The Basics of Dezincification

Larry Muller
Director, Metallurgy and Technical Services
Chase Brass and Copper Company, LLC.
Montpelier, OH
Presentation Summary

1. Why understanding dezincification is important
2. Brass basics
3. Dezincification definition and consequences
4. Why and how of dezincification
5. What brasses are vulnerable
6. Control and evaluation
7. Interpreting test results
Why is this topic important?

Corrosion occurs in every material under the proper conditions, but understanding the fundamentals can allow you to make an effective choice for:

1. correct alloy selection for new applications
2. guiding corrective actions to address field failures
3. concerns about the changing corrosiveness of water
4. dealing with changing standards, legislation or codes which disqualify the use of traditional materials
What is brass?

1. It is an alloy of copper and ≥5% zinc (the highest volume brass rod alloy contains ~35% zinc)

2. It can contain optional performance enhancing elements (to improve machinability, corrosion resistance, etc.)

3. It contains residual elements (from the materials melted to make new brass) which can be neutral or harmful to corrosion performance.

4. It is a versatile alloy that can be cast, wrought or forged
What brasses are involved in this web class?

1. Rod alloys for machining and forging
2. 56 – 92% copper
3. 0 – 4% lead
4. Alloys with corrosion resistance additions
5. Thermally treated brass (forged or annealed)
# What domestic brass rod alloys are popular for plumbing fixtures and fittings in the US?

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Copper (%)</th>
<th>Lead (%)</th>
<th>Silicon (%)</th>
<th>Phos. (%)</th>
<th>Zinc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Historical Alloys</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C36000</td>
<td>60 - 63</td>
<td>2.5 – 3.0</td>
<td>-</td>
<td>-</td>
<td>~ 35</td>
</tr>
<tr>
<td>C37700</td>
<td>58 - 61</td>
<td>1.5 – 2.5</td>
<td>-</td>
<td>-</td>
<td>~ 39</td>
</tr>
<tr>
<td><strong>Recent Additions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C27450</td>
<td>60 - 65</td>
<td>0.25 max</td>
<td>-</td>
<td>-</td>
<td>~ 38</td>
</tr>
<tr>
<td>C36300</td>
<td>61 - 63</td>
<td>0.25 – 0.7</td>
<td>-</td>
<td>0.04 – 0.15</td>
<td>~ 38</td>
</tr>
<tr>
<td>C37000</td>
<td>59 - 62</td>
<td>0.8 – 1.5</td>
<td>-</td>
<td>-</td>
<td>~ 38</td>
</tr>
<tr>
<td>C69300</td>
<td>73 - 78</td>
<td>0.09 max</td>
<td>2.7 – 3.4</td>
<td>0.04 – 0.15</td>
<td>~ 21</td>
</tr>
</tbody>
</table>

Ver. 9/22/17
What is dezincification and the problems it can cause?

1. Dezincification is the selective loss of zinc from brass.
2. It’s an electrochemical reaction between zinc and some chemicals found in water.
3. It results in a weak spongy copper layer at the water contact surface.
4. It can progress through the part causing leaks.
5. It can cause blockage of the water path if it forms a “meringue” deposit.
6. The loss of the wall’s cross section can cause mechanical failure by straight-forward fracture or increased vulnerability to stress corrosion cracking.
# What causes dezincification?

<table>
<thead>
<tr>
<th>Water Conditions</th>
<th>Dezincification Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>High O(_2) &amp; CO(_2), stagnant or slow moving water</td>
<td>Layer — Progression is slow &amp; along a broad front. Figures 1 &amp; 2 on pgs. 9 &amp; 10</td>
</tr>
<tr>
<td>Slightly acid water &amp; low salt content</td>
<td></td>
</tr>
<tr>
<td>Soft water, low pH, low mineral content</td>
<td></td>
</tr>
<tr>
<td>Waters high in chloride ions</td>
<td>Plug — Progression is faster and localized. Figures 3 &amp; 4 on pgs. 11 &amp; 12</td>
</tr>
<tr>
<td>Neutral / alkaline waters, high salt, ≥ room temperature</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1 – Layer type dezincification
Figure 2 – Layer type dezincification
Figure 3 – Plug type dezincification
Figure 4 – Plug type dezincification
What isn’t dezincification?

1. Stress corrosion cracking – rapid cracking in susceptible copper alloys caused by the combination of high stress and exposure to chemicals which attack the grain structure. Problem chemicals are ammonia, sulphates, mercury (figure 5, page 14).

2. Erosion – corrosion – loss of material caused by fluid moving rapidly over a part’s surface and can include mechanical wear and abrasion as contributors (figure 6, page 15).
Figure 5 – Stress corrosion cracking
Figure 6 – Erosion - corrosion
Why does dezincification happen?

1. Zinc has weaker atomic bonds than copper
2. Copper is more noble than zinc making it more resistant to corrosion
3. Zinc more readily forms compounds than copper
Are all brasses prone to dezincification?

1. No

2. 15% zinc has been the traditional maximum limit for avoiding dezincification

3. At ≤ 35% zinc, some additives and/or thermal treatments can prevent this corrosion
What are dezincification inhibitors for brass?

1) Minor additions (0.20% max)
   a) Arsenic (As)
   b) Antimony (Sb)
   c) Phosphorus (P)

2) Major additions (0.25 – 2%)
   a) Nickel (Ni)
   b) Tin (Sn)
   c) Aluminum (Al)
How do inhibitors work?

1. Two theories:
   a) They create a surface film which prevents zinc dissolution
   b) They interfere with soluble copper and zinc ion formation
When were inhibitors first tried?

1. Arsenic was added to brass for the boilers in the USS Oregon in 1898

2. R&D for additional inhibitor elements conducted from 1924 to 1941 resulted immediately in commercial use
What limitations are there to using inhibitors?

1. They can’t fully protect brasses with > 35% zinc
   a) Above this level, a second phase of brass with 45% zinc forms as stringers in the alpha brass
   b) The second phase is called beta phase (the alloy is then called duplex brass – figure 7, page 22)
   c) No alloying additives protect beta phase (it is chemically active – figure 8, page 23)

2. Too high a concentration can cause undesirable property changes
   a) Makes the alloy brittle
   b) Can cause other damaging forms of corrosion (see page 32)

3. They will combine with certain residual elements like iron and manganese which makes them ineffective
Figure 7 – Duplex brass structure in wrought brass rod

Extrusion Direction – Longitudinal Grain Orientation
Figure 8 – Preferential dezincification of beta phase in C27450 (38.2%Zn, 0.037%P)
Are there residual elements that promote dezincification?

1. Iron (Fe)
2. Manganese (Mn)
3. Cobalt (Co)
Is there anything else that promotes dezincification?

1. Poor manufacturing controls that stabilize beta phase at lower than normal zinc contents

2. Poor control of residual elements that promote beta phase

3. Poor control of copper and zinc that result in higher than specification zinc contents

4. Water conditions outlined on page 8
Can anything else improve dezincification resistance?

1. Thermal treatments break up the beta phase from stringers into small islands. Examples are:
   a) Forging
   b) High temperature anneal (e.g. ≥ 900F)

Notes:
   a) Thermal treatments are not completely effective in arresting dezincification as shown in Figure 9, page 27
   b) Thermal treatments reduce strength and machinability
Dezincification in Alpha and Duplex Brasses

Figure 8 – Dezincification in single phase brass, no inhibitor added.

Alpha phase brass (35% zinc)

Figure 9 – Dezincification in annealed duplex brass shows both phases are effected.

Duplex brass (41% zinc) inhibited with phosphorus and annealed
**How do you test for dezincification resistance?**

The most widely used test is ISO 6509 because it is a short term test that is simple to run but has correlated with long-term performance in the field (see footnote 1). As you can see, it is the basis for the other tests in the table.

<table>
<thead>
<tr>
<th></th>
<th>ISO 6509 (2&amp;3)</th>
<th>AS2345</th>
<th>UL199</th>
<th>EN12164</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Application</strong></td>
<td>General</td>
<td>General</td>
<td>Sprinklers</td>
<td>Rod</td>
</tr>
<tr>
<td><strong>Test Solution</strong></td>
<td>1% CuCl₂</td>
<td>1% CuCl₂</td>
<td>1% CuCl₂</td>
<td>1% CuCl₂</td>
</tr>
<tr>
<td><strong>Test Temperature</strong></td>
<td>75°C</td>
<td>75°C</td>
<td>75°C</td>
<td>75°C</td>
</tr>
<tr>
<td><strong>Test Length</strong></td>
<td>24 Hr.</td>
<td>24 Hr.</td>
<td>144 Hr.</td>
<td>24 Hr.</td>
</tr>
<tr>
<td><strong>Max. Dezinc. Depth</strong></td>
<td>See note 3</td>
<td>-</td>
<td>200µ</td>
<td>200µ</td>
</tr>
<tr>
<td><strong>Avg. Dezinc. Depth</strong></td>
<td>L:300µ; T:100µ</td>
<td>-</td>
<td>100µ</td>
<td>-</td>
</tr>
</tbody>
</table>

(1) Initially developed to correlate with Swedish, Australian and South African field tests. Established in 1981

(2) Example of user defined pass/fail criteria: NSF 14 limit is 200µ plus passing the ASTM B858 ammonia SCC test.

(3) ISO6509-2 was approved on 3/6/2017 for the following limits:
   a) forgings & castings avg. 100µ, max. 200µ;
   b) extruded rod longitudinal avg. 300µ, max 400µ and transverse avg. 100µ and max 200µ
Can you show how inhibitors / thermal treatments effect ISO 6509 results? Part 1

ISO 6509 Dezincification Depth (Maximum)

Dezincification testing performed by Corrosion Testing Laboratories, Newark DE

Ver. 9/22/17
Can you show how inhibitors / thermal treatments effect ISO 6509 results? Part 2

See explanation of graph on page 31
What can I learn from this graph?

1. **Analytical**: The 15% zinc limit to avoid dezincification is not universal. The use of inhibitors and thermal treatments can protect brasses with up to 35% zinc.

2. **Cautionary**: The ISO 6509 test is an accelerated test designed to provide comparative information in 24 hours. Do not expect that an alloy will show as much dezincification in actual use in just 24 hours. It may take 30+ years depending on the alloy, manufacturing controls and chemical environment.

3. **Explanatory**: Why are there relatively few data points to the left of the 35% zinc line? Although many brasses with low zinc contents may be good for dezincification resistance, they aren’t as easy to produce on a large scale as those with at least 35% zinc. At 35% zinc, brass heated to over 1100F starts to form beta phase which is much easier to hot work than single phase alloys. Proper manufacturing controls eliminate or minimize beta phase as the alloy cools to room temperature.
Can you show how inhibitors can have a negative effect on corrosion performance?

Dezincification and Stress Corrosion Cracking Results
(Bar Height = Dezincification Depth, Cracked Note = SCC Failure)

Test Conditions:
1) Munich tap water with ammonia addition
2) Notched sample stressed to 95% of YS
3) Electrode potential of +0.4V
4) 200 hr test

Source: Reference 6

See explanation of graph on page 34
In the same test, how do some of the newer low-lead and lead-free alloys being used in the US compare to C36000?

Dezincification and Stress Corrosion Cracking Results
(Bar Height = Dezincification Depth, No Cracking Occurred)

Test Conditions:
1) Las Vegas water chemistry with ammonia addition
2) Notched sample stressed to 95% of YS
3) Electrode potential of +0.4V,
4) 200 hr test

Source: Reference 7

See explanation of graph on page 34

Ver. 9/22/17
What do these graphs mean?

1. These alloys were involved in the graphs on page 32 & 33 (remainder is zinc):

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Page</th>
<th>Copper (%)</th>
<th>Lead (%)</th>
<th>Bismuth (%)</th>
<th>Arsenic (%)</th>
<th>Silicon (%)</th>
<th>Phosphorus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C38500*</td>
<td>32</td>
<td>57 - 59</td>
<td>2.5-3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C37700*</td>
<td>32</td>
<td>57 - 59</td>
<td>1.6-2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muntz Metal*</td>
<td>32</td>
<td>63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C35330</td>
<td>32</td>
<td>61-63</td>
<td>1.7-2.8</td>
<td></td>
<td></td>
<td>0.02-0.15</td>
<td></td>
</tr>
<tr>
<td>CW724R</td>
<td>32</td>
<td>75-77</td>
<td>0.1 max</td>
<td></td>
<td>2.7-3.5</td>
<td>0.02-0.10</td>
<td></td>
</tr>
<tr>
<td>C49260*</td>
<td>33</td>
<td>58-63</td>
<td>0.09 max</td>
<td>0.5-1.8</td>
<td></td>
<td></td>
<td>0.05-0.15</td>
</tr>
<tr>
<td>C27450*</td>
<td>33</td>
<td>60-65</td>
<td>0.25 max</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C27451*</td>
<td>33</td>
<td>61-65</td>
<td>0.25 max</td>
<td></td>
<td></td>
<td></td>
<td>0.05-0.20</td>
</tr>
<tr>
<td>C36000*</td>
<td>33</td>
<td>60-63</td>
<td>2.5-3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C69300</td>
<td>33</td>
<td>73-77</td>
<td>0.09 max</td>
<td></td>
<td>2.7-3.4</td>
<td></td>
<td>0.04-0.15</td>
</tr>
</tbody>
</table>

2. The samples were subjected to water with different ammonia levels while they were under stress and +0.4 volts.
3. Dezinification was higher in alloys without an inhibitor or contained beta phase (alloys with asterisks) than alloys with an inhibitor and no beta phase
4. Only the sample with arsenic suffered stress corrosion cracking
How do the alloys on page 6 perform in the ISO 6509 test?

See explanation of graph on page 36

Ver. 9/22/17
What does this graph mean?

1. This high-average-low graph presents results for multiple tests of each alloy.

2. The values used in the analysis were the maximum dezincification depths reported by an independent laboratory.

3. Example: of all the tests performed on C36000, the average of the maximum dezincification depths was 450 microns. The highest and lowest maximums were 640 and 270 microns respectively.
Technical Summary

1. Defined dezincification
   a. Mechanism and types (layer, plug)

2. Described what brasses are prone to dezincification
   a. > 15% Zn although brasses with up to 35% can be made resistant
   b. Alloys containing beta phase

3. Discussed the most popular method of how to test for dezincification performance
   a. The ISO 6509 test is the most popular and useful

4. Discussed how to improve dezincification resistance
   a. inhibitors, thermal treatments, proper manufacturing controls

5. Provided test results on:
   a. Dezincification depth vs alloy, inhibitor & treatment
   b. Dezincification and stress corrosion resistance performance
   c. Dezincification resistance of seven currently popular alloys
General Summary

1. Every material corrodes under the right conditions

2. Dezincification performance is a function of alloy chemistry, manufacturing controls, protective treatments and the operating environment.

3. Information is available to provide you with the tools for making knowledgeable choices or to ask the right questions
References

2. “A Note on the Dezincification of Brass and Inhibiting Effect of Elemental Additions”, D. Davies, CDA, July 1993
5. Dr. Peter Dierschke, Research work performed by Seppelfricke Armatutren GmbH, Germany, July 2006
7. Exova Report G301009