

Why Oxygen is Number 3 in Cosmic Abundance

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Occurrence

- Milky Way
- Solar System

Due to gas giants, H and He still dominate. But note the peaks for oxygen and iron.
Let’s talk about OXYGEN
From the stellar forge to the Earthly anvil

Occurrence

- Milky Way
- Solar System
- Earth

Earth
A distilled planet: small size, low gravity and proximity to the sun. Mainly heavy elements retained.
- Fe 32%
- O 30%
- Si 15%
- Mg 14%
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Occurrence

- Milky Way
- Solar System
- Earth
- Earth’s Crust (the slag layer)

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Occurrence

- Milky Way
- Solar System
- Earth
- Earth’s Crust
- Fire, water, iron and cyanobacteria
- The Iron Ore Age ends
- The Air Age begins

Source Graeme Churchard
OXYGEN AND METALS

Message from Metals: Who wants my excess electrons?

Answer from Oxygen: I do!

- Free Energy Diagram
- Ag₂O vs Cu₂O vs MgO
OXYGEN SOLUBILITY IN SILVER

Effect of pressure - Sievert’s Law

\[ N_{Ag} = K p_{O_2}^{1/2} \]

Solubility in molten silver
Solubility in solid silver
Supersaturation?

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solubility (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.3</td>
</tr>
<tr>
<td>900</td>
<td>61.4</td>
</tr>
<tr>
<td>973</td>
<td>3,050</td>
</tr>
<tr>
<td>1024</td>
<td>2,950</td>
</tr>
</tbody>
</table>
## SUMMARY OF SURVEY RESULTS

Responses: 18 GD Silver Refiners from 12 countries – Thanks!

<table>
<thead>
<tr>
<th>Raw material for furnace</th>
<th>Crystals (17); grain (2); scrap (2); bars (1) unrefined bullion (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting furnace type</td>
<td>Induction (13); Gas fired crucible (3); Resistance (1); Reverberatory (1)</td>
</tr>
<tr>
<td>Limiting $O_2$ absorption during melting</td>
<td>Carbon* cover (11); Reducing flame (3); Carbon &amp; Flame (1); Carbon rod “poling” (2); Nitrogen purge (1)</td>
</tr>
<tr>
<td>Analysis of oxygen in molten silver</td>
<td>4 answered “yes” – mostly occasionally finding ~20-40 ppm</td>
</tr>
<tr>
<td>Use of flame polishing for casting</td>
<td>Yes (12); No (6); Graphite block covers on mould (2)</td>
</tr>
<tr>
<td>Need for physical treatment of bars</td>
<td>Yes (13) not all related to needle removal; No (5)</td>
</tr>
<tr>
<td>Physical treatment of cast bars</td>
<td>Hammering (4); Hand Grinding (5); Wire brushing (4); milling (2) Polishing or buffing (2) (incl some combinations)</td>
</tr>
<tr>
<td>Analysis of oxygen in cast bars</td>
<td>5 answered “yes” – but not routinely, finding variously from 20-235 ppm</td>
</tr>
</tbody>
</table>

* Carbon included graphite blocks, activated charcoal, briquettes and lump coal