Corrosion of brass in drinking water with high alkalinity

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Summary

In Danish drinking water installations, brass has been the most commonly used material for fittings such as stop valves and control valves; dezincification resistant (DZR) brass of the type CuZn36Pb2As being the dominating alloy. DZR brass has traditionally been considered sufficiently corrosion-resistant to be used in all Danish water types, and previous experience has been good. However, today, an increasing number of severe water damage caused by corrosion of DZR brass in areas with hard, high conductivity ground water has increased the focus on corrosion of copper alloys and, as a consequence, recommendations have changed. In the Copenhagen area and other areas with similar water quality, it is now recommended to use fittings of gun metal or stainless steel (AISI 316 or better).

This paper focuses on examples of failures leading to the changed recommendations and the technical methodology including scanning electron microscopy and metallographic examinations applied to study brass corrosion. Examinations include failure analyses and condition assessments of brass fittings from real drinking water installations throughout the Copenhagen area. In alfa-phase DZR fittings, intergranular corrosion rates ranging from 50-300 µm/year were observed. In fittings with coherent beta-phase taken from the same installations, selective dezincification values of up to approximately 100 µm per year were observed. The appearance of dezincification attacks was strongly dependent on the microstructure. In failed DZR fittings, the cause of failure was stress corrosion cracking (SCC) promoted by notch-shaped intergranular corrosion attacks. In most cases, failure had occurred after less than five years of operation.

Examinations confirm that the traditional copper alloys have unacceptably short life expectancy in the hard, high conductivity water types found in Denmark. A major reason is believed to be that the preferred pipe material has changed from hot-dip galvanised steel to stainless steel and plastic.

1 Introduction

1.1 Copper Zinc alloys for drinking water

Brass is the common denominator for a large variety of copper-zinc alloys with more than 50 % copper. The main types of brass are defined by the alloy crystal structure:

- α-brass with a copper content above approximately 63 %. α-brass has single phased micro structure with $\alpha-$crystals only. Zinc is found as solid solution in copper.

- $\alpha+\beta$-brass with copper content between approximately 54-63 %. $\alpha+\beta$-brass has a two-phased microstructure with $\alpha+\beta-$crystals.

- β-brass with a copper content between approximately 50-54 %. β-brass has single-phased microstructure with β-crystals only.

The microstructure is primarily governed by the relation between copper and zinc but for many brasses heat treatment, cooling rate and annealing temperature may affect the microstructure considerably. As an example, one of the most commonly used DZR free turning brasses, CuZn36Pb2As, can end up with unacceptable amounts of coherent β-phase if heat treated incorrectly, thus being susceptible to selective dezincification. The relation between copper- and zinc-content and the crystal structure of brass can be seen from figure 1, Copper-zinc phase-diagram.

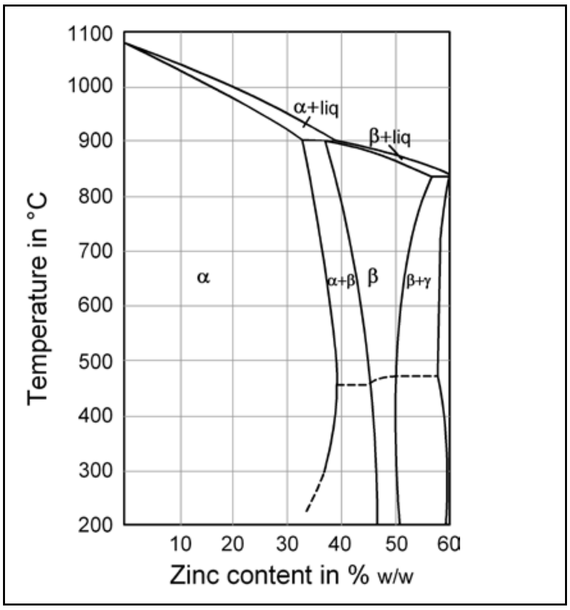

Figure 1. Copper-zinc phase-diagram

The properties of brasses may be controlled even further by adding additional alloying elements. Examples of alloying elements found in commercially available brasses are aluminium, arsenic, cobalt, iron, manganese, nickel, phosphor, lead, silicon and tin. Changes of both mechanical and corrosion properties due to alloying constituents can be quite significant.

In drinking water the number of alloys used in practice is limited. The two types of brasses most widely used are $\alpha+\beta-$brass with approximately 58-60 % copper and DZR brass, which is $\alpha-$brass with approximately 63-64 % copper alloyed with small amounts of arsenic (typically 0.02-0.15 %). Arsenic is added to inhibit dezincification of the $\alpha-$phase. In Denmark the most commonly used of the two above mentioned is DZR brass with arsenic used as inhibitor. More complex copper zinc alloys are finding their way into the market but long term practical experiences from drinking water installations are still limited.

In table 1 examples of the brasses used most often in Danish drinking water installations are shown. The examples are all so called free turning brasses that have been added lead (1.7-3.5 %) to enhance the cutting properties. Alloys developed for sand casting and hot working may hold small variations in composition just like various standards can have various limits for the constituents. However, for most reasons the corrosion properties will be comparable.

Table 1: Typical compositions of brasses used in the plumbing industry (DS/CEN/TS 13388:2008).

Material designation		**Composition in w%**														
Symbol	**No.**	Element	Cu	Al	As	Co	Fe	Mn	Ni	P	Pb	Si	Sn	Zn	Others total
CuZn36Pb2As	**CW602N**	Min. Max.	62.5 64.0	- 0.05	0.02 0.15		- 0.1	- 0.1	- 0.3		1.7 2.8		- 0.1	Rem. -	- 0.1
CuZn39Pb3	**CW614N**	Min. Max.	57.0 59.0	- 0.05	- -		- 0.3	- -	- 0.3		2.5 3.5		- 0.3	Rem. -	- 0.2
CuZn40Pb2	**CW617N**	Min. Max.	57.0 59.0	- 0.05	- -		- 0.3	- -	- 0.3		1.6 2.5		- 0.3	Rem. -	- 0.2

1.2 Corrosion of brass in drinking water

Corrosion processes on brass are strongly dependent on:

- Water quality
- Alloy composition and micro structure
- Processing (heat treatment, casting, machining)
- Geometry of the finished product
- Contact with other metals.

In Denmark drinking water is untreated ground water often with high carbonate hardness and high conductivity. In table 2 parameters for typical water qualities in the Copenhagen area are listed.

Table 2: Parameters for typical water qualities in the Copenhagen area.

Parameter		**Value**
pH		7.2 - 7.6
Conductivity, 25 °C	mS/m	80-100
Total hardness	°dH	15-30
Hydrogen carbonate	mg/l	300-450
Chloride	mg/l	50-150
Sulphate	mg/l	50-150

In water types such as the ones found in the Copenhagen area corrosion is a challenge and have to be considered carefully when choosing materials for drinking water installations. Possible corrosion forms to be considered when choosing between copper alloys for use in drinking water installations are listed in table 3 below.

Table 3: Corrosion forms to be considered when selecting copper alloys.

Alloy	**Corrosion forms at risk**
$\alpha+\beta-$beta brass with 58-60 % Cu e.g. CuZn39Pb3 / CuZn40Pb2	Dezincification Stress corrosion cracking (erosion corrosion)
DZR brass e.g. CuZn36Pb2As	Stress corrosion cracking Intergranular corrosion (erosion corrosion)
Gunmetal e.g. CuSn5Zn5Pb5	Uniform corrosion (erosion corrosion)

Copper and its alloys in general show relatively good corrosion resistance in drinking water and DZR brass has been considered sufficiently resistant for all Danish water types. However over the last years a substantial increase in corrosion damages has been observed in areas with hard water types with high conductivity. Corrosion attacks occur from the water side and in DZR brasses failures are caused by SCC leading to severe water damages. A number of reasons for the increase in corrosion failures are suggested. An important reason to be considered is the use of more corrosion resistant pipe materials.

Traditionally the preferred pipe material for large drinking water installations in Denmark has been hot-dip galvanised steel. However changes in installation practice due to legislation, demands for better functionality and changes in consumer behaviour have led to unacceptable corrosion problems with hot-dip galvanised steel. As a consequence the preferred pipe materials have changed to polymers and stainless steel over the past 10-15 years.

The influence on corrosion due to change in pipe materials is illustrated in figure 2.

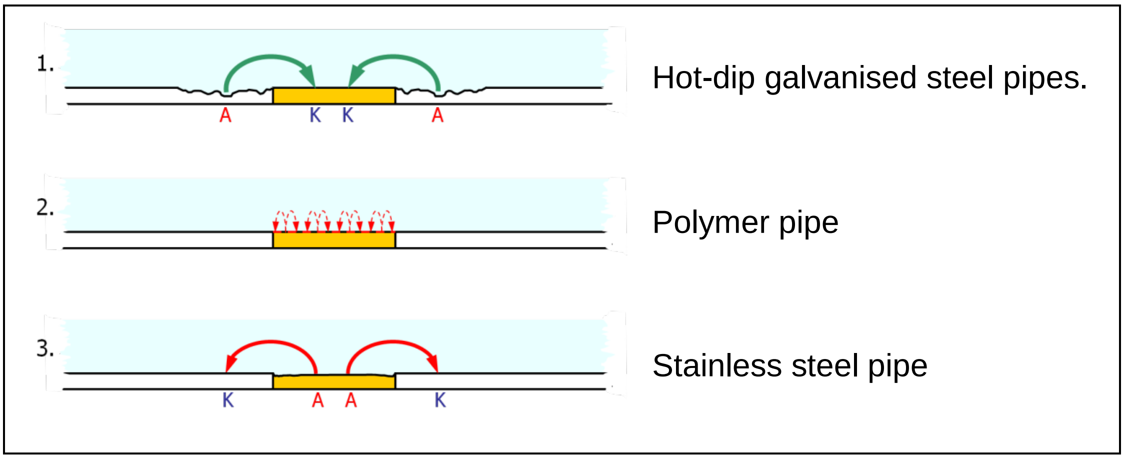

Figure 2. Corrosion of small brass parts in contact with different pipe materials. **1:** Small parts of brass are cathodically protected due to the contact with the less noble hot-dip galvanised steel pipes. Corrosion on the hot-dip galvanised steel pipe is enhanced due to bimetallic corrosion. **2:** Polymer pipes do not affect corrosion of the brass part. Corrosion is governed by the corrosion properties of the bras part itself. **3:** Stainless steel suitable for use in drinking water is more noble than brass. Corrosion of the brass part will be slightly enhanced due to bimetallic corrosion.

Bimetallic corrosion on brass parts in contact with stainless steel is enhanced in water types with high conductivity due to the larger area included in the cathodic reaction.

Examples of corrosion in brass fittings and valves will be given in the following sectors to illustrate dezincification, intergranular corrosion and stress corrosion cracking.

2 Dezincification as observed in drinking water installations in the Copenhagen area

In α+β-brasses dezincification may occur in the zinc-rich β-phase dissolving the β-phase selectively. During dezincification both copper and zinc dissolve. Copper redeposits leaving the original shape more or less intact but now porous and without the original mechanical strength. In soft water types dezincification often forms pure white and very voluminous zinc corrosion products. Subsequent dezincification in these water types is often referred to as meringue corrosion. In most Danish water types dezincification usually form very thin layers of discoloured corrosion products.

In figure 3 examples of dezincification in brass fittings from drinking water installations in the Copenhagen area are shown.

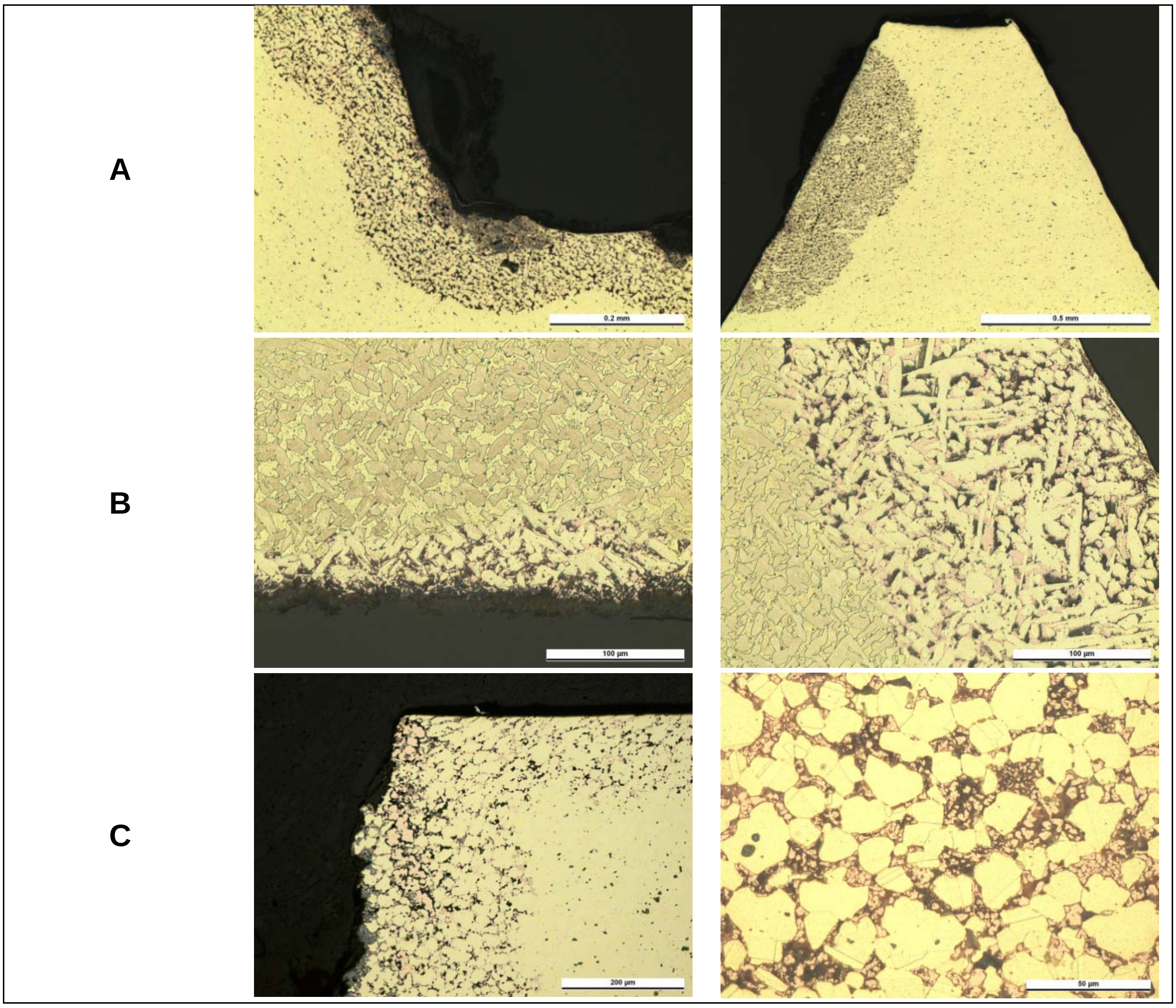

Figure 3. Examples of selective dezincification of β-phase in α+β-brasses. Examples A and B have been examined as part of condition assessments of drinking water installations. Example C has been examined due to breakdown of the fitting. **A:** Cross section of a hot worked DN20 ball valve, α+β-brass. The valve was mounted in a 2-3 years old installation for warm water and in contact with stainless steel pipes (AISI 316). 100-250 μm deep selective dezincification attacks of the β-phase are observed. **B:** Cross section of a 3 year old threaded fitting for mounting water meters. The fitting have been mounted in the installation for cold water and in contact with other brass fittings. 75-200 μm deep selective dezincification attacks of the β-phase are observed. **C:** Cross section of a 11 year old DN15 ball valve, leaded α+β-brass. Selective dezincification attacks of the β-phase are observed. β-phase is estimated to constitute approximately 30-35 %.

Rapidly occurring failures due to selective dezincification in α+β-brasses are no longer common in Denmark. The main reason being that the α+β-brasses have been replaced by DZR brasses. In cases where α+β-brasses are used in water types similar to the water quality in the Copenhagen area corrosion rates of up till approximately 100 μm are observed. Higher corrosion rates may be observed in crevices and below diffusion-open gaskets.

3 Intergranular corrosion in DZR brass as observed in drinking water installations in the Copenhagen area

In connection with the increased use of polymer and stainless steel pipes very fast intergranular corrosion has been observed in parts of DZR brass of the type CuZn36Pb2As when installed in hard water types with high conductivity similar to the water types found throughout the Copenhagen area. During the first years of operation corrosion rates of 100 μm per year are not uncommon and corrosion rates of up till 300 μm per year have been observed.

Some investigations suggest that the corrosion rate decreases after a period of time. However further investigations and preferably test rig experiments have to be carried out to fully confirm this.

Figures 4 and 5 show examples of intergranular corrosion attacks on DZR fittings taken from drinking water installations in the Copenhagen area.

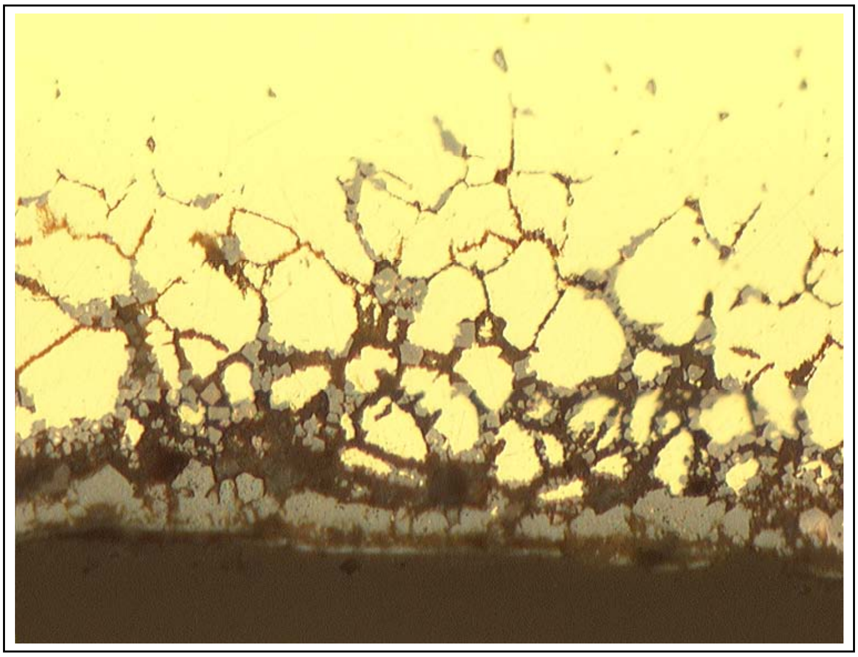

Figure 4. Cross section of nickel plated stop valve examined after 1 year of operation in the Copenhagen area. The valve has been assembled with a stainless steel fitting in an installation for cold drinking water.

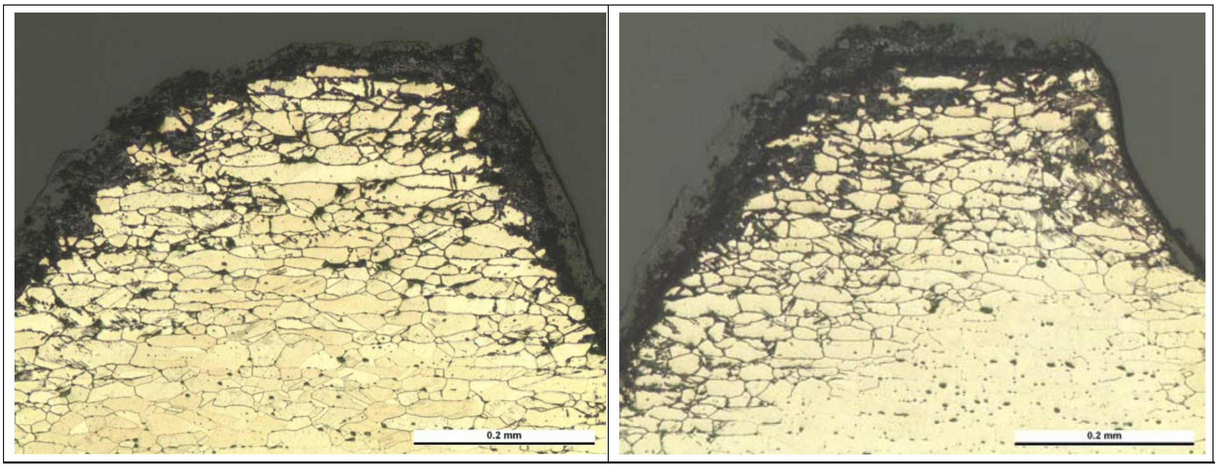

Figure 5. Examples of intergranular corrosion as seen in the Copenhagen area. Cross section of DN 15 nipple-muff (left) and DN15 stop valve (right) taken from the same installation after 2-3 years of operation. Both showing 200-300 μm deep intergranular corrosion attacks. Both parts have been assembled with other brass fittings in an installation for cold drinking water.

The precise mechanism of intergranular corrosion attacks observed on DZR brass is not fully understood. One widely accepted explanation is that impurities form inter-metallic compounds with arsenic that precipitate in the grain boundaries leaving an arsenic depleted zone around the grain boundaries, which is susceptible to dezincification [1]. Impurities of iron, manganese and nickel are suspected to have the above effect. Recommendations are to use DZR brass with iron contents below 0.1% and for the manufacturer to take these mechanisms into account when heat treating products.

Figure 6. Clamp ring fitting after 5-6 years of operation. Fracture on the bushing due to intercrysalline corrosion.

Despite the high corrosion rates Intergranular corrosion is seldom the direct reason for failures. One exception is bushings used in clamp ring fittings. These bushings often have very thin wall thickness and will in many cases corrode from both sides.

An example can be seen in figure 6. Failures of bushings in clamp rings seldom give rise to severe water damages.

Even though intergranularintergranular corrosion in DZR brass fittings and valves are seldom the direct reason for failures the reduction of wall thickness can increase tensile strength which together with the notch shaped corrosion attacks promote SCC.

4 SCC in DZR brass as observed in drinking water installations in the Copenhagen area

SCC is caused by a specific chemical environment in combination with the presence of tensile stress.

Tensile stress in brass products for use in drinking water installations may originate from production and as a result of mounting the product in the installation. Depending on the level of tensile stress present the composition and harshness of chemical environments that can cause SCC will differ. Historically the best known chemical compound to cause SCC on brass is ammonia. Many environments can be polluted with small amounts of ammonia e.g. originating from paints, cleaning agents, toilets and even insulation materials.

In the past SCC on brass in drinking water installations almost exclusively occurred from the outside on brass mounted in installations for cold drinking water where condensation keeps the outer surfaces moist and able to absorb any ammonia vapours if present.

Over the past years a significant increase in failures of DZR brass due to SCC has been observed. Failures occur from the water side and in nearly all cases SCC has been promoted by intergranular corrosion. SCC is observed in installations for both warm and cold water but primarily in areas with hard, high conductivity ground water. DZR brass fittings and valves with small dimension, DN15 and DN20, are overrepresented.

In one case an apartment building experienced more than 100 SCC failures in small DZR ball valves over a two year period after 3-5 years of operation. Examined ball valves were in conformity with standards for alloy composition and microstructure.

Fortunately such extreme cases are rare but due to the severe water damage caused by SCC and the general increase in failures DZR brass is no longer considered sufficiently corrosion resistant in areas with hard, high conductivity ground water comparable to the water quality found in the Copenhagen area. As a consequence it is now recommended to use fittings of gun metal or stainless steel (AISI 316 or better).

Examples of SCC in DZR brass may be seen in figures 7 and 8.

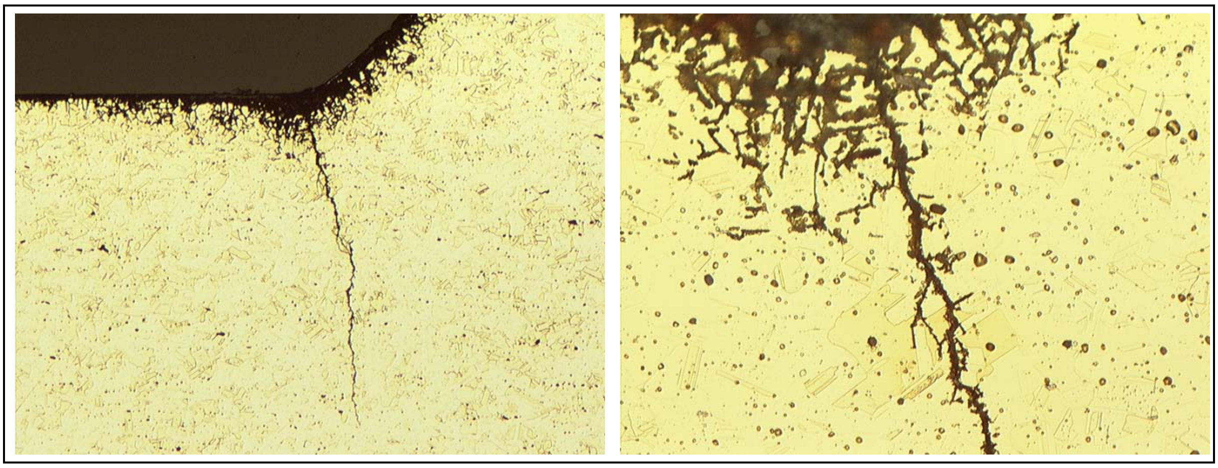

Figure 7. Cross section of DZR nickel plated stop valve examined after 1 year of operation in the Copenhagen area. The valve has been assembled with a stainless steel fitting in the installation for cold drinking water. Intergranular corrosion attacks from the water side in combination with high tensile stress have led to SCC.

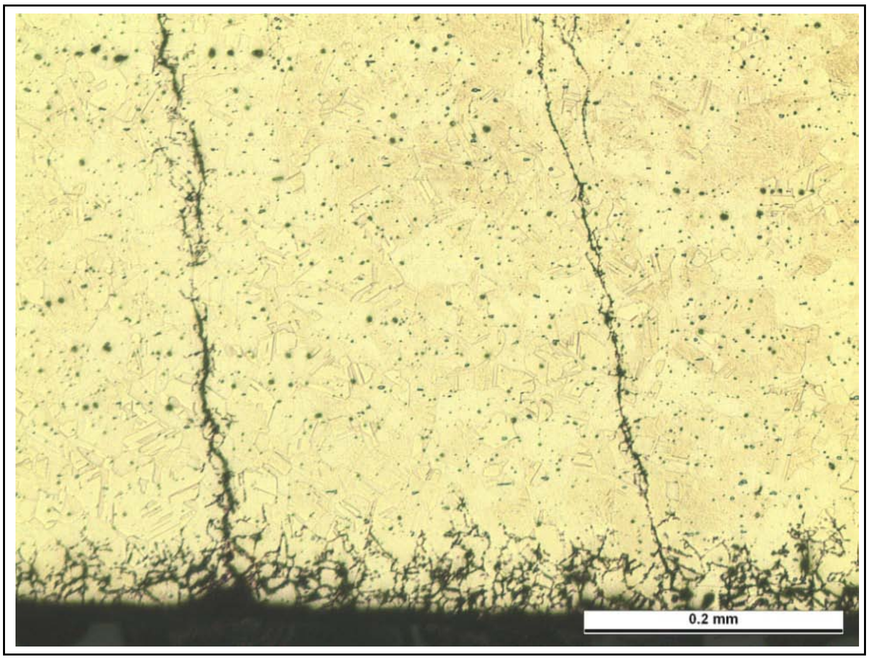

Figure 8. Cross section of a DZR stop valve taken from an installation for warm drinking water after 2-3 years of operation. Investigated due to failure. The cross section shows two cracks due to SCC from the water side. Intergranular corrosion attacks of app. 100 μm are observed on the surface.

The nature of failures due to SCC makes it possible for layman to mistake the failure with failures due to mechanical overload. In many cases this justifies a thorough examination to ensure legal responsibility is not incorrectly placed on the plumber.

Figures 9 and 10 show examples of thorough analyses of valves that failed due to SCC. Elements such as visual examination of the failed valve and fracture, examination of the fracture in SEM and examination of cross sections in light optical microscope before and after etching are important to define the cause of failure. In some cases it can also be beneficial to make an analysis of the exact alloy composition.

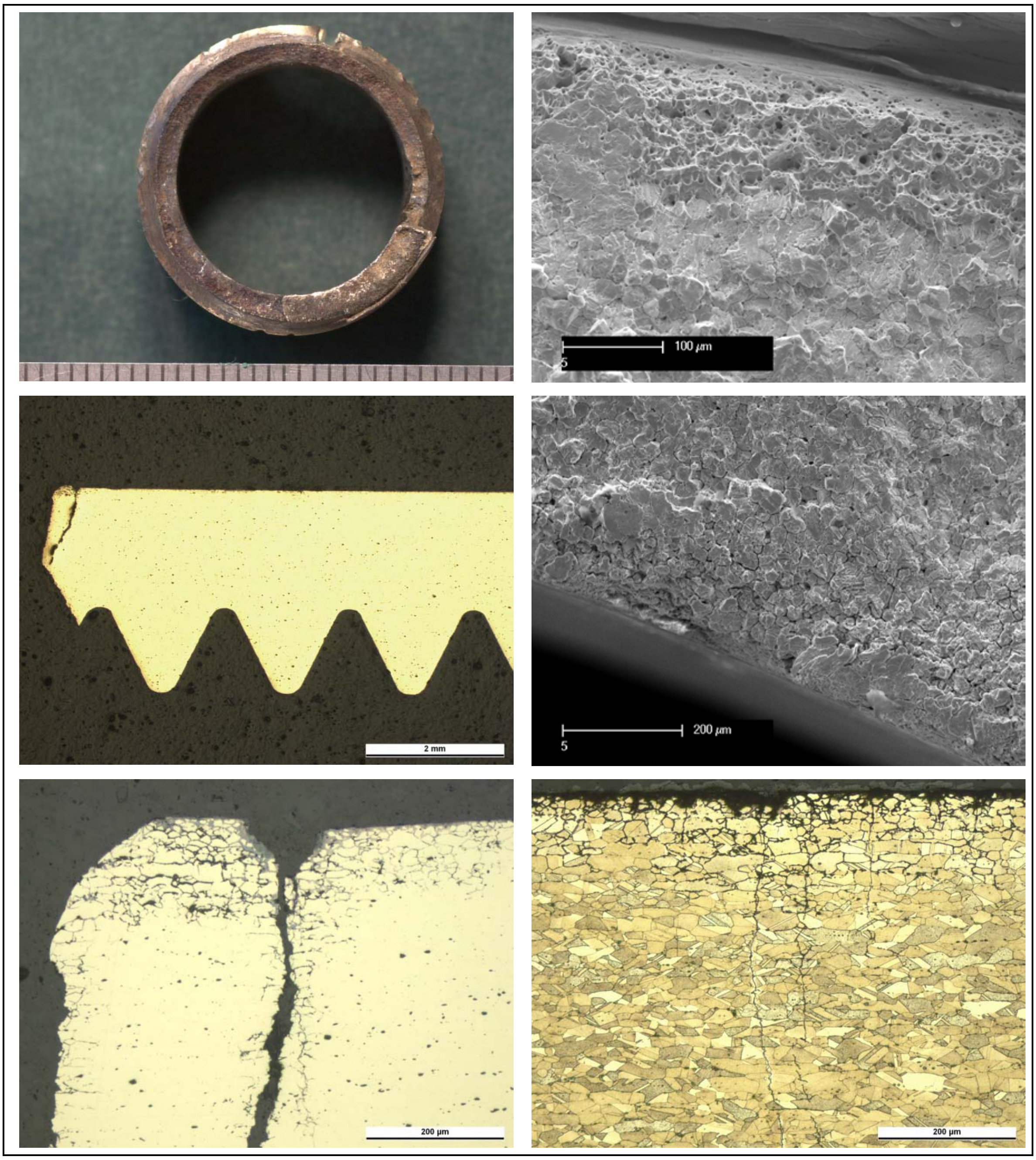

Figure 9. Examination of failed DN20 drain valve from a 10 year old installation with stainless steel pipes (AISI 316). **Top left:** Fracture surface, overview. No sign of plastic deformation. **Top right**

and middle right: SEM images of the fracture surface. The image, middle right, shows an intergranular fracture from the water side. Closer to the outer surface, top right, the fracture gradually shows more transgranular characteristics. **Middle left:** Cross section of thread, overview. The fracture is seen on the left. **Bottom left:** Cross section of the thread. The fracture can is observed on the left. Parallel to the fracture another stress corrosion crack is observed. On the water side intergranular corrosion attacks of approximately 200 micrometer can be seen. **Bottom left:** Cross section after etching shows α-structure and no visible β-phase. Deep intergranular corrosion attacks are observed on the water side as well as several stress corrosion cracks.

5 References

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