Corrosion Testing of Silver-Brazed Stainless Steel Joints in Tap Water

Chloride concentrations in tap water influenced the corrosion rates of two brazing filler metals but had little effect on another.

BY H.-D. STEFFENS, B. WIELAGE AND W. BRANDL

ABSTRACT. Three different silver-based brazes (B-Ag 56 Cu-In-Ni, B-Ag 60 Cu-Sn and B-Ag 72 Cu) were investigated with respect to their corrosion behavior in tap water. As a result, it was found that the chloride concentration possesses a significant influence on the resistance of the joints produced with the filler metals B-Ag 56 In-Ni and B-Ag 60 Cu-Sn. While the former can be used in water up to 50 mg Cl⁻/L without showing knife-line attack, the latter is feasible for higher chloride concentrations. For the braze B-Ag 72 Cu, it was determined that an increasing Cl⁻ content does not associate with a higher corrosion rate.

Introduction

The corrosion behavior of stainless steels and their brazed joints have been, and continue to be, the subject of numerous investigations. Due to the heavy increase in water consumption and the accompanying increasing pollution of effluents, the corrosive aggressiveness of the waters carried in sanitary installations will increase over the next several years, at least in central Europe. The chemical aggressiveness of these media will, of course, vary widely, with pollution being heavy in densely populated industrial centers and less pronounced in predominantly agricultural and more thinly populated areas.

Experimental Materials

The material selected for the base metal was Cr-Ni-Mo-Ti 18-10 stainless steel. The brazing alloys used were B-Ag 56 Cu-In-Ni (620-730), B-Ag 60 Cu-Sn (600-720) and B-Ag 72 Cu (780) - Table 1.

Production of Brazed Joints

For the production of brazed joints, seamless cold-drawn pipe with an internal diameter of 15 mm (0.6 in.) and a wall thickness of 1.5 mm (0.06 in.) was used, brazing being done with braze fittings. The braze filler metal was available in wire form (thickness 1.2 mm/0.05 in.). Rings were made from the wire for brazing. Brazing was done with a fluxing agent in air for the first two brazes mentioned and in a vacuum furnace for the third. The joint clearance for the furnace brazed was set at 0.05 mm, and for brazing in air, a joint clearance of 0.1 mm was used.

The structure of the brazed joint produced with Braze B-Ag 56 Cu-In-Ni 620-730 is shown in Fig. 1. It is composed of three phases. The copper-rich α-phase in the brazed joint is visible in the form of large-area, dark regions and occurs at the base-to-braze interface as a coherently precipitated phase. The matrix consists of silver-rich α₁ phase (large, light-colored regions in Fig. 1). The finely precipitated phase in the matrix is the Ag-In β-phase.

Table 1—Chemical Composition of Brazing Alloys

<table>
<thead>
<tr>
<th>Brazing Alloy</th>
<th>Chemical Composition</th>
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<tbody>
<tr>
<td>B-Ag 56 Cu-In-Ni (620-730)</td>
<td>Ag 56 Cu 26 Sn 4 Ni 14</td>
</tr>
<tr>
<td>B-Ag 60 Cu-Sn (600-720)</td>
<td>Ag 60 Cu 30 Sn 10 Ni</td>
</tr>
<tr>
<td>B-Ag 72 Cu (780)</td>
<td>Ag 72 Cu 28 Ni</td>
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H.-D. STEFFENS, B. WIELAGE and W. BRANDL are with the University of Dortmund, Dortmund, West Germany.

the braze-to-base interface.

The eutectic structure of the silver-braze B-Ag 72 Cu 780 is shown in Fig. 3.

Methods of Investigation

To investigate the corrosion behavior of the brazed joint in Dortmund drinking water (Table 2), electrochemical tests were made. The influence of the chloride content of the water on the polarization behavior of the brazed joints was investigated. Chloride contents were varied from 25 to 500 mg/L.

In order to reproduce the conditions existing in pipelines in regard to oxygen content and flow patterns, an experimental device was used in which fresh water flowed over the specimen at a constant rate—Fig. 4.

Corrosion Testing Device

The work cell of the corrosion testing device is made of polyvinylchloride. A contact pin is provided whereby the specimen is connected to the work electrode via the anode rod. The auxiliary electrode is arranged in a circle around the work electrode. Potential measurement was made via the salt bridge probe with the aid of the reference electrode. For all measurements, a saturated calomel electrode was used as the reference electrode. Observation of the specimen during the test was made possible through the Plexiglas pane by means of a stereomicroscope. The electrolyte flowed through the work cell from end to end and the probe was positioned in the direction of flow. The rate of flow was variable.

The continuous, metered addition of sodium chloride solution required for variation of the chloride content was achieved with the aid of a micropump. Prior to the test, the specimens were ground and polished with diamond paste to a 1 μm finish.

Test Results

Experimental Results in Tap Water

The current density versus potential curves of the base metal Cr-Ni-Mo-Ti 18-10 stainless steel brazed with the three different silver brazes in tap water with a chloride content of 25 mg/L are shown in Figs. 5-7. For the purposes of comparison, the current density versus potential curve of the base material is also shown in these figures. The steady-state potentials of the brazed joints are, without exception, more positive than those of the base material. Appearance of the braze joint in its initial state at potential P1 alters during the polarization test at different potentials referred to as P2, P3, P4 and P5.

Figure 8 shows the change in the structure of the braze joint during the polarization test carried out on the Cr-
Fig. 5—Polarization curve of Cr-Ni-Mo-Ti 18-10 stainless steel/B-Ag 56 Cu-In-Ni joint in tap water

Fig. 6—Polarization curve of Cr-Ni-Mo-Ti 18-10 stainless steel/B-Ag 60 Cu-Sn joint in Dortmund tap water

Fig. 7—Polarization curve of Cr-Ni-Mo-Ti 18-10 stainless steel/B-Ag 72 Cu joint in Dortmund tap water

Fig. 8—Appearance of B-Ag 56 Cu-In-Ni brazed joint during electrochemical polarization. A—Initial structure at −400 mV; B—corrosive attack begins, +190 mV; C—brownish layer forms, +260 mV; D—corrosion grows into a dense, firmly adhering layer, +400 mV
Ni-Mo-Ti 18-10 stainless steel/B-Ag 56 Cu-In-Ni brazed joint.

The initial structure of the brazed joint (Fig. 8A) at -400 mV (Point P₁ on the current density versus potential curve — Fig. 5) begins to change from about +190 mV (Point P₂) onward. There are indications of corrosive attack on the α-Cu phase in the joint and at the braze-to-base interface — Fig. 8B. This incipient corrosion grows as the anodic polarization increases, which is associated with a steep rise in current density — Fig. 5.

With the fall of the current density at P₃ (Fig. 5) a brownish layer begins to form (Fig. 8C), with the formation completed at about +260 mV; the formation of this layer starts from the α-Cu phase. The renewed rise in current density from 260 mV onward (Fig. 5) is associated with an attack on the silver matrix (α₁-Ag-rich phase). As the α₁-Ag phase goes into solution, however, a dense, firmly adhering layer grows in these areas of the brazed joint — Fig. 8D.

The original structure of the brazed joint (Fig. 9A) changes from about +50 mV onward (Point P₂ in Fig. 6). The α-Cu phase sustains the initial corrosive attack — Fig. 9B. With increasing polarization, up to about 225 mV (Point P₃), there is a massive rise in current density. The incipient corrosion of the copper-rich phase intensifies and a layer begins to form from the α-Cu phase — Fig. 9C. At the highest current density of the polarization curve (at about 290 mV, P₄ in Fig. 6) the formation of a second layer begins — Fig. 10A. This layer covered the entire brazed joint at increasing polarization and exhibited no tendency to be flushed off — Fig. 10B. Figure 10C illustrates the strong adhesion of this layer after a minute’s polishing; a light-colored covering layer (top layer) was formed, which had grown beyond the edge of the brazed joint. In contrast to Braze B-Ag 56 Cu-In-Ni, only minor corrosive attack was detected on the remaining structure.

In polarizing the Cr-Ni-Mo-Ti 18-10 stainless steel/B-Ag 72 Cu brazed joint, some initial corrosive attack was noted at +25 mV (Point P₂ in Fig. 7). The appearance of the brazed joint at +25 mV is shown in Fig. 11A.

In the eutectic structure, the copper-rich solid solution is preferentially attacked. In the further stages of the current density versus potential curve, the current density drops. This drop is accompanied by the formation of a layer. The renewed steady rise in current density, which points to increased dissolution of the silver-rich phase, subsequently levels off slightly at about 210 mV. It is here that a further layer begins to form starting at the edge of the brazed joint (Fig. 11B) completely covering the brazed joint at 400 mV. Extended polishing proved incapable of removing this layer, indicating how firmly adhered it was.

In summarizing the test results of the Dortmund tap water, one can state that under these conditions of water composition and temperature, i.e., room temperature (Table 2), all three brazes exhibited good stability, with Braze B-Ag 72 Cu performing best. With this particular braze, the depth of attack was the lowest, while the top layer, which forms in the process, adheres firmly. No corrosive attack was noted on the base metal. While Braze B-Ag 56 Cu-In-Ni with the copper-rich α-phase does sustain some
corrosive attack, no knife-line attack was observed at the chloride ion concentrations used in this work.

**Experimental Results in Tap Water with Different Chloride Contents**

With the stepwise increase of the chloride content, Braze B-Ag 56 Cu-In-Ni showed increased corrosive attack in the brazed joint (Fig. 12) and knife-line attack for chloride ion concentrations from about 50 mg/L or higher.

Figure 13 shows the current density versus potential curve for this brazed joint at chloride concentrations in Dortmund tap water of 25, 100, 200 and 500 mg/L.

The curves hardly differ from one another up to chloride contents of 200 mg/L. However, the appearance of corrosion at the brazed joint is very diverse—Figs. 8D and 14.

At 25 mg/L chloride, no knife-line attack could be detected at the braze-to-base interface (Fig. 8D), and at 100 mg/L chloride, the interface has been partly dissolved, while at 200 mg/L chloride, it is completely dissolved—Fig. 14. This phenomenon is even more pronounced at the maximum chloride concent...
tent of 500 mg/L - Fig. 14. For these chloride concentrations, the current densities are, by comparison, considerably higher - Fig. 13.

The corrosive attack of Cr-Ni-Mo-Ti 18-10 stainless steel/B-Ag 60 Cu-Sn-brazed joints increased with increasing chloride content, too. The attack on the α phase, as well as the associated layer formation, undergone a shift towards more negative potentials. The same also applies to the corrosive attack on the silver-rich phase and the layer formation proceeding from it. Nevertheless, no preferential attack could be detected at the braze-to-base interface.

With the joint made with brazing alloy B-Ag 72, a phenomenon was found, as yet unexplained. At low (25 mg/L) and high (500 mg/L) chloride contents, firmly adhering layers form, which completely cover brazed joint. Yet, after polishing, they vary in appearance, suggesting differences in composition - Fig. 15.

At intermediate chloride contents (100 and 200 mg/L), only incomplete coverage of the brazed joint occurs (Figs. 16B and C), with the structure having been attacked only slightly.

Clarification of these phenomena, possibly attributable to the influence of chloride content on carbonate equilibrium, is the subject of further work.
Conclusion

The Braze B-Ag 56 Cu-In-Ni can be used in cold drinking water up to approximately 50 mg of chloride per litre. At higher chloride contents, increasing susceptibility of knife-line attack must be expected. According to present findings, this susceptibility is not due to the constant precipitation of the less noble α phase at the brazed joint, but rather to a very thinly formed intermediate layer, which still requires exact identification — Fig. 17. The preferred attack of this intermediate layer probably leads to the failure of the joint.

While the joint made with the Braze B-Ag 60 Cu-Sn is subject to stronger attack at rising chloride contents, no preferred attack at the base-to-braze phase boundary takes place. Hence this braze, on the basis of the electrochemical tests, can also be used in drinking water with higher chloride contents.

The test results obtained on the joints made with the Braze B-Ag 72 Cu indicate that an increasing chloride content of the electrolyte, e.g., tap water, is not necessarily associated with a higher rate of corrosion. The variations in the formation of the covering layer that were found here, are to be clarified in further research work by correlating electrochemical tests and the results of plant corrosion tests with surface-analytical measuring techniques, especially Auger Electron Spectroscopy. Since this method allows the composition of the layer with depth to be determined (by incremental removal of material by argon sputtering), inferences as to the formation mechanisms of the covering layers with regard to the polarization potential and water composition may be deduced.