Stainless steels and nickel alloys are widely used in chemical plants for equipment in contact with very corrosive solutions such as sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and hydrochloric acid (HCl). As molybdenum (Mo) and nickel (Ni) are beneficial elements to improve the corrosion resistance, high Mo containing Ni alloys such as UNS N10276 or N06022 have been successfully used, although these expensive elements increase material costs. Researchers have found that copper, which is less expensive, can also improve corrosion resistance.

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Depending on the corrosiveness of the application environment, selecting Ni alloys may result in poor cost-effectiveness. Some researchers have reported that copper (Cu), which is less expensive than Mo and Ni, is beneficial to improve corrosion resistance of stainless steels and other alloys. For example, it is said that the corrosion resistance in stainless steels in sulfuric acid was improved by the formation of a Cu layer on the surface.

In this study, Cu was focused as the element to substitute Mo of Ni, and the effect of Cu and Mo contents on the corrosion resistance was evaluated for 46Ni-23Cr-4W-Fe alloy in reducing acids.

Based on the laboratory corrosion test results, by optimizing both Cu and Mo contents to achieve comparable corrosion resistance with N10276 and N06022, new Ni alloy with 3%Cu and 6%Mo, UNS N06845 was proposed. Corrosion resistance of N06845 was evaluated in 3% HCl solution at 60°C for 6 hours, 20% H\textsubscript{2}SO\textsubscript{4} solution at 80°C for 24 hours, boiling 40% HNO\textsubscript{3} solution for 24 hours and 3 different types of mixed acids (0.1% HCl and 0.1% H\textsubscript{2}SO\textsubscript{4}).

**Laboratory corrosion tests**

Corrosion tests on 46Ni-23Cr-4W-Fe alloys with various Cu contents were conducted to evaluate the influence of Cu on corrosion resistance. Incidentally Cr and W was added to ensure high resistance to corrosion by oxidizing acids and local corrosion, respectively. The chemical compositions of tested materials are shown in Table 1 comparing with conventional Ni alloys. Ingots were made in a 180kg vacuum induction melting furnace, then hot forged and hot rolled to plates with 20mm thickness. After annealing at 1150°C for 10 minutes followed by quench, these plates were cold rolled to 12mm thick and subjected to solution heat treatment at 1150 °C. Coupon specimens (3mm thickness x 10mm width x 40mm length) were cut from the sheets, and their surface was mechanically ground by a 600 grit emery paper, followed by ultrasonic cleaning in acetone. After that the specimens were weighed. Corrosion tests were conducted in 3% HCl solution at 60°C for 6 hours or 20% H\textsubscript{2}SO\textsubscript{4} solution at 80°C for 24 hours. After the immersion, specimen was ultrasonic cleaned in acetone to remove the surface corrosion products, and was weighed to determine the corrosion rate.

Based on the results of these corrosion tests, a new Ni alloy with 3% Cu and 6% Mo, which is registered as N0 6845, has been developed. Corrosion resistance of N06845 was evaluated in 3% HCl solution at 60°C for 6 hours, 20% H\textsubscript{2}SO\textsubscript{4} solution at 80°C for 24 hours, boiling 40% HNO\textsubscript{3} solution for 24 hours and 3 different types of mixed acids (0.1% HCl and 0.1% H\textsubscript{2}SO\textsubscript{4}).

**Table 1. Chemical composition of the laboratory test alloys (mass %)**

<table>
<thead>
<tr>
<th>Mark</th>
<th>C</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>0.008</td>
<td>-</td>
<td>45.85</td>
<td>22.70</td>
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<td>4.0</td>
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<td>B</td>
<td>0.008</td>
<td>1.00</td>
<td>46.14</td>
<td>23.02</td>
<td>-</td>
<td>4.1</td>
</tr>
<tr>
<td>C</td>
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<td>3.01</td>
<td>46.04</td>
<td>23.04</td>
<td>-</td>
<td>3.9</td>
</tr>
<tr>
<td>D</td>
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<td>6.98</td>
<td>46.01</td>
<td>23.02</td>
<td>-</td>
<td>4.0</td>
</tr>
<tr>
<td>E</td>
<td>0.009</td>
<td>3.02</td>
<td>46.32</td>
<td>22.98</td>
<td>-</td>
<td>4.1</td>
</tr>
<tr>
<td>F</td>
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<td>2.95</td>
<td>46.25</td>
<td>23.10</td>
<td>3.07</td>
<td>3.9</td>
</tr>
<tr>
<td>G</td>
<td>0.006</td>
<td>2.99</td>
<td>46.30</td>
<td>23.00</td>
<td>6.02</td>
<td>4.3</td>
</tr>
<tr>
<td>H</td>
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<td>0.10</td>
<td>5.99</td>
<td>23.01</td>
<td>6.01</td>
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</tr>
<tr>
<td>N08825</td>
<td>0.02</td>
<td>2</td>
<td>40</td>
<td>21</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>N10276</td>
<td>0.005</td>
<td>-</td>
<td>57</td>
<td>16</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>N06022</td>
<td>0.005</td>
<td>-</td>
<td>59</td>
<td>21</td>
<td>13</td>
<td>3</td>
</tr>
</tbody>
</table>

*) UNS No.
+ 0.5% H$_2$SO$_4$, 2% HCl + 10% H$_2$SO$_4$, 2% HCl + 10% HNO$_3$) to compared with existing Ni alloys (N08825, N06022 and N10276).

**Alloy design based on the laboratory tests**

Figure 1-a) shows the mean corrosion rate of 46Ni-23Cr-0Mo-4W-Fe alloys as the function of Cu content. With increasing Cu content up to 3% the corrosion resistance to both HCl and H$_2$SO$_4$ was improved. However, over 3% Cu, the effect is saturated. Based on these results, the Cu content was determined as 3%.

Figure 1-b) shows the mean corrosion rate of 46Ni-23Cr-3Cu-4W-Fe alloys as the function of Mo content. With increasing Mo content the corrosion resistance to H$_2$SO$_4$ was improved. On the other hand, the material adding 3% Mo showed maximum corrosion rate, and the material adding 6% Mo show the excellent corrosion resistance, whose corrosion rate was about 0.04mm/year. The cause that the material adding 3% Mo showed high corrosion rate in HCl will be discussed as a future work.

Based on these results, the chemical composition of new alloy; UNS N06845 was determined as 46Ni-23Cr-3Cu-6Mo-4W. N06845 had been registered in ASTM B163, B423, B424 and B425 as shown in Table 2 and ASME Code Case.2794.

Figure 2 shows the mean corrosion rate in H$_2$SO$_4$, HCl and HNO$_3$ solution. N06845 showed comparable corrosion resistance to N10276 and N06022 in both oxidizing (HNO$_3$) and reducing acids (HCl, H$_2$SO$_4$).

Corrosion resistance of N06845 in the mixed acids was also evaluated as shown in Figure 3. N06845 showed even better corrosion resistance than other Ni alloys.

**Surface analysis**

To investigate the properties of surface film in H$_2$SO$_4$ conditions, surface analysis with X-ray photoelectron spectroscopy (XPS) was carried out. The specimens were analyzed with XPS using monochromatic-AlK$_\alpha$ X-rays (h $\nu$= 1486.6eV) over an area of about 0.2mm diameter from the surface to 30nm depth. High-resolution spectra for the statement analysis were recorded with 23.50eV pass energy. Surface of the specimen was analyzed at 45 degree take-off angle. The surface
was sputtered by Ar+ ion gun to investigation depth distribution of Cu, Ni, Mo Chromium (Cr) and Iron (Fe). Sputtering rate was 0.8nm/min as SiO2 conversion.

**Effect of Cu to improve the corrosion resistance**

Figure 4 shows the results to measure the concentration distribution of the material with 0.1% Cu and 3% Cu after the corrosion test in H2SO4. Figure 5 is the magnified result of the Cu profile in Figure 4. Within the range of 4 nm portion from the surface, the peak of Cr oxide is detected for both materials, and Cu is concentrated under Cr oxide. It is considered that this Cr oxide was formed in the air atmosphere after the corrosion test because H2SO4 has reducing property. That is, in H2SO4 solution, Cu is seemed to be concentrated at the beneath of surface. This may indicate that Cu which dissolved with mother material at first reaction aggregates around the surface, then corrosion reaction is inhibited by Cu deposition to the surface of material. 

These results show Cu addition is one of the best ways to improve corrosion resistance to the acids as a substitute of Mo in the terms of cost-effectiveness.

**Field test at chemical plant**

N06845 has shown better corrosion resistance to sulfuric acid than existing alloys (N06022 and N10276) in the laboratory corrosion test to verify applicability to a commercial plant, N06845 was evaluated for 1 year in the commercial sulfuric plant. Existing alloys N06022 and N10276 were also evaluated under the same conditions.

The chemical compositions of tested alloys are shown in Table 3. The 3.5 ton ingot of N06845 was made in a vacuum induction melting furnace. After that, ingot was hot forged and hot extruded to the seamless pipe with 204 mm OD and 9.5 mm WT. After annealing at 1100 °C in air, this pipe was cold rolled to 168.5 mm OD and 6.95 mm WT. Then solution heat treatment at 1100 °C was conducted. Two Coupon specimens were cut from this pipe to 6mm thickness x 15mm width x 50mm length and butt-welded by GTAW with the welding filler of AWS ERNiCrMo-10.

![Figure 4. Surface analysis by XPS after immersion in 20%H2SO4 solution at 80°C for 24 hours.](image1)

![Figure 5. Surface analysis by XPS after immersion in 20%H2SO4 solution at 80°C for 24 hours.](image2)

*Table 3. Nominal chemical composition of the field tested alloys (mass %)*

<table>
<thead>
<tr>
<th>Mark</th>
<th>UNS No.</th>
<th>C</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
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<td>A18</td>
<td>N06845</td>
<td>0.01</td>
<td>3</td>
<td>46</td>
<td>23</td>
<td>6</td>
<td>4</td>
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</tr>
<tr>
<td>HC22</td>
<td>N06022</td>
<td>0.005</td>
<td>-</td>
<td>59</td>
<td>21</td>
<td>13</td>
<td>3</td>
<td>ERNiCrMo-10</td>
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<tr>
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<td>N10276</td>
<td>0.005</td>
<td>-</td>
<td>57</td>
<td>16</td>
<td>16</td>
<td>4</td>
<td>ERNiCrMo-4</td>
</tr>
</tbody>
</table>

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4. Corrosion resistance of N06845 was comparable to N10276 and N06022 in the reducing acids, and superior to them in oxidizing acids in the laboratory tests.

5. In spite of reduced Mo and Ni content, since N06845 shows excellent corrosion resistance in various severely corrosive environments, N06845 is expected to be the most economical alloy in chemical plants.

6. Excellent corrosion resistance of N06845 has been proven in various commercial plants as well as in laboratory tests.

Coupon specimens of N06022 and N10276 were also cut from commercially available plates and butt-welded by GTAW with the welding filler of AWS ERNiCrMo-10 and AWS ERNiCrMo-4, respectively. All test specimens were mechanically ground with 600 grit emery paper, followed by ultrasonic cleaning in acetone. The test specimens were exposed at the outlet of an H2SO4 tank containing a little NH4SO4 for 1 year. After the exposure, the metallographic cross section of the specimen surface was investigated using an optical microscope.

Figure 6 and 7 shows the appearance and the cross sections after the exposure, respectively. N06022 is attacked to about 50µm depth at weld metal and N10276 also overall attacked to 70µm depth at the heat affected zone (HAZ). However, N06845 shows only 15µm intergranular attack at HAZ. This is considered that N06022 and N10276 were corroded by oxidants such as NH4SO4 in the environment because N06022 and N10276 contained lower Cr than N06845. Because N06845 showed even or better corrosion resistance to N06022 and N10276 in the commercial plant, it is confirmed that N06845, containing Cu and lower Mo, was the practical and economical material in this application.

Conclusions
1. Effect of Cu and Mo contents on corrosion resistance in 46Ni-23Cr-4W-Fe alloy was investigated under a reducing acid environment in the laboratory test. Both Cu and Mo were confirmed to improve corrosion resistance.
2. Since copper seems to concentrate beneath the surface of the corrosion test specimen, the corrosion reaction was considered to be inhibited by Cu deposition to the surface of material.
3. Copper bearing new nickel alloy (UNS N06845, 46Ni-23Cr-6Mo-4W-3Cu) was proposed with optimized Cu and Mo contents.

References available on request

About the author
Mitsuru Yoshizawa is a senior manager of Nippon Steel & Sumitomo Metal Corporation (NSSMC) European office. NSSMC was formed by the merger of Nippon Steel and Sumitomo Metals in October 2012. Mr. Yoshizawa started his career as a researcher of heat resistant steel (mainly used for power plant) at Sumitomo Metals in 1997. He was transferred to Amagasaki Works in 2009 where he was in charge of technical services for Asian customers of seamless tubes & pipes (mainly stainless steel and Ni base alloy). In January 2014, he was transferred to European office (Dusseldorf, Germany) and is engaged in the technical services for their European seamless tubes & pipes customers in the petrochemical, chemical, subsea and power plant industries.
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