Microstructure-corrosion interrelations in new low-lead and lead-free brass alloys

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Abstract

In new low-lead and lead-free brass alloys, it is not understood how the corrosion properties, such as dezincification, are related to material composition as well as annealing temperature and duration. This study aims to fill this knowledge gap by mapping sixteen annealing conditions and three different brass alloy compositions to their respective microstructure and dezincification performance. It was found that high dezincification depth was a result of annealing temperatures at 300°C – 400°C, which promoted precipitation of intermetallic AlAs-particles along grain boundaries, twins and lead particles as well as precipitation of β-phase along grain boundaries. Their presence was correlated to high micro additions of aluminium or iron in the material composition. An additional compositional factor contributing to precipitation of high amount of β-phase was low copper/zinc-ratio.
Svensk sammanfattning

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1 Introduction

Brass is a copper alloy with zinc as the most dominant alloying element [1]. To further enhance properties such as machinability, durability and resistance to certain types of corrosion attacks, it is common to add other alloying elements to the brass. One such alloying element is the highly poisonous metal lead (Pb), which significantly increases the machineability of the brass [2]. However, because many brass products involve contact with water, lead consequently will be depleted from the brass and enter the water system due to corrosion, thus putting human health in risk. Because of this, there is an interest from the Swedish government to promote the Swedish brass manufacturing industry to develop new lead free brass alloys, e.g. alloys with less than 0.2% lead, for plumbing and fittings applications [3]. The long term goal is to completely phase out the lead containing brass products from water systems. In addition, the 4 Member State (4MS) joint committee of the European Association for the Taps and Valves Industry, is further restricting the amount of Pb and Ni allowed in brass alloys in contact with drinking water, thus promoting the development of new lead-free brass alloys. [4]

However there is currently a lack of basic knowledge regarding the corrosion properties of brass and how these properties are influenced by processing parameters and alloy composition. In order to complete the long term goal to phase out lead free brass alloys from the infrastructure, this basic knowledge must be increased. This master thesis aims to contribute to this effort by investigating how the corrosion properties of three different brass alloys are affected by different heat treatment durations and temperatures. The goal is to map the corrosion properties to the resulting microstructure, which will contribute to the understanding of how different alloying elements are prone to interact with each other and the degree of impact that various detrimental phases have on the corrosion of brass.

1.1 Brass alloy design

As stated previously, brass’ main alloying element is zinc (Zn), and in its simplest form, brass is a binary Cu-Zn alloy with 4-43.5% Zn [5]. Its phase diagram is displayed in Figure 1 using Thermo-Calc with a custom database for brass alloys, developed by Swerea KIMAB [6].

At Zn-contents below 37% [1], Zn dissolves into the copper to form a phase with FCC-structure, and uniform composition. This phase called the α-phase displays good ductility at
room temperature and is thus desirable for cold working treatment. Brasses with such low zinc content are called “α brasses” or “cold working brasses” for this reason. However while these brasses are durable, ductile and more resistant to corrosion compared to brass alloys with higher zinc content and less α-phase, they have poor machinability and workability at high temperatures [1], and are thus more limited in their field of application from a design point of view. Furthermore, the high copper content will result in increased price. For these reasons are α-brasses more suited for cartridges for fire arms for instance, and have less prevalence for plumbing and fitting applications for water systems. For those applications, brasses with higher Zn-content have larger precedence.

![A binary Cu-Zn phase diagram, plotted using Thermo-Calc with a custom database for brass alloys, developed by Swerea KIMAB [6].](image)

For brasses with Zn-contents within 38–42%, a BCC-structured β-phase is prone to precipitate as indicated by the phase diagram in Figure 1. The β-phase will nucleate in the grain boundaries of the α-grains and precipitate. It will exist alongside the α-phase in the finished product, making it a “duplex brass”, also known as “α-β brasses” or “hot working brasses”. 
For brasses with higher Zn-content than 42%, a brittle γ-phase is prone to precipitate, as the phase diagram in Figure 1 predicts.

Duplex brass alloys are more commonly used in the plumbing and fittings applications for water systems [1]. At room temperature, the β-phase is harder and less formable than the α-phase at room temperature. At higher temperatures however, e.g. 750°C, the β-phase becomes more formable as the zinc content is increased inside the β-phase, thus making the duplex brass more formable and workable at higher temperatures, as illustrated in Figure 2, hence the name “hot working brasses”.

However, the β-phase is also less resistant to corrosive attacks compared to the α-phase, a subject discussed in section 1.2. For this reason, it is common to heat treat duplex brass products in this application in order to reduce the amount of β-phase in the microstructure, with careful control of the annealing temperature and cooling rate. However, it is important to note that complete riddance of β-phase in the microstructure is difficult to obtain because the zinc concentration is higher in the grain boundaries than the bulk of the grains due to microsegregation of Zn during solidification.

Figure 2: Visualization of how zinc content influences the deformation properties of the β-phase at 750°C [1].
In the industry, additional alloy elements are used to enhance the properties of the brass material. These include lead (Pb), aluminum (Al), iron (Fe), manganese (Mn), arsenic (As), phosphorous (P), silicon (Si), tin (Sn), antimony (Sb) and nickel (Ni).

**Lead** (up to 3 %): Unlike other alloying elements, lead does not dissolve when it is added in the liquid brass. As a result, it perseveres as undissolved spherical particles, and as the rest of the melt solidifies, the lead particles stay in the melt until the brass has completely solidified. Pb-particles will thus appear in the grain boundaries, the location of the lastly solidified melt, as undissolved particles. These comparably soft Pb-particles provide significantly increased machineability to duplex brasses, whilst not affecting the corrosion properties, bulk hardness or tensile strength of the material. In addition, if the lead particles melt, lead can penetrate the grain boundaries and grant a lubricating effect on the material that further increases machinability. However, as mentioned previously, lead will be depleted from the material into the environment due to corrosion, a subject that will be further described in section 1.2. [1]

**Aluminium** (0 – 1.7%): Aluminum is a β-phase stabilizing element in brass, and affects the mechanical properties of the brass by increasing hardness and castability. [7] The hardening mechanism is a combination of increased grain refinement of α-phase and increased stability of β-phase, which is harder than the α-phase at room temperature. How Al-additions affect the corrosion properties of the brass, more specifically the dezincification resistance, is not cemented; some sources [1] claim that Al inhibits dezincification, while others [8] conclude that it either offers no dezincification resistance at all or merely retards the dezincification.

**Iron** (≤ 0.3%), **Manganese** (≤ 0.1%) and **Nickel** (0 – 0.3%): These elements are used in duplex brasses to improve the compression strength and hardness [1]. For castings, Fe is used for grain refinement. However, investigations [8] have concluded that duplex brasses with 0.5% Fe or 0.5% Mn accelerate the dezincification rate. Another important aspect to mention is that Fe, Mn and Ni can form stochimetric phases with other elements in in the brass, which will affect the properties of the brass further. This subject will be further described in section 1.2.
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**Arsenic** (0 – 0.2%), **Phosphor** and **Antimony** (0 – 0.01%): Brass is doped with As to improve the corrosion resistance of the brass. It namely improves the dezincification resistance in the α-phase by dissolving into it [1]. The mechanism is further described in section 1.2. It is believed that Sb and P have a similar purpose in the brass composition [8]. However As, Sb and P form stoichiometric intermetallic phases with other elements, such as Fe or Mn, which can remove their inhibiting dezincification function upon heat treatment and annealing. This will also be further described in section 1.2.

**Silicon** (0 – 0.03%): Brass alloys that contain Si are more wear resistant, harder and display finer grains of α-phase [9] compared to unalloyed CuZn40-brass. It is an alloying element that also stabilizes the formation of β-phase, similar to Al, as well as slight stabilization of γ-phase. Similar to As, P and Sb, Si can form hard intermetallic phases with tramp elements such as Fe [1]. For dezincification resistant alloys, this is favourable since it can prevent the formation of intermetallic phases such as FeAs, which can deplete the corrosion resistance provided by As.

**Tin** (0 – 0.3%): Similar to Si, Sn increases hardness and stabilizes β- and γ-phase. Sn is also believed to increase the corrosion resistance of the brass [1]

### 1.2 Corrosion of brass

Corrosion is the concept of the material degenerating due to interactions with the environment. Because of its copper content, brass is considered to be a metal with good corrosion resistance compared to conventional carbon steel or cast iron [1]. Pure copper is a noble metal, i.e. corrodes slowly in neutral salt water.

However, due to the presence of the far less noble metal, Zn, brass is often subject to the corrosion mechanism called dezincification, dealloying of Zn or selective removal of Zn [10]. This mechanism describes the process of removal of Zn from brass material as a result of prolonged exposure to aerated water with high CO$_2$ and/or chlorides, preferably in a slow-moving stagnant solution. The loss of Zn leaves a porous Cu-matrix with poor mechanical properties that can easily be subject to cracks and failure. There are two predominant theories that describe this mechanism: one suggests that Zn is selectively dissolved from the brass leaving a porous Cu-residue, while the second theory suggests that Zn and Cu are both
dissolved followed by reprecipitation of pure Cu on the material surface, for being the more noble element [11]. There are however indications [10] that both mechanisms can occur in separate, yet overlapping electron potential intervals, as illustrated in Figure 3. An important note in this regard is that the reprecipitation of copper is a result of accumulated Cu-ions redepositing on the surface, and thus is the amount of reprecipitated copper is dependent on properties of the solution, such as concentration of chlorides and copper, the electrode potential or if the solution is stirred.

Figure 3: Illustration of the potential regions that yields either separate or simultaneous dissolution of Zn and Cu, as well as whether it results in dezincification/reprecipitation of copper in chloride solutions. [10]
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Dezincification can either happen in the bulk of the material uniformly or as a localized attack that only affect the grain boundaries due to the increased diffusion of elements there, yielding accelerated corrosion of those areas [1]. The latter is referred to as intergranular attack (IGA) by other studies. Both mechanisms contribute to Pb leaching to the drinking water.

One established method used to protect brass against dealloying of Zn is to dope the brass with As, P or Sn, where As is the most effective. The said alloying element will dissolve into the lattice of the α-phase, and inhibit the dezincification of that phase. Exactly how this inhibits dezincification is not conclusive [8] [11] [12] [13]. One theory suggests that As traps the vacancy pairs formed in the lattice by the presence of Cl- in the medium, which the Zn-atoms otherwise use to diffuse through the material [12]. Another suggests that the dezincification inhibitor, As for instance, forms As-rich As-Cu-Zn passive layer barrier that either prevents dissolution of Cu and Zn or prevents reprecipitation of Cu on the surface [11] [13].

However, the current dezincification inhibitors merely enhance the dezincification resistance in the α-phase [1]. This makes brasses with a higher amount of α-phase desirable for dezincification resistant applications, such as plumbing or fittings for water drinking. Indeed, the amount of β-phase should be minimized for these alloys by careful choice of composition and controlled heat treatment, as further described in section 1.2.1. If both phases exist, the β-phase should preferably be present as isolated fragments as opposed to a continuous network to decrease failure propagation rate.

1.2.1 Heat treatment and depletion of inhibitor properties

For brasses designed for high dezincification resistance it is desired to obtain 100% α-phase due to its higher resistance to dezincification, which is a result of its ability to dissolve agents that retard dezincification (As, P and Sn) into its lattice structure. [1] Thus are these brasses annealed at 500°C – 600°C, a choice motivated by the phase diagram in Figure 1 in order to promote maximum growth of α-phase and minimization of β-phase precipitation. This annealing process is referred to as β-annealing.

However, in the temperature range generally between 300°C – 400°C, i.e. just below the β-annealing temperature, tramp elements in the brass such as Fe, Mn or Ni are prone to interact with the dezincification inhibitors such as As, P and Sn, and form stoichiometric intermetallic phases such as FeAs or Fe2P [14]. This affects the performance of the dezincification resistance since the removal of dezincification inhibitors from the solid solution in the α-
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Phase depletes the corrosion resistance in the α-phase [1]. Slow cooling after the β-annealing increases thus the risk of intermetallic phases forming, resulting in higher susceptibility of dezincification of the α-phase.

This phenomenon is promoted by increased diffusion of elements [1]. Since diffusion of elements can occur faster in the grain boundaries due to the structure being more disordered there in contrast to the bulk of the grains, the precipitation of intermetallic phases is more prominent in the grain boundaries. As a result, the grain boundaries and the local zones around them are especially sensitive to depletion of dezincification resistance in α-phase, which yields a loss of strength that is able to yield intergranular fracture. The phenomenon is for this reason considered as intergranular attack (IGA).

In addition, if the material is quenched after obtaining 100% α-phase during β-annealing, no intermetallic phases have time precipitates [1]. However, the fast cooling can result in residual stresses in the material, which can cause stress corrosion cracking (SCC). To eliminate the residual stresses, the material can be annealed to relax the material. However, the temperature of this stress relieving heat treatment overlaps to some extent with the range in which intermetallic phases are prone to form: 300°C – 400°C. Stress relieving heat treatment can thus unintentionally sensitize the brass to IGA.
2 Materials

Prior to this study, three specimens of duplex brass alloys had been extruded and drawn to bar at Nordic Brass Gusum AB. One alloy was a dezincification resistant Pb-free (Pb-content less than 0.3 wt%) brass alloy: CW511L, which had a diameter length of 75.7mm. The other two were more conventional Pb-containing brass alloys: CW625N and CW626N, with diameter length of 61.7mm and 71.2mm respectively. The difference in these two alloys is that CW626N is composed of slightly more Al. The chemical composition of each alloy was analyzed by Degerfors lab, given in Table 1.

CW511, commercially referred to as Aquanordic, contains the lowest amount of alloy elements beyond copper and zinc. The Zn-amount is the highest of the three alloys, which for CW511 results in the lowest relative amount of Cu. The resulting Cu/Zn-ratio is equal to ~1.78. Furthermore, it has been doped with <0.1 wt% arsenic in order to enhance resistance to dezincification, as described in section 1.1. The remaining elements are unintentional additions as a result of the processing of the bar.

CW625 and CW626 are similar in composition. Both of them contain 1.2-1.3% lead and have been micro alloyed with 0.01% – 0.1% arsenic and iron as well as containing 0.6–0.7% aluminium, as displayed in Table 1. The main difference between them is the Cu/Zn-ratio; for CW625 it is ~1.83 and for CW626 it is ~1.95.
### Materials

Table 1: Chemical composition, given by Degerfors Laboratorium AB in weight percent.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu (wt%)</th>
<th>Zn (wt%)</th>
<th>Al (wt%)</th>
<th>As (wt%)</th>
<th>Fe (wt%)</th>
<th>Mn (wt%)</th>
<th>Cr (wt%)</th>
<th>Ni (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW511L</td>
<td>63.8%</td>
<td>35.9%</td>
<td>&lt; 0.05%</td>
<td>&lt; 0.1%</td>
<td>0.05%</td>
<td>&lt; 0.01%</td>
<td>&lt; 0.02%</td>
<td>0.02%</td>
</tr>
<tr>
<td></td>
<td>Mg &lt; 0.05%</td>
<td>Bi &lt; 0.01%</td>
<td>P &lt; 0.01%</td>
<td>Pb 0.20%</td>
<td>Sb &lt; 0.01%</td>
<td>Si &lt; 0.04%</td>
<td>Sn 0.04%</td>
<td></td>
</tr>
<tr>
<td>CW625N</td>
<td>63.7%</td>
<td>34.8%</td>
<td>0.6%</td>
<td>&lt; 0.1%</td>
<td>0.11%</td>
<td>&lt; 0.01%</td>
<td>&lt; 0.02%</td>
<td>≤ 0.2%</td>
</tr>
<tr>
<td></td>
<td>Mg &lt; 0.05%</td>
<td>Bi &lt; 0.01%</td>
<td>P &lt; 0.01%</td>
<td>Pb 1.3%</td>
<td>Sb &lt; 0.01%</td>
<td>Si &lt; 0.04%</td>
<td>Sn 0.06%</td>
<td></td>
</tr>
<tr>
<td>CW626N</td>
<td>64.6%</td>
<td>33.2%</td>
<td>0.70%</td>
<td>0.03%</td>
<td>0.11%</td>
<td>0.008%</td>
<td>&lt; 0.005%</td>
<td>0.05%</td>
</tr>
<tr>
<td></td>
<td>Mg 0.001%</td>
<td>Bi 0.01%</td>
<td>P &lt; 0.01%</td>
<td>Pb 1.23%</td>
<td>Sb &lt; 0.005%</td>
<td>Si 0.02%</td>
<td>Sn 0.05%</td>
<td></td>
</tr>
</tbody>
</table>
3 Experimental details

In order to map the corrosion properties to the microstructure of the brass, samples of the three brass alloys were heat treated to result in different microstructures using the different heat treatment parameters: temperature and heat treatment duration. Each sample underwent two types of heat treatments followed by testing of the corrosion properties. Between each step, the microstructure was analyzed in an attempt to understand what aspect of the process affected the material properties. The entire process is illustrated in Figure 4.

Figure 4: An illustrative overview of all the experimental steps in this study.
3.1 Heat treatment

Each sample underwent two types of heat treatments; the β-annealing followed by the post β-annealing. The following section describes the methodology used for each heat treatment.

3.1.1 Pre-heating, β-annealing

Each alloy bar was cut into 16 smaller bars of equal height, one for each planed post-β-annealing heat treatment, which will be described in section 3.1.2.

In order to minimize the amount of β-phase, and simultaneously ensure that all samples were in the same thermodynamic starting state, all samples were β-annealed, e.g. heat treated at 550±2°C for 2h. The temperature of the material and the furnace ambience was measured using two thermocouples connected to a multimeter. In order to acquire a representative temperature of the samples during each heat treatment, a 15mm deep hole with a diameter of 2.5mm was drilled prior to the heat treatment in centre of the one sample in the extrusion direction, in which one of the thermocouples would be placed during the heat treatment. To minimize the risk of all samples not reaching the desired temperature, the sample which would require the longest time to reach the desired temperature was chosen. Because the bars from CW511 exhibited the largest diameter, it was assumed that those samples would require the longest time to reach the desired temperature. Thus, a CW511-sample selected as the sample from which the temperature inside the brass was measured.

While the first thermocouple was placed inside the hole drilled in CW511 to measure the internal temperature of the material, the second thermocouple was freely exposed to the air of the furnace to measure the ambient temperature of the furnace for increased process control. The 2 hours annealing time was set to start after CW511 reached 550±2°C. After the 2 hours, all samples were cooled in room temperature.

3.1.2 Heat treatment, post-β-annealing

The idea of the heat treatment post-β-annealing was that after this heat treatment, all three alloys have four sets that each consists of four samples (16 samples in total per alloy). Each set represented a temperature, while the four samples within the set represented different exposure durations for each temperature. The four sets of temperatures were chosen as: 250°C, 300°C, 350°C and 400°C. The four exposure durations within each set were selected as 2h, 10h, 100h and 1000h. A visual summary is displayed in Table 2. Inside a Carbolite VCF 12/5 Furnace the samples exposed to 250°C – 300°C were heat treated, while the 350°C
– 400°C were heat treated in a Naber Industrieofenbau D-2804. The thermocouples were utilized in the same way as described in section 3.1.1. The measured values of the thermocouples were logged over time using the software EasyView version 5.5.1.5. After the heat treatment duration was over, the samples were placed in room temperature to cool to 25°C. This cooling of the material was also registered in using the thermocouple to increase the process control.

Table 2: A summary displaying how the samples were categorized after the heat treatment post-β-annealing.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>CW511</th>
<th>CW625</th>
<th>CW626</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Set with respect to exposure temperature</strong></td>
<td>250°C</td>
<td>300°C</td>
<td>350°C</td>
</tr>
<tr>
<td>Samples within each set with respect to exposure duration</td>
<td>2h</td>
<td>2h</td>
<td>2h</td>
</tr>
<tr>
<td></td>
<td>10h</td>
<td>10h</td>
<td>10h</td>
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<td></td>
<td>100h</td>
<td>100h</td>
<td>100h</td>
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<tr>
<td></td>
<td>1000h</td>
<td>1000h</td>
<td>1000h</td>
</tr>
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### 3.2 Corrosion testing

The corrosion properties of the brass samples that were heat treated after β-annealing were tested with respect to dezincification and intergranular attack respectively. The following section describes the sample preparation of each corrosion test.

#### 3.2.1 Dezincification

The sample preparation and solution for accelerated of dezincification testing was followed using standardized testing method SS-EN ISO 6509-1:2014 “Determination of dezincification resistance of copper alloys with zinc” [15]. The samples were cut into 10mm x 10mm x 10mm cubes, which were mounted in the phenolic resin compound Phenocure black Bakelite using Buehler SimpliMet™ 4000 Mounting system and Buehler SimpliMet™ XPS1 Mounting system, with the extrusion direction of the sample facing outwards. The bottom of the disc-shaped phenolic resin was then cut so that the sample can stand during the dezincification test.
The distance from bottom of the brass sample to the bottom of the phenolic resin was minimum 15mm. A visual representation of the process is displayed in Figure 5 and Figure 6. The exposed surface of each sample was then ground using wet silicon carbide abrasive paper in the following order: 180p, 320p and 600p. The grinding was performed using a Stuers Abramin automatic grinding machine with the paper disc rotation speed at 300 rpm and 100N pressing power. The sample surface was ground for 60 seconds with 150N pressing power for the first and most coarse abrasive paper, and 90 seconds each with 100N pressing power for 320p and 600p paper.

Figure 5: Illustration of how the samples for accelerated dezincification testing were cut from extruded brass bars. The extrusion direction of the bar is marked with an X.

Figure 6: Illustration of how the cut samples were mounted in phenolic resin and how the bottom of the cylinder was cut in order to create a stable foundation of the sample to stand on. The extrusion direction of the brass is marked with an X.

Following ISO 6509-1:2014 [15], the solution of the dezincification was produced by dissolving 12.7g copper (II)chloride dihydrate (CuCl$_2$ $\times$ 2 H$_2$O) per 1 L deionized water. The
result is a 1% CuCl₂ solution. The total amount of solution of each corrosion test is calculated with respect to the amount of exposed brass surface area using the ml solution/surface area ratio recommended by the ISO 6509-1:2014: 250 ml/mm². The samples were exposed to the CuCl₂-solution for 24h ± 30min at 75°C. The solution containing the samples were concealed using lid consisting of a plastic bag sealed with rubber bands. The setup is illustrated in Figure 7. After the test, the samples are rinsed and dried using ethanol and forced hot air convection. How the dezincification depth was measured in the light optical microscope (LOM) is described in section 3.3.2.

**Figure 7:** An illustration of the test apparatus used to perform the accelerated dezincification, as recommended by ISO 6509-1:2014 [15]

<table>
<thead>
<tr>
<th>Key</th>
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<tbody>
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<td>5</td>
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</tbody>
</table>
3.2.2 IGA

The testing of IGA-depth follows the method conducted and described by F. Mazza and S. Torchio [14] in their study “Factors influencing the susceptibility to intergranular attack, stress corrosion cracking and de-alloying attack of aluminium”. The samples were cut into cuboids as illustrated in Figure 8, with geometries 10mm x 10mm x 20mm (± 1mm), the exception being CW625 which was limited by its smaller bar diameter, and therefore had the following dimensions: 10mm x 10mm x 15mm (± 1mm). A hole with 2.5mm diameter was drilled through the top of the sample in the extrusion direction in order to fit a string from which the samples could hang in the corrosive solution. All sides of the samples were mechanically grinded with 320p followed by a 600p surface finish.

The polish was done chemically by emerging the samples in 100ml phosphoric –nitric–propionic (2:1:2 vol) acid solution in 5 seconds followed by rinsing in distilled water and greasing in 400ml ethanol-ethylc ether (1:1 vol) for 5 seconds and dried using forced air convection. The acid solution was produced by mixing 40ml 99.5%-Propionic acid followed by 20ml 68%-nitric acid and finally 85%-phosphoric acid, followed by carefully stirring.

After the polish was complete and the samples were dried, each sample received a layer of protective coating on each side of sample, as illustrated in Figure 8, in order to retain a reference area unaffected by the corrosive attack as comparison to the rest of the sample.

Figure 8: Illustration of how the samples for accelerated IGA-testing were cut and processed before testing.

The solution of accelerated intergranular attack (IGA) was a “chloride-citrate” solution [14] consisting of Trisodiumsulphate-Sodiumchloride-Copper(I)chloride with a pH 4.0. The
The chemical composition of the acid and the chloride-citrate solution is displayed in Table 3. The mixing of this solution was done as instructed in the study by Mazza and Torchio, and conducted in batches that would contain 2000ml of the IGA-solution. The mixing procedure was performed as following: Trisodiumsulphate and sodium chloride were dissolved in 500-700ml distilled water. The pH of this solution was carefully adjusted from 7.89 to 4.30±0.01 using 50–10ml additions of acid to successively reach the desired pH value. The CuCl was then added into the solution followed by further careful pH adjustment to pH 4.0±0.02, using the same procedure as previous pH-adjustment. Then the remaining water amount was added, and using a stirring magnet, the solution was stirred for 16 hours in order to homogenize the pH-value of the solution.

The samples were individually immersed in cups containing 200ml each of chloride-citrate solution. It should be noted that not all the cups were of same size, but were able to contain 200ml. After the 100 hours, the samples were rinsed in distilled water and dried using ethanol and forced air convection. The pH-value of the chloride-citrate solution in each cup was then measured and the volume of solution left in each cup was noted.

Table 3: The chemical composition of the chloride-citrate solution in two 2000ml flasks.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Amount of measured compound [g/2000ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flask 1</td>
</tr>
<tr>
<td>Trisodium sulphate</td>
<td>147.05</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>116.88</td>
</tr>
<tr>
<td>CuCl(I)</td>
<td>2.6 – 2.7</td>
</tr>
</tbody>
</table>

3.3 Microstructure analysis and sample preparation method

3.3.1 β-phase analysis using LOM

The heat treated samples were cut so that the surface displays the extrusion direction. The surface of each sample was then grinded using wet silicon carbide abrasive paper in the following order: 180p, 320p, 600p, 1200p, 2500p and 4000p. The samples were grinded for 90 seconds for the most coarse abrasive paper and 60 seconds for the remaining papers. The
grinding was performed using a *Stuers Abramin* automatic grinding machine, using 100N pressing power with 300 rpm paper disc rotation rate.

The grinded surface was polished using diamond polishing in the following size and order: 3µm, 1µm and 0.25µm. A paste containing the diamonds was applied to three different polishing cloths, one per diamond size. The 3µm diamond paste was applied to a *Struers MD DAC™* polishing cloth, while 1µm diamond paste and 0.25µm diamond paste were applied to *Struers MD Nap™* polishing cloths respectively. The polishing was performed in a *Stuers Abramin metal polisher*, using 100N pressing power and 300 rpm polishing cloth disc rotation speed. The polishing duration was 30 seconds for 3µm, 60 seconds for 1µm and 90 seconds for 0.25µm. The samples were then degreased, followed by washing under distilled water. Finally the samples were dried using ethanol and forced hot air convection.

A Klemm I etching solution was produced by dissolving 25g sodium thiosulfate in 100ml distilled water assisted by stirring. One the salt was completely dissolved 5g of potassium metabisulfite was added and dissolved into the solution, assisted by stirring.

The samples were then etched in this solution in 15 seconds to make the β-phase visible without etching the grain boundaries in the microstructure. In the light optical microscope (LOM), the brightness and contrast is adjusted so that the β-phase appears as yellow while the α-phase appears as white. Five pictures of random locations in each sample were then captured from the LOM using the software *Kappa ImageBase* version 2.8.4.14051. Using the software *ImageJ*, the quota of yellow pixels occupying the image could be calculated, and the average amount could be calculated with the five images. With this method, the amount of precipitated β-phase could be calculated for each sample.

### 3.3.2 Average dezincification depth

After the dezincification exposure was complete, the samples were rinsed in distilled water and dried using ethanol and forced air convection. The samples were then cut along the extrusion direction so that the depth of the dezincification was exposed as demonstrated in Figure 9. The resulting piece was then mounted in Transoptic resin.
Figure 9: Illustration of how the mounted samples were cut after the corrosion test in order to study the dezincification depth.

The exposed surface was grinded and polished as described in section 3.3.1; mechanical grinding (180p, 320p, 600p, 1200p, 2500p and 4000p) and diamond polishing (3μm, 1μm and 0.25μm).

The depth of dezincification could then be estimated using LOM, according to the ISO 6509-1:2014 [15]. The method aims to measure the size of localized dezincification and layer dezincification as illustrated in Figure 10. [15] Thus, two types of measurements were employed to encompass both types of attacks. To this end was the maximum dezincification depth and average dezincification depth was recorded for each sample. The maximum dezincification was recorded by measuring the distance from the top metal surface to the finishing point. The average dezincification was measured by dividing the sum of recorded dezincification depths of each contiguous field of the microscope, with the number of contiguous fields. The dezincification depth in each contiguous field was recorded by measuring the distance between the top of the metal surface and the intersection point of a vertical line in the middle of the field and a line drawn connecting the extremity on each side of the vertical line as exemplified in Figure 11. If a dezincification front was not detected on both sides the depth of the dezincification in that field was recorded as zero.
Microstructure-corrosion interrelations in new low-lead and lead-free brass alloys
Experimental details

3.3.3 Average depth of intergranular attack

In order to study the microstructure of the corroded samples, they were cut in the extrusion direction to study the IGA-depth. The samples were mounted in the phenolic resin “Phenocure black Bakelite” with the cut surface facing outwards, as illustrated in Figure 12. The surface was then grinded and polished as described in section 3.3.1.

Figure 10: The dezincification attack propagates from left to right. The illustration highlights the different types of dezincification and importance of measuring both maximumdezincification and the size of the layer dezincification.

Figure 11: Example of how dezincification depth is measured in a contiguous field as ISO 6509-1:2014 instructs. The encircled areas represent identified extremities on each side of the imaginary vertical line in the middle of the sample.
Figure 12: Illustration of how the IGA-tested-samples were cut in order to study the depth of the intergranular attack in the extrusion direction, followed by mounting the samples in phenolic resin with the cut surface facing outwards.

The IGA-depth was estimated by comparing the depth of the attack to the level of the applied coating on all four visible sides in LOM, resulting in four different depths: \(d_{1}^{IGA}, d_{2}^{IGA}, d_{3}^{IGA}\) and \(d_{4}^{IGA}\) as illustrated in Figure 13. It is important to note that the exposed part of the material right next to the protective coating usually was more corroded than the rest. Therefore, \(d_{1}^{IGA}, d_{2}^{IGA}, d_{3}^{IGA}\) and \(d_{4}^{IGA}\) were measured as far away from the edge of the coating as possible. The average depth of the attack was calculated using Equation 1.

*Equation 1*

\[
d_{average}^{IGA} = \frac{d_{1}^{IGA} + d_{2}^{IGA} + d_{3}^{IGA} + d_{4}^{IGA}}{4}
\]
3.3.4 SEM-analysis and sample prep.

In order to detect possible precipitated intermetallic phases in the microstructure, selected samples were analysed in a scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS). The surfaces of these samples were polished using oxide polishing suspension (OPS) polishing.

To map the EDS-signals to crystalline phenomena such as grain boundaries or β-phase, some samples were using SEM with electron backscatter diffraction (EBSD) functionality in addition investigated in addition to EDS-analysis. To accommodate this investigation, the surfaces of interest of these samples were polished using electrolyte polishing.

3.3.4.1 Oxide polished samples, EDS-analysis

The samples selected for this analysis, which are displayed in Table 4, were polished using active oxide polishing suspension (OPS) in order to minimize the amount of scratches and chemical artefacts. These samples were specifically chosen to compare the difference between alloys, as well as comparing the 400°C heat treatment to the 250°C heat treatment for CW626.

Table 4: List of samples that were OPS-polished and analysed in SEM-EDS.

Figure 13: Illustration of how the depth of the intergranular attack (IGA) in the extrusion direction of the sample was estimated.
To prepare the samples for the OPS-polishing, the brass samples were cut so that the surface displays the extrusion direction. The samples were then casted in phenolic resin. The exposed surface is then grinded as described in 3.3.1 and polished using diamond polishing with only 3μm diamonds with a similar setup described in 3.3.1.

The final polish of the samples was performed using oxide polishing with aqueous ammonia (NH₃ + H₂O) suspension. It was performed by hand in a Struers DAP-8 for 3 minutes using disc rotation speed of 300rpm followed by 30 seconds polishing using distilled water as suspension to remove excess oxidation products. The sample was then degreased followed by rinsing it in distilled water. Under hot air convection, the sample was dried using 95%-ethanol.

The surface of the polished sample was analysed in a scanning electron microscope (SEM) LEO 1530 with Gemini column, upgraded to a Zeiss Supra 55 with Channel 5 software from HKL Technology. The SEM-image was captured using emissions of secondary electrons with 15kV acceleration voltage and 120μm aperture size in a random location in the bulk to avoid edge specific defects of the sample. The EDS-measurements were obtained using a 50mm² X-Max Silicon Drift Detector (SDD) from Oxford Instruments.

3.3.4.2 Electrolyte polished samples, EBSD-EDS-analysis

By using the EBSD-functionality of the SEM-equipment, details regarding the crystal structure and their orientation could be analyzed. The samples listed in Table 5 were chosen in order to investigate the influence of temperature and thermodynamic phase stability on the microstructure and relate this to the corrosion performance.
Table 5: List of the samples that were electrolyte polished and analysed with SEM-EDS-EBSD.

<table>
<thead>
<tr>
<th>Electrolyte polished samples</th>
<th>CW511</th>
<th>CW625</th>
<th>CW626</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy:</td>
<td>CW511</td>
<td>CW625</td>
<td>CW626</td>
</tr>
<tr>
<td>Sample heat treatment:</td>
<td>-</td>
<td>400°C for 1000h</td>
<td>400°C for 1000h</td>
</tr>
<tr>
<td></td>
<td>300°C for 1000h</td>
<td>350°C for 1000h</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No HT</td>
<td>No HT</td>
<td></td>
</tr>
</tbody>
</table>

The surface of the sample was mechanically grinded and mechanically polished with a procedure similar to the one described in 3.3.4, including the oxide polishing. Following the oxide polishing, the sample was cut out of the phenolic resin to be polished using electrolyte. The electrolyte polishing was performed using a *Struers Lectropol-5* at flow rate of 18 UNIT, voltage of 56V and operation time of 6 seconds with a mask large enough to make the bulk and edge of the brass exposed to the electrolyte. The electrolyte consisted of 500ml distilled water, 250ml phosphoric acid, 250ml ethanol, 50ml propanol and 5.0gm carbamide (CO(NH$_2$)$_2$). The sample was the degreased followed by rinsing it in distilled water. Under hot air convection, the sample was dried using 95%-ethanol. The polished sample was then analysed in the same scanning electron microscope as described in section 3.3.4.1 with the same settings. In this analysis however, the sample was tilted 70° in order to enhance the grain orientation, with the same settings as described in 3.3.4.1. The EBSD-image was then analysed using the EBSD post-processing software *Tango* by *Oxford Instruments*. This would allow for study of grain orientation mapping, which was used to highlight grain boundaries, twins and deformed areas, and in addition be overlapped with the EDS-analysis, which was used to observe if concentrations of chemical signals overlapped with the various defects.

### 3.4 Thermodynamic calculation

To assist in the analysis of how compositional elements and heat treatment conditions impact the microstructure, a property diagram for each alloy was calculated using the software *Thermo-Calc* by *Thermo-Calc Software AB*. This software utilizes the calphad-method to predict various thermodynamic outcomes, such as which phases are able to precipitate in a complex multi-component alloy system. In its user interface, the thermodynamic material
database, material composition, system size, pressure and temperature are parameters that can be used to regulate the properties of the system.

The calculated property diagram would display the amount of each stable phase at each heat treatment temperature, under the assumption that the system has reached equilibrium. For this purpose, a custom database developed by Swerea KIMAB [6]. This database did not contain all elements present in the material, including Mg, Cr, Mn, Ni, Sn and Bi. The composition used to calculate the property diagram is displayed in Table 6. The system pressure and size was set as $10^5$ Pascal and 1 mole respectively.

Table 6: Displays the values of the compositional parameters used in Thermo-Calc to calculate amount of phases in equilibrium, representing each alloy.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>wt%Zn</th>
<th>wt%Pb</th>
<th>wt%Al</th>
<th>wt%Fe</th>
<th>wt%As</th>
<th>wt%P</th>
<th>wt%Sb</th>
<th>wt%Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW511</td>
<td>35.9</td>
<td>0.2</td>
<td>0.05</td>
<td>0.05</td>
<td>0.1</td>
<td>0.01</td>
<td>0.04</td>
<td>rem. (63.64)</td>
</tr>
<tr>
<td>CW625</td>
<td>34.8</td>
<td>1.3</td>
<td>0.6</td>
<td>0.11</td>
<td>0.1</td>
<td>0.01</td>
<td>0.04</td>
<td>rem. (63.03)</td>
</tr>
<tr>
<td>CW626</td>
<td>33.2</td>
<td>1.23</td>
<td>0.8</td>
<td>0.11</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>rem. (64.60)</td>
</tr>
</tbody>
</table>
4 Results

4.1 Corrosion test results

The brass alloys CW511, CW625 and CW626 were heat treated at 250°C, 300°C, 350°C and 400°C. The alloys were exposed to these temperatures at four different durations: 2h, 10h, 100h and 1000h. Samples from each temperature and exposure duration were then prepared and tested with respect to each corrosion test. In the following section, the result of each alloy will be described separately.

4.1.1 Dezincification performance

The samples were prepared and tested for dezincification by following the guide lines provided by standardized testing method SS-EN ISO 6509-1:2014 [15]. The dezincification depth was estimated using average dezincification depth and maximum dezincification depth. The results of the measurements are displayed in Figure 14 – Figure 18.

For alloy CW511, Figure 14 shows that the dezincification only occurs on a local level, as exemplified in Figure 15 with low depth of dezincification of < 25μm. The general observed tendency was that the local dezincification was more evident within the samples with higher heat treatment durations. The notable exception was the samples heat treated in 350°C, where the local dezincification was larger at lower heat treatment durations. However, the local dezincification did not occur often enough in CW511 to conduct an average dezincification depth. Overall, the dezincification depth of CW511 is not substantial initially nor significantly affected by the heat treatment.
Figure 14: Dezincification depth of the CW626-samples. The average depth was measured using the SS-EN ISO 6509-1:2014 [15] method and the depth of the largest detected dezincification depth (Max) was noted.

Figure 15: Example of the local corrosion depth in CW511-250°C-1000h.
For alloy CW625 in Figure 16, the dezincification performance is displayed. The samples heat treated at 250°C only displayed isolated local dezincification attacks, but these did not occur often enough to produce an average dezincification depth.

![Dezincification depth (µm), CW625](image)

*Figure 16: Dezincification depth of the CW626-samples. The average depth was measured using the SS-EN ISO 6509-1:2014 method [15] and the depth of the largest detected dezincification depth (Max) was noted.*

Compared to the sample with no heat treatment a significantly large dezincification depth was detected in the samples heat treated at 300°C, 350°C and 400°C, i.e. larger dezincification depths for higher heat treatment temperature.

In addition, it was observed that this depth of dezincification increased for samples with longer heat treatment durations. A notable exception to this trend was observed in CW625-400°C-10h. This sample displayed a larger dezincification depth compared to the sample with longer heat treatment duration, 100h. However, compared to the samples with longer heat treatment, the 10h-sample displayed a more selective zone in which the dezincification
occurred more aggressively, as Figure 17 illustrates. This subject is further investigated in 4.3.3.

Figure 17: Images of the samples CW625-400°C-10h and CW625-400°C-100h after exposure to the dezincification solution. A) View parallel to the extrusion direction. B) View perpendicular to the extrusion direction.

In terms of comparing how the heat treatment duration impacted the dezincification depth in Figure 16, samples with higher heat treatment duration generally displayed larger depth of dezincification, with 250°C being the exception for which the performance remained unaffected by the heat treatment. However, the depth did not increase successively for the samples heat treated at 300°C-400°C. Instead, an abrupt increase in average dezincification depth, from the range 10μm–25μm to 300μm–500μm, was observed. For CW625, the 350°C-samples did not display this behaviour until the transition from 100h to 1000h, while the 300°C- and 400°C-samples reached 300μm –500μm as early as the transition from 10h to 100h. It is not possible to tell if 400°C could have reached it even earlier because of the anomaly presented in the 400°C-10h sample. However, the general observation was that the
300°C-samples and 400°C-samples abruptly increased from the range 10μm–25μm to 300μm–500μm at shorter heat treatment durations compared to the 350°C-samples.

It should also be noted that the 300°C-sample displayed the largest average dezincification depth. 350°C however, displayed the largest local dezincification depth.

**For alloy CW626,** dezincification performance is displayed in Figure 18. It shows that the average dezincification depth was low (10μm–25μm) for the samples heat treated at 250° and 300°C as well as the sample with no heat treatment.

![Dezincification depth (µm), CW626](image)

*Figure 18: Dezincification depth of the CW626-samples. The average depth was measured using the SS-EN ISO 6509-1:2014 method [15] and the depth of the largest detected dezincification depth (Max) was noted.*

CW626-300°C-1000h displayed a large spike of local dezincification attacks as illustrated in Figure 19. The attacks were however not frequent enough to result in a large average dezincification depth (300μm–500μm). Large average dezincification depths could not be observed until 300°C at 100h–1000h and 400°C 10h–1000h, i.e. higher heat treatment temperatures at longer durations.
Compared to CW625, the dezincification depths of CW626 were observed to be lower, especially at lower heat treatment temperatures. The depth of dezincification in CW626 was observed to be generally higher in the samples heat treated for a longer duration, i.e. the same trend as observed in CW625.

It should be noted however that in the samples heat treated at 400°C for 100h and 1000h respectively, it was observed that both the average dezincification depth and the maximum local dezincification was lower compared in the 1000h duration compared to 100h, possibly indicating that the data has entered a steady state.

Figure 19: Images of the samples CW626-300°C-1000h after exposure to the dezincification solution displaying large local dezincification attacks. A) View parallel to the extrusion direction. B) View perpendicular to the extrusion direction.

4.1.2 Performance of IGA-solution

The depth of the IGA was measured in heat treated alloy samples after being exposed to a chloride-citrate solution for 100h. Not all samples investigated in Table 1; the only investigated samples were those heat treated at 400°C and 250°C for 2h, 10h, 100h and 1000h respectively, as well as 300°C for 2h, 10h and 100h. In the following section, the observations in each alloy will be described separately.

For CW511, the IGA-depth consistently remained within 45-70μm as observed in Figure 20. The two samples that drastically deviated from this trend were the two samples heat treated for 250°C and 400°C for 1000h. At 250°C-1000h CW511 displays significantly higher IGA-
depth while at 400°C-1000h it displays a lower IGA-depth. The sample solutions had a pH-value within 3.97 – 4.06, as disclosed in Figure 20.

Figure 20: Average height of surface exposed to IGA-solution relative the height of unexposed surface for alloy CW511 as well as the pH-value of each solution after 100h.

For CW625, samples heat treated at 300° and 400°C showed a common trend: depth of the IGA decreased as the duration of the heat treatment increased. Samples heat treated at 250°C show a trend with a more constant value within 85–83µm, with the single exception being the sample heat treated for 2h displaying ~53µm IGA-depth. The pH-value of the sample solutions in the 250°C- and 300°C-samples as well as the 400°C-1000h consistently remained within 3.95 and 4.03. In the samples heat treated at 400°C for 2h, 10h and 100h the pH-range was lower, within 3.87 and 3.92.
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Figure 21: Average height of surface exposed to IGA-solution relative the height of unexposed surface for alloy CW625 as well as the pH-value of each solution after 100h

For CW626, the trend of IGA-depth for the samples heat treated at 400°C was similar to the samples heat treated at 400°C and 300°C in CW625; IGA-depth decreased as the duration of the heat treatment increased. The pH value for the CW625-400°C-samples displayed the opposite trend; lower pH at 3.78 for the 2h-sample with increased pH-value in the solution for the samples with longer HT-duration. The remaining samples exposed to chloride-citrate solution displayed a depth between 103–89μm, with the exception being 250°C-2h which displayed 77μm IGA-depth. The pH-value for these samples displayed a stable value between: 3.94 – 4.05.
Figure 22: Average height of surface exposed to IGA-solution relative the height of unexposed surface for alloy CW625 as well as the pH-value of each solution after 100h

4.2 Thermodynamic calculations

Thermodynamic calculations were performed using Thermo-Calc with a database by Swerea KIMAB especially designed for brass systems in order to assist the understanding of the microstructure that each heat treatment would yield in the different alloys. The missing elements in the database are: Mg, Cr, Mn, Ni, Sn and Bi. A property diagram displaying the amount of phases at a thermodynamic steady state was calculated for each alloy.

For CW511, displayed in Figure 23, β-phase should precipitate at 250°C and 300°C with decreasing amount as the temperature rises, according to the calculations. In the range 250°C – 300°C, the stoichiometric intermetallic phases AlAs and FeAs are stable and should precipitate, AlAs being the more prominent specimen. At temperatures higher than ~375°C the stoichiometric intermetallic phase FeCu2AsSb is stable enough to precipitate instead of FeAs. Finally, the specimen Fe2P is stable throughout the calculated temperature range 250°C–500°C.
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Figure 23: Property diagrams of CW511, displaying amount of phases if system has homogeneous composition and is in a steady state.

The result of CW625 is displayed in Figure 24. The property diagrams shows that β-phase should be stable and precipitate within the range 250°C–370°C, with decreased amount as the temperature converges on 370°C. The stoichiometric intermetallic phase AlAs should also precipitate within that range as well as the phase BCC(Fe-Si-Al). Above 370°C, BCC(Fe-Si-Al) and AlAs decreases in stability in favour of the growth of FeCu₂AsSb. At 390°C, BCC(Fe-Si-Al) has dissolved in stability completely.

Compared to CW511, CW625 displays a higher amount of stoichiometric intermetallic arsenide phases, β-phase and Pb(s). The amount of Fe₂P in the two alloys is equal however.
Results

Figure 24: Property diagrams of CW625, displaying amount of phases if system has homogeneous composition and is in a steady state.

The results of CW626 show the same resulting precipitated specimens as CW625, as displayed in Figure 25. The calculations indicate however that the β-phase is prone to precipitate only within 250°C–280°C for CW626. Further differences from CW625 display that AlAs precipitates lower amount than BCC(Fe-Si-Al) within 250°C–370°C, and when FeCu2AsSb precipitates AlAs dissolves while BCC(Fe-Si-Al) remains, which decreases in amount as the temperature rises.
4.3 Microstructure analysis

4.3.1 β-phase-etching

The β-phase contain no dezincification inhibitors in α-brasses, and is thus especially susceptible to dezincification, and as result it is one of the culprits causing dezincification in As-containing brasses.

The β-content in the samples was investigated for this reason. The samples were cut parallel to the extrusion direction, and the exposed surface was grinded, polished and etched as described in section 3.3.1. The treatment made the β-phase appear as distinctly yellow in juxtaposition to the white α–phase–matrix, as illustrated in Figure 26. Using the software ImageJ, the amount of yellow surface area relative to the non-yellow area could be calculated to represent the amount β-phase in each sample. In Figure 27 the resulting amount of β-phase is illustrated for all three alloys, only including samples that were heat treated for 1000 hours as well as the samples that received no additional heat treatment. The result of each alloy will be described in the following order: CW511, CW625 and CW626.

Figure 25: Property diagrams of CW626, displaying amount of phases if system has homogeneous composition and is in a steady state.
Figure 26: A view of sample CW625-300°C-1000h in light optical microscope (LOM), etched in Klemm I solution. The yellow area is etched β-phase, while the white matrix is α-phase. The black spots are undissolved particles.
Microstructure-corrosion interrelations in new low-lead and lead-free brass alloys

Results

Figure 27: Average amount of β-phase in all samples heat treated for 1000h and the samples with no heat treatment, including pre-heat treatment.

CW511

As displayed in Figure 27, the samples of alloy CW511 heat treated for 1000h show no precipitation of β-phase regardless of temperature of the heat treatment.

CW625

From observing Figure 27, the amount of β-phase appearing in CW625 at 1000h of heat treatment time is overall the highest out of the three alloys within this study. The sample with no additional heat treatment, including pre-heating, only displayed a slight amount of isolated areas of β-phase. The 300°C-1000h-sample however, displayed 2% – 4% of β-phase along the grain boundaries of the α-phase, as represented in Figure 26. The 350°C-1000h-sample had also precipitated β-phase in the grain boundaries, but rather as small isolated islands than a continuous network. The heat treatment at 400°C-1000h resulted in a similar pattern as
350°C-1000h, but with a smaller size as well as lower overall frequency of appearance. The trend is displayed in Figure 27 and it indicates that the heat treatment post- β -annealing with higher temperature than 300°C decreases the amount of precipitated β-phase.

![Figure 28: A representative image of the β-phase appearance in CW625-350°C-1000h, etched in Klem I solution. The white represents the α-phase, the yellow represent the β-phase and the black spots are undissolved particles.](image)

In the sample heat treated at 250°C for 1000h no β-phase appeared as yellow by the etching. However, grey shaded areas appeared in both along grain boundaries as exemplified in Figure 29, and free in the matrix in the same shape as the observed yellow β-phase in the previous samples. These areas were not taken into account in the ImageJ calculation.
Microstructure-corrosion interrelations in new low-lead and lead-free brass alloys

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Figure 29: A diamond polished surface of sample CW625-250°C-1000h, etched in Klem’s solution. Light grey areas appearing in grain boundaries and as free in the matrix is highlighted.

CW626

The β-phase in CW626 mostly appeared as isolated round or elongated islands, close to α-grain boundaries or in contact with a Pb-particle as exemplified in Figure 30.

In the sample with no additional heat treatment, CW626-No Pre-HT, only a slight amount of isolated β-phase precipitated (0.00%–0.05%). The heat treatment at 250°C for 1000h resulted even lower amount of visible β-phase (0.00%–0.01%). At 300°C, the highest amount of β-phase precipitated (0.2% – 0.5%), similar to the amount and appearance as CW625-350°C-1000h. 350°C yielded less β-phase than 300°C (0.1–0.2%), and 400°C displayed no β-phase visible in the light optical microscope. The trend of the data can be observed in Figure 27.

As observed in Figure 27, the β-content was lower in CW626 than the CW625, but the data followed the same trend; the amount of β-phase peaks at 300°C and decreases as the temperature further increases. At 250° and 400°C, no β-phase was observed using the light optical microscope.
Microstructure-corrosion interrelations in new low-lead and lead-free brass alloys

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Figure 30: CW626-300°C-1000h, etched in Klemm’s I solution. Illustrates how the β-phase (yellow) has formed alongside α-phase grain boundaries and often in close proximity to undissolved Pb-particles.

In the sample heat treated in 250°C for 1000h, grey areas appeared along grain boundaries or free in the metal matrix, as represented in Figure 31; a similar result as the one given in CW626-250°C-1000h.
Figure 31: A diamond polished surface of sample CW626-250°C-1000h, etched in Klemm I solution. Grey areas appear as either free in the matrix or along grain boundaries is highlighted.
4.3.2 Chemical analysis in microstructure

4.3.2.1 OPS-polished samples, EDS-analysis

From the EDS-analysis of the samples polished using active oxide polishing suspension (OPS) listed in Table 4, three main enriched areas observed: Pb-rich areas, As-rich areas and Fe-rich areas, upon which enrichment of other elements would overlap. Additionally, for CW626-250°C-1000h featured Zn-enriched areas. Each major group of enriched elements will be described.

The Pb-enriched areas appeared as spherical or elongated particles, and these areas were clearly visible as white spots in the electron image without EDS. Their size and frequency shifted with the alloy composition; CW511 displayed smaller areas with less frequency, while CW625 and CW626 displayed larger areas with larger frequency. They did not exclusively appear on grain boundaries. In the samples with OPS-polished surface, the Pb-rich areas could also overlap with Bi-enriched areas.

The As-enriched areas detected with EDS appeared in conjuncture with unindexed areas on the SEM-images that used the detector of secondary electrons to create a picture. These black spots appeared as black spots in the image and were either isolated in the matrix or connected to the Pb-rich particles as illustrated in Figure 32 and Figure 33. The As-enriched areas often overlapped with Al-enriched areas in CW625 and CW626, represented in Figure 33. In CW511 however, they instead overlapped with Fe-enriched and P-enriched areas, as shown in Figure 34.

In the comparison of the samples CW511-400°C-1000h, CW625-400°C-1000h and CW626-400°C-1000h the amount As-enriched in CW511 was 0.025%–0.030%. CW625 displayed 0.055–0.045% and CW626 displayed 0.100–0.140%. In addition, sample CW626-250°C-1000h exhibited no detectable As-enriched area.
Figure 32: A digitally magnified image of OPS-polished sample CW626-400°C-1000h, displaying how As-enriched areas (teal) typically appeared in CW626 and CW625: free in the bulk (A) or attached to a Pb-enriched area.
Results

Figure 33: Illustrates how As-, Pb- and Al-enriched areas overlap in CW625 and CW626 heat treated at 400°C for 1000h. A. exemplifies how Al and As overlap and B. how As-enriched areas can exist without overlapping with Al.
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Figure 34: Illustrates how Fe-enriched areas on OPS-polished CW511-400°C-1000h overlap with As-enriched areas (A), P-enriched areas (B) or both (C).

The Fe-enriched areas were detectable using EDS, and similarly to the As-enriched areas they appeared on black spots in electron image, i.e. locations with low electron signal output. As illustrated in Figure 35, these black spots appeared similarly to the As-enriched areas; either freely in the bulk or in conjuncture with the Pb-particles. In CW625 and CW626, the appearance of the Fe-enriched areas would often overlap with areas exhibiting high P-, Cr- or Si-concentration respectively, as represented in Figure 36, while CW511 they overlapped instead with As-enriched and P-enriched areas, as shown in Figure 34.

In the comparison between the samples CW511-400°C-1000h, CW625-400°C-1000h and CW626-400°C-1000h, all samples displayed 0.032% – 0.046% Fe-enriched area relative the total area of the captured image. CW626-250°C-1000h displayed 0.010% Fe-enriched areas.
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Figure 35: A digitally magnified image of OPS-polished sample CW626_400°C_1000h displaying how Fe-enriched areas appears freely in the bulk on black dots on the electron image (A) or in conjunction with Pb-rich particles (B).
**Figure 36**: EDS-mapping of CW626-400°C-1000h with OPS-polished surface, displaying how typically Fe-enriched areas can overlap with Cr- and P-enriched areas respectively. The layered image display how the three areas overlap with the Electron Image from the SEM.

**Zn-enriched areas** were only found in CW625-250°C-1000h. These areas were not detectable without EDS. In addition, they did not overlap with any other area of enriched element.
4.3.2.2 Electrolyte polished samples, EDS and EBSD

In order to correlate chemical analysis to defects and grain boundaries, selected samples were polished using electrolyte and high voltage and analysed in SEM with both EDS and EBSD. The electrolyte polishing would allow EBSD-equipment to analyse the surface with minimal deformations in crystal lattice left by the mechanical grinding and diamond polishing. To enable a detailed EBSD-analysis, the sample had to be tilted by 70° to the electron beam. The selected samples are listed in Table 5. In order to further enhance defects and grain orientation mapping, EBSD pictures were analysed using EBSD Post-processing software Tango by Oxford Instruments.

In terms of enrichment of alloy elements in CW625 and CW626, the EDS-analysis of the listed samples in Table 5 revealed a similar result as the OPS-polished results described in 4.3.2.1; the As-enriched areas overlapped with Al-enriched areas, while Fe-enriched areas overlapped with enriched areas of Cr, Si or P. In addition, the secondary electron detector of electrolyte polished samples revealed that As-enriched areas could overlap with reflective spherical areas in the topography of the metal’s surface, as represented by Figure 38.

Figure 37: EDS-mapping of CW626-250°C-1000h with respect to Zn-content, displaying the location of Zn-enriched areas of the microstructure.
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Figure 38: Electrolyte polished surface of CW626-350°C-1000h in SEM, using secondary electron emission signals. The highlighted areas exemplifies how As-enriched areas overlap with unindexed areas.

The P-enriched areas however were far more prominent in the electrolyte polished samples compared to the OPS-polished samples, as represented in Figure 39, and overlapped more with Pb in addition to Fe.

Figure 39: A comparison of the amount of P-enriched areas in two samples of the same alloy (CW626) and equal heat treatment (400°C for 1000h). To the right the sample has been electrolyte polished and to the right the sample has been OPS-polished.
The gathered results of the EDS-analysis in Figure 40, indicates an increase in As-enriched areas, Fe-enriched areas and Pb-enriched areas as the temperature of the heat treatment rises. As illustrated in Figure 41 however, the magnification of the pictures used to perform this comparison is lower in the samples heat treated at 400°C than the samples heat treated at 300°C, 350°C as well as the samples with no heat treatment. This will affect the values of analysis since lower magnification results in more of the large clusters of enriched areas such as Pb, to be taken into account when calculating the amount of enriched area in ImageJ.

![Graph showing enriched areas of CW625 and CW626](image)

**Figure 40:** Graphs displaying the element enriched surface area/total surface area - ratio of Fe, As and Pb in each electrolyte polished sample image respectively.
**Results**

Figure 41: Layered images of CW626 with equal heat treatment duration, but different heat treatment temperatures: I) Sample with no heat treatment II) 350°C for 1000h III) 400°C for 1000h. Highlighted is band contrast (BC), As, Pb and Fe.

As with the EDS-analysis of the OPS-polished samples, As and Fe appeared in the electrolyte polished samples as either free in the bulk of the metal or in conjuncture with Pb-enriched areas. However, the addition of EBSD also revealed that the As-enriched and Fe-enriched areas overlapped with various defects, including grain boundaries, twins and Pb-rich areas as highlighted in Figure 42 using the post processing Tango software. According to this data, As and Fe can both overlap with recrystallized material, substructured material and deformed material, with no clear preference. It also shows trends that indicates that Pb overlaps with local areas of deformed material in the microstructure.
Figure 42: A composite image of sample CW626-350°C-1000h consisting of the result of EDS-analysis of As, Fe, and Pb as well as the EBSD-analysis of band contrast, grain boundaries and recrystallized fractions including Deformed-, Substructured and Fully recrystallized material. The highlighted areas exemplify how As and Fe overlap with A) High angle grain boundaries, B) Twins (60°-boundaries) and C) Pb-particles.

The EBSD functionality was also able to identify β-phase in the microstructure. β-phase appeared as isolated pixels in all of the samples. The exception being CW625-300°C-1000h, which displayed minor clusters of β-phase that were adjacent to the grain boundaries of the sample. In addition, these clusters overlapped with Zn-enriched areas as displayed in Figure 43.
This sample also exhibited Cu-enriched areas along the grain boundaries, as displayed in Figure 44. These areas overlapped areas with low electron emission output, thus appearing as black spots in the electron image. Other low input areas were also detected in the bulk of the grains. These however, exhibited presence of O, P and S as opposed to Cu.

In addition, Fe-enriched and As-enriched areas appeared adjacent to all types of low output electron emission areas in CW625-300°C-1000h, regardless of their composition. This is represented in Figure 45.

![EDS-EBSD Layered Image CW625-300C-1000h Electrolyte Polished](image)

**Figure 43:** Layered image of sample CW625-300°C-1000h, displaying band contrast (BC), α-phase (Copper), β-phase (Brass-beta) and enriched areas of Zn.
Results

Figure 44: Layered image of sample CW625-300°C-1000h, with a spectrum analysis of three areas in the image. The table displays the composition of each spectrum.
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4.3.3 Grain size distribution for CW625

In CW625-400°C-10h an aggressive dezincification attack was observed in a selective area of the sample. To provide further details about the microstructure, the sample was etched in Klemms I solution for 7 minutes. The result is presented in Figure 46.

The etching revealed a zone below the area which had been aggressively corroded. This zone possessed a very fine grain size compared to the surrounding area. This zone was found in other samples of the alloy CW625, including 400°C-100h, 400°C-2h and 300°C-100h, however it should be mentioned that not all CW625-samples were investigated. Further investigation with etching using Klemm’s solution on a sample of alloy CW625 heat treated at 400°C for 100h, cut with the intent to display profile of the bar, showed a similar zone which was located in the centre extruded bar, as represented in Figure 47.
Results

Figure 46: Sample CW625-400°-10h after dezincification.

Figure 47: Images of a special sample cut with the intent to visualize the grain size distribution along the extruded bar profile. A) View parallel to the extrusion direction B) View perpendicular to the extrusion direction I) Area viewed in light optical microscope, which displays the zone of fine grain size distribution.
5 Discussion

5.1 Investigation of β-phase

5.1.1 Heat treatment temperature related to amount of β-phase

In this section, the amount of β-phase will be discussed with respect to each heat treatment temperature. The result will be correlated to the results of the thermodynamic calculations to determine if the displayed results are justified.

At 250°C the thermodynamic calculations indicated that amount of β-phase should be high. The observed amount in the microstructure did not reflect this. However, further analysis revealed that the miscoloured unknown grey phases along grain boundaries observed in Figure 29, the etched diamond polished sample of CW625-250°C-1000h were matching in size and form with the Zn-enriched areas spotted by the EDS-analysis of OPS-polished sample of the same alloy with the same heat treatment temperature and duration in Figure 37. In the EDS-EBSD-analysis of electrolyte polished sample CW625-300°C-1000h these types of Zn-enriched areas were revealed to be closely correlated to precipitated areas of β-phase, as indicated by Figure 43. Furthermore, a similar study performed by C. Comas in 2016 [16] investigating the amount of β-phase in brass alloy CW625 heat treated at 250°C for 250 hours revealed β-phase etched to a yellow colour as illustrated in Figure 48, and no grey unknown phases, further indicates that β-phase is expected to appear when the sample is heat treated at 250°C for an extended duration. This, in addition to the thermodynamic calculations predicting high amount of precipitated β-phase, could indicate that these unknown grey phases observed in CW625-250°C-1000h are precipitated β-phases coloured in an unexpected way. However, the etching procedure of diamond polished CW625-250°C-1000h was performed for equal duration in the same solution as CW625-300°C-1000h, which coloured the β-phase yellow as expected. The sample was in addition investigated in LOM directly after etching was performed. Thus there is no clear reason for why the β-phase in CW625-250°C-1000h would behave differently in the etching solution compared to CW625-300°C-1000h.
Figure 48: Image from a previous study. The alloy is CW625 that has been heat treated for 250h in 250°C, diamond polished followed by etching in a Klemm I solution to highlight areas of β-phase in a yellow shade. [16]

Even if the grey phases observed at 250°C-1000h are miscoloured β-phase, they are neither as large nor appearing as frequently as the β-phase observed in 300°C-1000h. This can be explained by the diffusion of Zn at lower temperatures; if the formation of β-phase is a reaction controlled by diffusion of Zn, then higher temperature will increase the diffusion rate of Zn-atoms. Thus, it could be a possibility that the formation of β-phase at 300°C occurs at a higher rate in compared to 250°C and can thus form into a larger amount. However, increasing the temperature of the heat treatment beyond 300°C can result in less β-phase being formed, as indicated by comparing the amount of precipitated β-phase in the 350°C-samples of CW626 and CW625 to the corresponding samples for 300°C in Figure 27. From the thermodynamic calculations it was revealed that the stability of β-phase decreases with increasing temperature. There is thus a possibility that lower stability of β-phase at 350°C is too much of a limitation in the system to allow the amount of β-phase at 350°C to exceed the amount of precipitated β-phase at 300°C, in spite of diffusion of Zn-atoms being higher at higher temperatures.

5.1.2 Influence of β-phase on dezincification

In this section, it is discussed how the amount of observed β-phase in the microstructure is correlated to the results of the dezincification test.

It is plausible to assume that the dezincification occurs as result of multiple sources of dezincification, and not only as a result of precipitated β-phase since there are samples that
displayed significant dezincification depth and no visible β-phase such as CW626-400°C-1000h. One such additional source is the presence of intermetallic particles containing As, which implies that there are parts of the α-phase which has been sensitized as a result of the heat treatment. This is exemplified in CW625-300°C-1000h and CW626-350°C-1000h, which display As-enriched areas in addition to β-phase. Thus it becomes challenging to separate dezincification caused by As-particles from the dezincification caused by β-phase, since all samples with β-phase also contain As-enriched areas.

An additional aspect of the results that further obscures the extent of which the β-phase impacts the dezincification depth is whether the grey shaded areas discussed in 5.1.1 observed in the CW625 and CW626 heat treated at 250°C for 1000h are precipitated areas of β-phase. If the etching method is correct, and there is no precipitated β-phase at 250°C, then the small dezincification depth is understandable, since absence of both As-enriched areas and β-phase would yield such result. However, if the β-phase indeed precipitates at 250°C, then there is an instance in which β-phase has precipitated without causing a considerable dezincification depth in the material. This may be linked to the fact that the precipitated areas are small and isolated from each other, thus not contributing to a large dezincification attack.

One way to determine the influence of β-phase is to analyse the difference between CW625 and CW626, since the amount of visible β-phase between differs drastically between these two alloys in the temperature range 300°C and 350°C as illustrated by comparing Figure 50 and Figure 51. One can assume the dezincification caused by precipitation of As-enriched areas is constant for the two alloys since the comparison in Figure 40 displays that the amount of As-enriched areas in CW625 and CW626 heat treated for 1000h are comparable. This is further substantiated by their composition; the amount of As, Fe and Al is similar between the two alloys, since that would result in the same amount of particles forming. For this reason it is plausible to assume that main difference in dezincification between the two alloys is a result of the differing amount of β-phase in the samples heat treated at 300°C and 350°C.

By further comparing Figure 50 and Figure 51, it is observed that for the samples of CW625, heat treated at 300°C or 350°C for 1000h, larger dezincification depth was yielded, both average and maximum, compared to the corresponding samples in CW626. In addition, drastically larger amount of β-phase was also observed in CW625. Since the amount of particles could be assumed as the same amount in the two alloys, this indicates that the likely reason for higher dezincification depth in CW625 is due to higher amount of β-phase.
In regards to why more $\beta$-phase precipitates in CW625 than CW626, the thermodynamic stability of the $\beta$-phase was compared in the two alloys using Thermo-Calc. From the comparison it is evident that $\beta$-phase is more stable in CW625 as a result of its lower Cu/Zn-ratio compared to CW626, as illustrated in Figure 49. Since both alloys contain similar amount of Al and Fe, the kinetics of the reaction controlling the formation of $\beta$-phase should also be the similar, leaving the stability of $\beta$-phase as the determining factor of how much $\beta$-phase is formed in CW625 compared to CW626 since remaining parameters are constant for the two heat treated alloys.

![Figure 49](image-url)  

*Figure 49: Two overlapping thermodynamic phase property diagrams displaying with different Cu/Zn-ratio in order to illustrate how that factor impacts the stability $\beta$-phase and thus controlling the amount of $\beta$-phase able to precipitate.*

The results provided by the calculations in Thermo-Calc do not however explain how fast the $\beta$-phase precipitates. Furthermore, the amount of precipitated $\beta$-phase was not investigated for
samples heat treated at lower heat treatment durations. Thus, it is not clear if the dezincification depth at lower heat treatment durations is a result of absence of β-phase.

Figure 50: The dezincification depth after the dezincification test and the amount of β-phase plotted together for CW625.

Figure 51: The dezincification depth after the dezincification test and the amount of β-phase plotted together for CW626.
5.1.3 Absence of β-phase in CW511

When studying the thermodynamic properties in Figure 23 – Figure 25 and comparing CW511 to CW625 and CW626, it is expected that β-phase should precipitate at 300°C or 350°C in CW511, and precipitate more than CW626. However, as represented in Figure 52, no such phase in any CW511-sample was observed in the LOM, while CW626 displayed a significant amount.

Figure 52: The dezincification depth after the dezincification test and the amount of β-phase plotted together for CW511.

To explain this, one can either assume that the database of the thermodynamics is inaccurate or that the absence of β-phase is due to slow kinetics of the reactions that controls its formation. Since their heat treatments were identical, the latter explanation suggests that the compositional difference between CW511 and the other two alloys allow for more rapid evolution of β-phase in CW625 and CW626.

As to what compositional difference could cause more rapid formation of β-phase in CW625 and CW626 compared to CW511, the amount of Fe and especially Al in CW511 is negligible compared to CW626 and CW626, as displayed in Table 7. This might indicate that their presence accelerates the β-phase evolution.
Table 7: Summarizing the experimental observations with the results of calculations and chemical composition related to the β-phase.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Thermodynamic stability of β-phase</th>
<th>Amount of β-phase at 300C and 350C</th>
<th>Cu/Zn-ratio</th>
<th>Al-content</th>
<th>Fe-content</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW511</td>
<td>Moderate</td>
<td>-</td>
<td>1.78</td>
<td>&lt; 0.05%</td>
<td>0.05%</td>
</tr>
<tr>
<td>CW625</td>
<td>High</td>
<td>High</td>
<td>1.83</td>
<td>0.60%</td>
<td>0.11%</td>
</tr>
<tr>
<td>CW626</td>
<td>Low</td>
<td>Moderate</td>
<td>1.95</td>
<td>0.70%</td>
<td>0.11%</td>
</tr>
</tbody>
</table>

The topic of which elements contribute to acceleration of formation of β-phase has not been subject to investigation by other studies. However, there are investigations that indicate that presence of Al and Fe contribute to higher amount of β-phase or dezincification properties, which could indicate that the elements are involved in kinetics of formation of β-phase as well. Al has been reported [7] to stabilize formation of β-phase, while micro additions of Fe were reported [8] to accelerate dezincification in 60/40 Cu-Zn brasses, although not disclosed if this was because of increased amount of β-phase.

The other substantial difference in composition between the alloys is the Cu/Zn-ratio, as represented in Table 7. As illustrated in Figure 49, higher Cu/Zn-ratio results in higher thermodynamic stability of β-phase, which yields larger amount of β-phase being formed for the system in equilibrium. While the Cu/Zn-ratio of CW511 resulted in higher thermodynamic stability compared to CW626, it did not result in any visible β-phase precipitating in CW511. In contrast, β-phase clearly precipitated in CW626 and CW625. This further supports that the absence of β-phase in CW511 is not related to the stability of β-phase, but the speed in which it is formed.

5.1.4 Impact of electrolyte polishing

In sample CW625-300°C-1000h, β-phase was clearly visible in a pattern that indicated that it had precipitated along the grain boundaries, as illustrated in Figure 26. However, upon investigating the grain boundaries in the sample further by the use of SEM-EBSD, large unindexed areas were found instead, which could possibly be translated as vacancies in the topography. Thus, dissolution or corrosion of the β-phase during the electrolyte polishing may be attributed to the absence of β-phase. Figure 44 and Figure 45 implies that these unindexed areas along the grain boundaries were either rich with Cu-content or rich with Zn-content. The fact that Zn-enriched areas overlap with clusters of β-phase signals, as illustrated in
Figure 45, lends support to the hypothesis that these areas were once occupied by β-phase. It is not known how the electrolyte etches the β-phase during the electrolyte polishing or what parameters control the etching outcomes. In theory [10], the applied high voltage, the turbulent flushing as well as no intentional additions of Cu and Cl in the solution, should simply dissolve the surface. So it is possible that an unintentional error has been committed during the polishing that has resulted in β-phase being subject to selective dezincification or selective etching.

5.2 Precipitation of stoichiometric intermetallic phases

5.2.1 As-precipitation

The experimental results imply that As-enriched areas in the samples have precipitated as the intermetallic particles AlAs (for CW625 and CW626) or FeAs (CW511). The literature [1] and thermodynamic phase property diagram in Figure 24 – Figure 25 supports this, that precipitated As-rich phases should appear as intermetallic particles. The literature specifically mentions that they should precipitate in the Cu-Zn matrix [1], preferably along grain boundaries. The experimental samples displayed that As-enriched areas did indeed precipitate along grain boundaries, but in addition to this also precipitated adjacent to other defects, including Pb-particles and twins, as observed in Figure 42. This could be for same reason as why they precipitate in grain boundaries, which is due to higher lattice disorder which allows for As-atoms to diffuse faster, allowing the transformation to proceed faster. Since both Pb and twins provide lattice disorder they should provide suitable sites for nucleation as well.

Furthermore, the observed trend was that EDS-signals from As consistently overlapped with unindexed areas in the secondary electron image, as observed in Figure 32 and Figure 38. Since unindexed areas could be translated as vacancies in the topography, this could imply that As-particles previously present in the microstructure were either partly dissolved or that the areas on which the As-particles nucleated were dissolved, thus leaving slight residue of As-particles detectable by the EDS-analysis.

5.2.1.1 As-particles – Corrosion properties – correlation

All samples in which the average dezincification depth has occurred to a significant amount, such as CW625-400°C-1000h, contained a significant amount of As-particles. In contrast, samples with low average dezincification depth, such as CW626-250°C-1000h, contained much lower amounts of As-particles. These results indicate that increased presence of As-
particles is significantly correlated to increased average dezincification of the material. This is supported by the literature, which describe that presence of As-particles deplete As from the α-phase, thus making it more susceptible to dezincification [1].

It was also observed that CW625-300°C-1000h with a heat treatment that resulted in both precipitation of β-phase and As-particles resulted the largest average dezincification depth. This indicates that precipitation of β-phase in conjunction with precipitation of As-particles can contribute to larger dezincification depths compared to when merely the precipitation of As-particles is the cause of the dezincification such as CW625-400°C-1000h.

5.2.1.2 As-particles – HT – correlation

When studying the impact of the heat treatment, it was observed in the experiments that the amount of As-particles precipitated in the sample with no heat treatment was less compared to the samples with merely heat treatment post-β-annealing. The indication of the results is that the As-particles precipitated as a result of the additional heat treatment, as opposed to existing in the microstructure prior to it.

When comparing the experimental results to the thermodynamic calculations, there are some phases that are notably absent, including FeCu₂AsSb. According to the property diagram, this phase should precipitate at 400°C. However since the EDS-analysis never displayed simultaneous overlap between enriched areas of As, Fe, Cu and Sb, there is an indication that these particles do not exist.

This infers that the FeCuAsSb-phase either:

- Never appeared in the microstructure during the heat treatment
- Reverted back to either AlAs or FeAl during the cooling procedure
- Was undetected by the instrument using instrument settings of this investigation
- Was removed by etching artefacts in the sample preparation procedure

The implications that the FeCuAsSb-phase never appeared in the microstructure are that the data used to calculate phase-property-diagram in Thermo-Calc is flawed or that the formation of FeCuAsSb-phase is a slow process.

The fact that not all elements, such as Cr or Si which interact with Fe according to the experimental results, are represented in the database utilized to calculate the phase-property-diagram, lends support to the implication that the phase-property-diagrams are displaying inaccurate representations in some aspects of the microstructure. However, since the diagram
was able to predict some information accurately, such as appearance of Fe$_2$P, there is no clear indication of the extent of the inaccurate aspects of the diagram.

Furthermore, one has to consider that the formation of phases is controlled by the kinetics of the reactions in addition the thermodynamic stability of the phases. In this regard, there is a slight possibility that formation of FeCuAsSb is too slow to form a detectable amount after 1000h or that it happens so quickly that it can revert back to FeAl or AlAs during the cooling procedure. However, there exists no data regarding the possible reactions that control formation FeCuAsSb and their kinetics. Thus no accurate conclusion can be expressed in this aspect of the study.

5.2.2 P-precipitation

P-enriched areas appeared consistently in the EDS-study of the samples. As exemplified in Figure 36, P-enriched areas often overlapped with Fe-enriched areas and appeared in unindexed areas in the secondary electron image. However, their frequency of appearance was significantly higher in the electrolyte polished samples compared to the OPS-polished samples. Furthermore, in the electrolyte polished samples they also overlapped with Pb-particles to a higher degree.

It should be mentioned that the electrolyte polished samples have been exposed to phosphoric acid during the polishing procedure. For this reason it is very possible that the additional P-enriched areas in the electrolyte polished samples include residue from the sample preparation procedure, i.e. chemical artefacts.

Since the OPS-polished samples do not include aggressive etching with phosphor, it is less likely that the exhibited P-enriched areas in those samples are chemical artefacts from the sample preparation procedure. This is supported by the thermodynamic calculations, as displayed in Figure 23 – Figure 25, which accurately predicts that the phase Fe$_2$P should precipitate. Furthermore have other studies [11] have found that phosphorus reacts with tramp elements, such as Fe to form Fe$_2$P-particles in similar alloys.

5.3 Chloride-citrate solution influence

The depth of the intergranular attack (IGA) yielded by exposure to chloride citrate solution for 100h is evaluated in this section.

As displayed in Figure 20, Figure 21 and Figure 22, the samples of all the alloys heat treated for 2h display that with increased heat treatment temperature the depth of the IGA decreases.
The samples heat treated for 1000h display the opposite trend; decreasing corrosion depth as the temperature increases, i.e. the alloy heat treated for 1000h becomes more resistant to IGA as the temperature increases.

When comparing the variation in pH to the amount of solution left after 100h, it is clear that the decrease in pH is a result of evaporated water, as exemplified in Figure 53. The difference in amount of evaporated water is a result of the placement of the solution container and how exposed it was to forced air convection, which unintentionally accelerates the evaporation process of the water in the solution. However, there was no clear correlation between the solution pH and the depth of IGA, as displayed in Figure 20, Figure 21 and Figure 22.

![Figure 53: The pH-value of the chloride-citrate solution compared to solution volume left after the corrosion test.](image)

The resulting IGA-depth from exposure in chloride-citrate solution is compared to the resulting dezincification depth from the standardized testing method in Figure 54, Figure 55 and Figure 56. As discussed in the previous sections, there were indications that the number As-enriched areas in samples heat treated at 1000h increased as the temperature increased. In the previous section it has been implied that increased number of As-enriched areas, i.e. larger amount of As-depleted α-phase, yield higher corrosion depth. The corrosion results based on the exposure of the chloride-citrate solution however, implies that increased presence of As-
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Enriched areas yield smaller depth of IGA. This does not coincide with the established theories regarding the dezincification mechanisms in brass or the results from the standardized dezincification test. Since the heat treated samples exposed to the IGA-sensitive chloride-citrate solution consists of the same composition and heat treatment as the samples exposed to the standardized copper chloride solution, then it is probable that there is a fundamental difference in the way that the respective solutions react with the various phases in the brass alloy. It is also not clear how the solution reacts on grain size and amount of twins in the microstructure. The results acquired in this study are however not enough to identify this fundamental difference, since it has merely focused on the presence of β-phase and As-enriched areas.

It should be noted that the report by Mazza and Torchio [14] that was used as a template for this experimental study did not provide a detailed explanation of how the IGA-depth has been measured in the light optical microscope. Thus, there is a possibility that the experiment was not successfully reproduced due to a misconception of the experimental details.

Figure 54: Graph displaying the standardized dezincification test result compared to the non-standardized depth of IGA in the alloy CW625.
Figure 55: Graph displaying the standardized dezincification test result compared to the non-standardized depth of IGA in the alloy CW626.
Figure 56: Graph displaying the standardized dezincification test result compared to the non-standardized depth of IGA in the alloy CW511.
6 Conclusions

Three alloys of single α-phase brass were heat treated with extreme durations to promote precipitation of detrimental phases contributing to dezincification in order to map how these phases impact the dezincification. These three alloys were: CW511 (lead-free), CW625 (low-lead) and CW626 (low-lead). The heat treatment was performed at 2h, 10h, 100h and 1000h within temperatures that are associated with annealing and recrystallization of said brass alloys; 250°C, 300°C, 350°C and 400°C. From the investigation, the following conclusions were conceived:

1. The considerably low dezincification of CW511 could be linked to the absence of β-phase and lower amount of AlAs-particles compared to CW625 and CW626, regardless of heat treatment. The lower amount of Al and Fe in the composition of CW511 was concluded to be the reason for this.

2. The difference in dezincification properties between CW625 and CW626 were found to be a result of different amount of β-phase in their respective microstructures. The higher amount of β-phase in CW625 could be related to its lower Cu/Zn-ratio using thermodynamic calculations. The amount of AlAs-particles between the two heat treated alloys was found to be comparable, and thus not a factor contributing to the difference in dezincification between the two alloys.

3. In samples heat treated for 1000 hours, precipitation of β-phase in CW625 and CW626 was the most significant at 300°C followed by 350°C, 250°C and lastly 400°C. At 400°C it was not observed by any circumstances and at 250°C there were merely slight indications of β-phase appearing. The amount of AlAs-particles in CW625 and CW626 increased as the annealing temperatures increased up to 400°C. In addition, the intermetallic particles were found to form on grain boundaries, twins and lead-particles, with no clear preference, using the EDS-detector and EBSD-camera.

4. Thermodynamic calculations implied that the absence of β-phase in CW511 was a result of either error in the thermodynamic database or very slow formation of the phase. The latter could be linked to absence of Al or Fe in the composition, i.e. micro alloying with Al or Fe accelerates the formation of β-phase in the current alloys in addition to promoting formation of intermetallic As-particles.
5. The depth of intergranular attack in samples exposed to non-standardized chloride-citrate solution was not comparable to the standardized dezincification test. Furthermore, the results could not be correlated to amount of β-phase or As-particles.
7 Future work

- Why the area in sample CW625-400°C-10h with fine grain size was so selectively sensitive to dezincification, especially for low heat treatment durations, was never understood in this study and should be investigated further. It provides an interesting prospect in that grain size and recrystallization may have a significant impact on the depth of dezincification. Further investigation in this area and CW625-400°C-1000h would especially assist the industry since they normally use heat treatment durations below 10 hours.

- This study further cements that precipitation of AlAs-particles is detrimental for dezincification of brass. However, there exists no data regarding the reactions that control the how fast the formation of these intermetallic occurs. Further investigation of this subject would help to determine why some intermetallic As-phases predicted in theoretical calculations, such as FeCuAsSb, do not appear in the experimental samples. Furthermore, an EDS-analysis of a sample with lower HT-duration, such as 2h, would also assist in mapping the kinetics of the As-particles.

- Since there was no β-phase investigated for samples heat treated for lower heat treatment durations, such as 100h, it is not clear how fast the β-phase forms in the alloys. This is a relevant point to investigate in order to provide a reason for why corrosion occurred in samples heat treated for lower durations.

- The precipitations of Fe-particles in CW625 and CW626 follow a similar trend as the As-enriched areas, in terms of where they appear and their amount as a function of annealing temperature. How their appearance is correlated to the dezincification performance of the alloys is a subject to further reflection and investigation.

- There is no explicit reason that explains why the samples with longer HT-duration exposed to chloride-citrate solution display lower IGA-depth compared to the samples with lower HT-duration. Understanding this can increase knowledge of how the corrosion mechanisms function differently with respect to different corrosive mediums. This is relevant in order to further understand the application limitations in which brass can be used as an industrial material.

- How the chloride-citrate solution specifically interacts with β-phase is not conclusive in this study since the data points in samples which had the amount of β-phase investigated using light optical microscope were not exposed to the chloride citrate
solution. Mapping the amount of β-phase to the heat treatment time, temperature and IGA-depth can fill this knowledge gap.

- In this study, it is heavily implied that the electrolyte polished samples have lost a lot of valuable information, such as appearance of β-phase, due to unintended etching effects. In addition, OPS-polished samples displayed scratchy surfaces with deformed grains due to the mechanical procedure of the polishing, which limits the accuracy of EBSD-analysis. Further research is recommended to be invested in finding alternative methods of polishing brass samples, that can display information of crystal orientation and chemical analysis with minimum amount of chemical- and crystal orientated artefacts.
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9 References


