Corrosion Resistance of New Copper Alloy Castings Registered in JIS H 5120:2016 Copper Alloy Castings

Hiroshi Yamada1, Masaaki Yamamoto1, Toshimitsu Okane2, Yoshiharu Kousaka3, Yoshiyuki Goto4 and Tomoki Ito5

1KURIMOTO, LTD, Osaka 559–0021, Japan
2National Institute of Advanced Industrial Science and Technology, Tsukuba 305–8564, Japan
3SAN-ETSU Metals Co., LTD, Tonami 939–1315, Japan
4Mitsubishi Shindoh Co., LTD, Sakai 590–0906, Japan
5Joetsu Bronz1 corporation, Joetsu 949–3112, Japan

Four kinds of dezincification corrosion resistance brass casting (JIS symbols CAC211, CAC221, CAC231 and CAC232) and two kinds of Bismuth bronze castings (JIS symbols CAC905 and CAC906) were suggested to Japanese Industrial Standards (JIS H2210, H5120 and H5121) as alloys applicable to tools related to water supply appliances. For the corrosion-resistant evaluation of those six new alloys (registered new materials), dezincification-corrosion test (ISO 6509-1981), erosion-corrosion test (jet-in-slit test) and stress-corrosion-cracking test were carried out, and the results were compared with JIS copper alloys (CAC203, CAC804, CAC902 and C3771). The dezincification corrosion resistance of the registered materials was better than CAC203 and equal to CAC804 and CAC902. In the erosion-corrosion test of the JIS copper alloys, CAC902 was excellent, followed by CAC804, C3771, and CAC203 (CAC902 >> CAC804 > C3771 > CAC203) in this order. Among the registered alloys, CAC211, CAC231, CAC905 and CAC906 showed good erosion-corrosion resistance equal to CAC902. The erosion-corrosion resistance of CAC221 and CAC232 was worse than CAC902 and equal or slightly better than CAC804. In addition, it was revealed that the erosion-corrosion resistance improved when tin was contained. In the stress-corrosion-cracking test, the stress-corrosion-cracking sensitivity of the registered materials was lower than C3771 and CAC203.

Keywords: dezincification corrosion, erosion-corrosion, stress-corrosion-cracking, corrosion resistance, lead-free alloy, copper alloy casting

1. Introduction

Recent amendment of water-quality standards in various countries has tended to strengthen the regulations against lead use globally. JIS H2202, H5120, and H5121, Japanese Industrial Standards related to copper alloys, have standardized several lead-free copper alloys such as bismuth bronze casting CAC902 and silzin bronze casting CAC804, as alternate materials of bronze casting CAC406 in amendments by 20091,2). Water supply instrument components to which these lead-free copper alloys are to be applied incorporate bronze and brass according to the usage environment. Therefore, evaluation of the corrosion resistance of candidate materials is an important factor when considering their conformity to the usage environment. Testing methods have been proposed that simulate various environments in the evaluation of corrosion resistance. Some examples are the dezincification test specified by ISO 6509, which is broadly used as a method of evaluating the corrosion resistance of copper alloys in a stationary environment. Other corrosion tests include erosion-corrosion tests that allow corrosion resistance evaluation under an environment with flow3–5) and the season cracking test as an evaluation method of stress corrosion cracking (SCC)6).

To date, brass castings of four types with improved dezincification property (CAC211, CAC2217), CAC231, and CAC232 in JIS H 5120:2016) and bismuth bronze castings of two types have been developed with reduced Sn and increased Zn (CAC9057) and CAC906 in JIS H 5120:2016) compared to the previous JIS (H 5120, H 5121, and H 2202). In 2016, these alloys are registered as applicable to water supply instrument components and similar uses. This article describes the corrosion resistance of six types of alloys that are newly registered (hereinafter, the new registered alloys) evaluated by ISO6509: 1981 dezincification test, erosion-corrosion test with a jet-in-slit tester8,9), and stress-corrosion-cracking test under ammonia atmosphere, in comparison to previous JIS copper alloys currently used as reference alloys for water supply instrument components.

2. Experimental

2.1 Test specimen

Table 1 presents chemical compositions of the new registered alloys and reference alloys used for this study. The new registered alloys of two kinds, A – nominal composition and D – composition prone to dezincification, and reference alloys of the nominal compositions were used for corrosion tests. Composition D of the new registered alloys was arranged to be prone to dezincification with the upper limit of the standard composition range of Al and Si of high zinc equivalent and the lower limit of Sn, P, Ni, Bi, and Sb, which are effective to suppress dezincification simultaneously. The reference alloys used were JIS H5120 silzin bronze casting CAC804 and bismuth bronze casting CAC902 widely used for water supply instrument components as lead-free copper alloys, and brass casting CAC203 and JIS H3250 forging brass bar C3771 as conventional brass alloys containing lead. Each test specimen was prepared using the fol-

---

*This Paper was Originally Published in Japanese in J. JFS 87 (2015) 830–835.
lowing procedure except for C3771, which was supplied as a forging brass bar of 30 mm diameter. The ingots of various alloys were melted with a HF induction furnace. Then the melt was cast into a sand mold (shell mold) to obtain JIS H5120 type-A test specimens. Figure 1 presents the type-A test specimen configuration and the collection positions of test pieces for each corrosion test. Test pieces for the dezincification test and the erosion-corrosion test were quarried from the parallel portion of the type-A test specimen, whereas test pieces for stress-corrosion-cracking tests were obtained from the grip part.

2.2 Dezincification test
Each test specimen was machined to a test piece of 12 mm diameter and 10 mm length. A dezincification test was conducted according to ISO6509:1981 reference using three test pieces \((n = 3)\) for each condition. After completion of the tests, the maximum dezincification depth was measured by optical microscopic observation of the radial cross-section of test surfaces. Then comparative evaluation of anti-dezincification property was conducted.

2.3 Erosion-corrosion test
Each test specimen was machined to 16 mm diameter and 12 mm length. Then erosion-corrosion tests were conducted using a jet-in-slit tester (Naigai Chemical Products Co. Ltd.). Figure 2 presents a schematic diagram of jet-in-slit erosion-corrosion test. A jet-in-slit tester allows evaluation of corrosion and erosion accompanying turbulence and shearing force of fluid flow, as presented in Fig. 2, the so-called erosion-corrosion\(^{11}\). Test conditions adopted include the following: test liquid, 1% copper chloride (II) aqueous solution same as for ISO6509, 1981 dezincification test; 40°C solution temperature; 0.4 L/min flow rate; 0.4 mm nozzle-test piece gap; 1.6 mm nozzle diameter; and 5 hr test time. The reason for selection of the test liquid was that

<table>
<thead>
<tr>
<th>Alloy</th>
<th>No.</th>
<th>Cu</th>
<th>Sn</th>
<th>Pb</th>
<th>Zn</th>
<th>Bi</th>
<th>Ni</th>
<th>P</th>
<th>Al</th>
<th>Si</th>
<th>Sb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC211</td>
<td>A</td>
<td>66.72</td>
<td>1.30</td>
<td>1.49</td>
<td>30.22</td>
<td>Tr.</td>
<td>Tr.</td>
<td>0.063</td>
<td>0.03</td>
<td>Tr.</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>D</td>
<td>65.73</td>
<td>1.15</td>
<td>1.47</td>
<td>31.41</td>
<td>Tr.</td>
<td>Tr.</td>
<td>0.05</td>
<td>0.07</td>
<td>Tr.</td>
<td>0.06</td>
<td>Tr.</td>
<td></td>
</tr>
<tr>
<td>CAC221</td>
<td>A</td>
<td>66.75</td>
<td>0.03</td>
<td>0.02</td>
<td>30.62</td>
<td>0.76</td>
<td>0.6</td>
<td>0.052</td>
<td>1.11</td>
<td>Tr.</td>
<td>Tr.</td>
<td>0.06</td>
</tr>
<tr>
<td>D</td>
<td>66.80</td>
<td>Tr.</td>
<td>Tr.</td>
<td>31.33</td>
<td>0.24</td>
<td>0.21</td>
<td>0.008</td>
<td>1.41</td>
<td>Tr.</td>
<td>Tr.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAC231</td>
<td>A</td>
<td>66.54</td>
<td>1.19</td>
<td>0.01</td>
<td>31.34</td>
<td>0.64</td>
<td>Tr.</td>
<td>0.067</td>
<td>0.06</td>
<td>Tr.</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>67.01</td>
<td>1.12</td>
<td>0.01</td>
<td>31.15</td>
<td>0.44</td>
<td>Tr.</td>
<td>0.051</td>
<td>0.09</td>
<td>Tr.</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAC232</td>
<td>A</td>
<td>67.73</td>
<td>0.9</td>
<td>0.03</td>
<td>29.64</td>
<td>0.64</td>
<td>0.03</td>
<td>0.006</td>
<td>0.47</td>
<td>0.45</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>68.21</td>
<td>0.65</td>
<td>Tr.</td>
<td>29.40</td>
<td>0.46</td>
<td>Tr.</td>
<td>0.002</td>
<td>0.53</td>
<td>0.71</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAC905</td>
<td>A</td>
<td>81.93</td>
<td>2.28</td>
<td>Tr.</td>
<td>15.00</td>
<td>0.62</td>
<td>0.15</td>
<td>0.021</td>
<td>Tr.</td>
<td>Tr.</td>
<td>Tr.</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>81.52</td>
<td>1.5</td>
<td>Tr.</td>
<td>16.48</td>
<td>0.39</td>
<td>0.09</td>
<td>0.022</td>
<td>Tr.</td>
<td>Tr.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAC906</td>
<td>A</td>
<td>81.45</td>
<td>2.42</td>
<td>0.04</td>
<td>14.46</td>
<td>1.54</td>
<td>0.03</td>
<td>0.012</td>
<td>Tr.</td>
<td>Tr.</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>80.55</td>
<td>1.91</td>
<td>0.04</td>
<td>16.35</td>
<td>1.07</td>
<td>0.02</td>
<td>0.022</td>
<td>Tr.</td>
<td>Tr.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAC804</td>
<td>A</td>
<td>76.51</td>
<td>0.06</td>
<td>Tr.</td>
<td>20.20</td>
<td>Tr.</td>
<td>0.095</td>
<td>Tr.</td>
<td>3.09</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>78.42</td>
<td>0.54</td>
<td>0.09</td>
<td>17.53</td>
<td>Tr.</td>
<td>0.05</td>
<td>0.103</td>
<td>Tr.</td>
<td>3.18</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAC804+Sn</td>
<td>A</td>
<td>86.98</td>
<td>4.75</td>
<td>0.21</td>
<td>5.95</td>
<td>1.56</td>
<td>0.23</td>
<td>0.018</td>
<td>Tr.</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>68.21</td>
<td>0.65</td>
<td>Tr.</td>
<td>29.40</td>
<td>0.46</td>
<td>Tr.</td>
<td>0.002</td>
<td>0.53</td>
<td>0.71</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAC203</td>
<td>A</td>
<td>60.82</td>
<td>-</td>
<td>2.44</td>
<td>36.74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>58.92</td>
<td>Fe+Sn = 0.45</td>
<td>2.19</td>
<td>38.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Tr: Trace

---

Table 1 Chemical compositions of specimens (mass%)

\[^{10}\] H. Yamada, et al.

---

Fig. 1 Shape and size of shell mold casting and collection position of test pieces\(^{10}\).

Fig. 2 Principle of Jet-in-slit erosion-corrosion test.
Cu²⁺ ions in the solution serve as an oxidant such as dissolved oxygen and chloride ions in tap water, so that the corrosion rate can be accelerated under a similar corrosion mechanism to that of the actual environment, and quick evaluation is attained after testing, test pieces were subjected to rinsing in water, ultrasonic cleaning, drying, and external observation on the test surface. Then the maximum corrosion depth and wear were measured. Subsequently, a comparative evaluation of anti-erosion-corrosion properties was conducted.

2.4 Stress corrosion cracking test

Each test specimen was machined into a cylinder with 20.7 mm external diameter and 28 mm length with Rc3/8 internal taper pipe threads. The test piece was then clamped to an R3/8 taper screw using torque of 29.4 Nm. Then stress corrosion cracking tests were conducted. Figure 3 depicts a test piece assembly. Each test piece was left in a desiccator filled with ammonia under torque of 29.4 Nm for 120 hr. After testing, test pieces were subjected to pickling. Then surface cracks were detected using a dye penetrant test and visual observation using stereomicroscopy with 10 times of magnification. Comparative evaluation was made of anti-stress-corrosion-cracking properties.

3. Results and Discussion

3.1 Dezincification test

Figure 4 presents measurement results of the maximum dezincification depth of the new registered alloys and reference alloys. The maximum dezincification depth of reference alloy CAC203 was as great as 727 μm, whereas that of composition A of the new registered alloys and reference alloys (CAC902 and CAC804) were 100 μm or less, so that these alloys showed excellent anti-dezincification properties compared to CAC203. Comparison between the maximum dezincification depths of composition A and dezincification-prone composition D of the new registered alloys (CAC211, CAC905, and CAC906) showed little difference, but greater dezincification depth of composition D compared with that of composition A of the new registered alloys CAC221, CAC231, and CAC232. Especially, the maximum dezincification depth of CAC221 and CAC232 with D compositions exceeded 200 μm, but still exhibited excellent anti-dezincification properties compared to those of the most-corroded reference alloy; CAC203. Figure 5 presents the microstructures of the most dezincified component, as observed using optical microscopy. Reference alloy CAC203 presented exfoliation corrosion by which dezincification is assumed to have advanced over the whole area from the corrosion test surface. In addition, the new registered alloys and reference alloys (CAC804 and CAC902) showed partial corrosion in which dezincification is observed partially from the corrosion test surface. Particularly, CAC221 and CAC232 of compositions D exhibited plug-shaped corrosion in which a part of intermetallic compound phases such as the β phase of CAC221 or the γ and the κ phases of CAC232 partially corroded selectively. This corrosion is presumably attributable to the effect of zinc equivalent on dezincification proposed by Guillet.

Figure 6 shows the relation between the apparent zinc content and the maximum dezincification depth of each alloy. The maximum dezincification depth increases as the apparent zinc content increases in brass alloys except for CAC804. Regarding CAC221, because 37.2% of the apparent zinc content of dezincification-prone composition D was larger than 35.3% of that of composition A, it is considered that a part of β phase was corroded preferentially due to a high fraction of β phase formed in the microstructure, and the maximum dezincification depth was enhanced. Similarly for CAC232, the apparent zinc content of composition A of 36.3% is increased to 37.5% in composition D, so that the fraction of intermetallic compounds of high Zn concentration such as γ phase and κ phase becomes greater than α phase. Accordingly, it is considered that a part of the intermetallic compound was corroded and the dezincification depth was extended. It must take into account the fact that it was difficult to judge influence of the casting defect observed in corrosion test pieces on dezincification.

3.2 Erosion-corrosion test

Figure 7 depicts results of erosion-corrosion tests for the reference alloys and the registered alloys of composition A. First, comparative evaluation of the appearance of the test surface of the reference alloys revealed double corrosion rings attributable to erosion-corrosion resulting from turbulence and shear force of fluid flow, as shown in the schematic diagram of Fig. 2 in CAC804, CAC804+Sn, CAC203, and C3771. However, no corrosion ring was observed in CAC902. A comparative evaluation of the maximum corrosion depth and wear loss revealed maximum corrosion depth...
of 400 μm or more and wear loss of 300 mg or more in CAC203, C3771, CAC804, and CAC804+Sn, whereas the maximum corrosion depth was 100 μm or less and the wear loss was less than 300 mg in CAC902. The test result presented above verified that the anti-erosion-corrosion property is excellent in the ascending order of CAC203 < C3771 < CAC804 < CAC804+Sn << CAC902. Particularly, CAC902 showed excellent anti-erosion-corrosion properties. Next, a comparative evaluation made of the composition A new registered alloys revealed no apparent large corrosion ring and maximum corrosion depth of 100 μm or less for CAC211, CAC231, CAC905, and CAC906, which were as much as CAC902. A corrosion ring was observed on the test surfaces of CAC221 and CAC232. Their maximum corrosion depths were 300 μm or greater. Consequently, CAC221 and CAC232 were inferior to reference alloy CAC902, but were equivalent or slightly-better in comparison to CAC804, and better than either C3771 and CAC203.

Figure 8 presents the effects of Sn content of each alloy on the maximum corrosion depth and wear loss. Sn-containing reference alloy CAC902 and new registered alloys CAC211, CAC231, CAC905, and CAC906 exhibited excellent properties compared to those of reference alloys CAC804, CAC203, and C3771, and new registered alloy CAC221, which contained no Sn. Furthermore, CAC804+ Sn, in which Sn was added to CAC804, and CAC232, which contains Sn in alloy composition, showed better performance than CAC804. Especially alloys to which 1% or more of Sn was added showed experiment results equivalent to that of CAC902. Consequently, the previously described jet-in-slit erosion-corrosion test revealed that especially Sn concentration in the composition of the new registered and reference alloys are correlated with evaluation results under conditions of this study using anti-erosion-corrosion copper chloride (II) aqueous solutions.

### 3.3 Stress corrosion cracking tests

Figure 9 depicts the results of stress corrosion cracking for the new registered alloys of composition A and reference alloys. Stress corrosion cracking was observed at the end face of the screw parts of test pieces in reference alloys (C3771 and CAC203). Comparison of the crack size between C3771 and CAC203 revealed large visible cracks extending toward the side from the end face in C3771. Cracks were observable visually on the end face using a stereomicroscope also in CAC203, but they are so small cracks compared with C3771, and that no visible crack was observed connecting to the side. It is noteworthy that no crack was found by visual check or using stereomicroscopy in the new registered alloys or reference alloys (CAC804 and CAC902) after a test time of 120 hr. Furthermore, no crack occurrence was found for the new registered alloys of composition D
with enhanced apparent Zn content by stress corrosion cracking tests for 120 hr. Results revealed that the new registered alloys have lower stress corrosion crack sensitivity than the reference alloys (C3771 and CAC203).

4. Conclusion

Evaluation of the corrosion resistance of the six types of the new registered alloys was conducted as a joint experiment for amending JIS standards by the joint committee of the Japan Foundry Society, Inc. and the Japan Foundry Engineering Society, obtaining the following findings. It is noteworthy, however, that the corrosion resistance tests of this study are acceleration tests, and that correlation with the corrosion status in a real usage environment remains unknown. Therefore, proper alloys should be selected according to the usage environment.

(1) The new registered alloys of representing compositions showed the maximum dezincification depth of 100 μm or less in dezincification tests, thereby demonstrating an anti-dezincification property equivalent to reference alloys CAC804 and CAC902.

(2) CAC221 and CAC232 showed large dezincification depth with increasing contents of Al or Si as a great zinc equivalent, but exhibited excellent anti-dezincification properties compared with reference alloy CAC203 for most corrosive dezincification.

(3) The new registered alloys CAC211, CAC231, CAC905, and CAC906 exhibited anti-erosion-corrosion properties equivalent to reference alloy CAC902 in erosion-corrosion tests using copper chloride (II) aqueous solution. However, the new registered alloys CAC221 and CAC232 and reference alloys CAC804, CAC804+Sn containing 0.54% of Sn, CAC203, and C3771, presented corrosion rings because of erosion-corrosion and the maximum corrosion depth of 300 μm or more, which brought about inferior anti-erosion-corrosion properties compared with reference alloy CAC902. Presumably, Sn content in alloy composition has strong correlation with erosion-corrosion properties under the test conditions used for this study.

(4) Stress corrosion cracking tests conducted for 120 hr revealed that the new registered alloys have lower stress corrosion crack sensitivity than those of reference alloys C3771 and CAC203.

Acknowledgments

The authors are grateful to Mr. Takafumi Akashi of Akashi Gohdoh Inc. for cooperation in casting of test specimens and to Mr. Hideaki Kobayashi of Nihon Bronze Co. Ltd. for cooperation with chemical analysis.
<table>
<thead>
<tr>
<th>No.</th>
<th>CAC211</th>
<th>CAC221</th>
<th>CAC231</th>
<th>CAC232</th>
<th>CAC90S</th>
<th>CAC906</th>
</tr>
</thead>
<tbody>
<tr>
<td>Result</td>
<td>No Crack</td>
<td>No Crack</td>
<td>No Crack</td>
<td>No Crack</td>
<td>No Crack</td>
<td>No Crack</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>C3771</th>
<th>CAC203</th>
<th>CAC804</th>
<th>CAC902</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stereooscopic microscope image (×10)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>Result</td>
<td>Crack (Visual)</td>
<td>Crack (microscope)</td>
<td>No Crack</td>
<td>No Crack</td>
</tr>
</tbody>
</table>

Fig. 9 Result of stress-corrosion-cracking test of new registered alloys and reference alloys.

REFERENCES

4) Bosei, Boshoku Gijyutusouran Editing Committee: Bosei, Boshoku Gijyutusouran (In Tech Information s. c. Ltd, Tokyo, 2000), 473–474
6) JIS H3250:2010 Copper and copper alloy rods and bars, (Japanese Standards Association, Tokyo, 2010).
13) Editing committee of Dogokinimono no seisangijyutsu: Dogokinimono no seisangijyutsu, (SOKEIZAI Center, Tokyo, 1997) p.58.