PROPERTIES OF SILVER BRAZING ALLOYS CONTAINING LITHIUM

The analysis of the influence of lithium on wetting properties of Ag-Cu brazing alloys and the shear strength of stainless steel/braze/stainless steel joint was conducted. The brazing alloys of designations and composition according to ANSI/AWS A5.8: BAg-8a (71÷3 wt.% Ag, 0.25÷0.50 wt.% Li, Cu) and BAg-19 (92÷93 wt.% Ag, 0.15÷0.30 wt.% Li, Cu) and a braze alloy containing 70÷72 wt.% Ag, 0.6÷0.7 wt.% Li and Cu were subjected to the investigations. The wettability properties of the brazing silver alloys were examined in a spread test. The shear strength of joints were measured on the joints of stainless steel in the tensile test. The comparison of results showed a beneficial effect of lithium on the spreading properties and the wettability of braze alloys as well as the quality and shear strength of the brazed joints. The observed slag inclusions in the solid braze did not affect considerably the mechanical properties of the prepared joints because of the intensive deoxidation of the brazing surfaces of stainless steel elements.

Keywords: brazing, vacuum brazing, silver brazing alloys containing lithium, brazing properties, strength of brazed joints of stainless steel.

1. Introduction

The alloys based on the silver matrix belong to one of the fundamental groups of brazing filler metals (filler metals with a melting point higher than 450°C (723 K)). They were used in antiquity and the Middle Ages to join elements of copper and silver [1, 2]. These brazing alloys are standardized in Poland according to PN-EN ISO 17672 and the use of brazing includes almost all metals and alloys except for light and low melting alloys. The wide range of silver braze alloys, apart from pure silver, includes alloys containing 5÷93 wt.% silver with copper, zinc, tin, cadmium, manganese, nickel, etc., of melting temperatures from 500 up to 1220°C (melting point of pure silver is 960°C). They exhibit high brazing properties and provide a relatively high quality and strength of brazed joints [1÷7]. However, the relatively high price is their disadvantage.

There is an important group among the silver brazing alloys of Ag-Cu type which additionally contains lithium. They are used mainly for brazing without a flux, in reduction atmospheres controlled and in vacuum to obtain high quality connections of nickel-chrome and chrome stainless steels. Lithium as a component of silver brazing alloys is meant to improve the wettability of steel. This kind of brazing alloys have been developed relatively recently and therefore there is a lack of detailed studies of their properties as well as the properties of joint [4÷6, 9÷11].

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One of the main applications of silver filler metal of Ag-Cu type is to produce responsible joints of stainless steel (nickel-chromium and chromium) elements, especially in chemical apparatus, aircraft, equipment for power engineering, electronic and vacuum apparatus, etc. Silver and copper brazing alloys wet iron and its alloys rather poorly, due to the high stability of chromium oxide on the surface of stainless steel. Therefore, they require surface active additions, like for example, lithium [1, 2, 4, 5, 10].

The brazing filler metals based on silver and modified by lithium which can be found in the literature [1, 2, 4, 5] and in the ANSI/AWS 5.8 (U.S.) standards as well as in 19 738 GOST (Russia) ones. They have the following chemical compositions (in wt.%): (99.5% Ag, 0.5% Li), (95.5±96.5% Ag, 0.15±0.25% Li, Cu), (91±93% Ag, 0.15±0.30% Li, Cu), (71±73% Ag, 0.25±0.50% Li, Cu), and (71.5±72.5% Ag; 0.7±1.3% Ni; 0.4±0.6% Li).

The impact of lithium on the properties of brazing alloys is concerned with one general process, that is the reaction of lithium with the metal oxides of materials brazed which in consequence causes the activation of the surfaces, improvement of wettability, spreading and penetration of liquid brazing alloy in the capillary gap between the joined elements. The study was proposed for the realization because of the long-time experience of the authors in the investigation of thermodynamic properties of binary and ternary lithium solutions [12-20] and in the ANSI/AWS 5.8 (U.S.) standards for the determination of properties of filler metals for brazing. Methodology of wettability of the joined materials in technological conditions. The assessment of this capacity in the cases of brazing is performed mostly using the test of filler metal spreading (spreading is the result of wetting) on the brazed material, taking into account the positive effects of many technological factors [2÷7].

The primary and essential condition for obtaining a brazed joint in a brazing process is wetting the materials to be joined with the filler metal. Therefore, tests of brazing properties usually assess their ability to wet the joined materials in technological conditions. The assessment of this capacity in the cases of brazing is performed mostly using the test of filler metal spreading (spreading is the result of wetting) on the brazed material, taking into account the positive effects of many technological factors [2÷7].

The measure of wettability is the size of filler metal spreading surface, or the maximum height of brazed alloy after spreading and the corresponding coefficients calculated using the mentioned parameters [1, 6, 7].

It should be also emphasized that there are currently no European and international standards of research methodology for the determination of properties of filler metals for brazing. Methodology of wettability of the brazing alloy can be found in "classical" guides on brazing [1÷7].

In ongoing studies, the attempts to spread the BAg-8a and BAg-19 filler metals on austenitic stainless steel plates with dimensions of 40x40x1 mm, grade X2CrNi18-9 (PN-EN 10088:1998), were carried out in a vacuum furnace type S -16 of TORVAC company, while the experiments with the use of AgLi brazing alloy were performed in the resistance furnace with the

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2. Brazing alloys used in studies

The following brazing silver alloys of Ag-Cu-Li type, in the form of tapes characterized by their chemical composition are presented in Table 1.

<p>| Chemical composition of Ag-Cu-Li brazing alloys used in experiments |
|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Lp</th>
<th>Braze alloy</th>
<th>Chemical composition, % wt. According to ANSI/AWS A5.8</th>
<th>According to chemical analysis(^{1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BAg-8a</td>
<td>71±73 Ag, 0.25±0.50 Cu</td>
<td>72.32 Ag, 0.37 Cu, 0.67 Li</td>
</tr>
<tr>
<td>2</td>
<td>BAg-19</td>
<td>92±93 Ag, 0.15±0.30 Cu</td>
<td>92.27 Ag, 0.27 Cu, 0.67 Li</td>
</tr>
<tr>
<td>3</td>
<td>AgLi(^{2})</td>
<td>-</td>
<td>70.34 Ag, 0.37 Cu, 0.67 Li</td>
</tr>
</tbody>
</table>

\(^{1}\) chemical analysis of brazing alloys carried out in the laboratory of the Institute of Welding in Gliwice.

\(^{2}\) this brazing alloy is not included in ANSI/AWS A5.8 Standards.

3. Testing of brazing properties

The impact of lithium on the properties of brazing alloys is concerned with one general process, that is the reaction of lithium with the metal oxides of materials brazed which in consequence causes the activation of the surfaces, improvement of wettability, spreading and penetration of liquid brazing alloy in the capillary gap between the joined elements. The study was proposed for the realization because of the long-time experience of the authors in the investigation of thermodynamic properties of binary and ternary lithium solutions [12-20] and in the ANSI/AWS 5.8 (U.S.) standards for the determination of properties of filler metals for brazing. Methodology of wettability of the joined materials in technological conditions. The assessment of this capacity in the cases of brazing is performed mostly using the test of filler metal spreading (spreading is the result of wetting) on the brazed material, taking into account the positive effects of many technological factors [2÷7]. The measure of wettability is the size of filler metal spreading surface, or the maximum height of brazed alloy after spreading and the corresponding coefficients calculated using the mentioned parameters [1, 6, 7].

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high purity argon atmosphere contained in a glove-box equipped with the purification system from oxygen, water vapor and nitrogen. The concentration of contaminations in argon was monitored continuously and it was held at the level much lower than 1 ppm including the O\textsubscript{2} and H\textsubscript{2}O. Nitrogen was not monitored but it was removed by the absorption in a titanium sponge at 1100°C. The relatively high lithium content (0.6±0.7 wt.%), in the braze alloy, was the reason to use a gas atmosphere instead of vacuum to avoid its intensive evaporation.

The research of brazing alloy spreading in the vacuum furnace was carried out under the pressure of 1.33×10\textsuperscript{−3}–1.33×10\textsuperscript{−4} mbar, at temperatures: 850°C, 900°C, 950°C and 1000°C, according to the recommendations found in technical literature [1, 8] and the authors experience [21]. The temperatures close to 900°C and sometimes much higher than the melting temperature of the filler metal were required for brazing the stainless steel with silver filler metals. The sample was held at the spread test temperature for 5 minutes.

Two parameters being the measure of the wettability were calculated. The first one, designated as \(K_P\), was equal to the surface area of the braze alloy after spreading (measured with a polar compensating planimeter KP-27’s Juices, Japan) according to the following equation:

\[
K_P = \frac{(P_m - P_o)}{P_o},
\]

where: \(P_m\) is the arithmetic average size of submergence area of the brazing alloy and \(P_o\) is the surface area of the projection of the spherical brazing alloy sample of the volume \(V\) at the ground plane. It was calculated according to the formula:

\[
P_o = \pi \left( \frac{3}{4\pi} V \right)^{2/3}
\]

The second parameter \(K_H\) equal to the height of brazing alloy after spreading was calculated from the following relation:

\[
K_H = \frac{(D_o - H_m)}{D_o} \cdot 100\%
\]

\(H_m\) in Eq. 3 is the arithmetic mean height of the brazing alloy layer after spreading and \(D_o\) is theoretical diameter of droplet brazing alloy of the volume \(V\) in the absence of wetting, calculated as follows:

\[
D_o = 1.24V^{1/3}
\]

The values of calculated spreading surface areas and heights of brazing alloy layers are shown in Table 2. Additionally, the values of the coefficients \(K_P\) and \(K_H\) for the analyzed brazing alloys are shown in Figures 1 and 2.

Analyzing the results presented in Table 2 and in Fig. 1, it was found that the silver brazing alloys wetted the stainless steel only at temperatures higher than 950°C. The alloys with a composition close to the eutectic, i.e. with a content of 72% Ag (Ag 272, BAg-8a) at 850°C almost did not wet the steel substrate, and at 900°C a small spreading (wettability) was observed. The silver filler metal contains 92% Ag (BAg-19) and due to higher melting point (891°C) spreads on the steel at 950°C. The study confirmed the beneficial effect of lithium on the wettability and spreading of silver brazing alloys. The results of spreading tests at temperatures 950°C and 1000°C were about 13 to 20% higher in comparison with the silver filler metal not containing this metal. Lithium therefore improved the wetting properties of silver brazing alloys in the case of brazing stainless steel elements. The use of silver brazing alloys modified with the lithium allowed to some extent the solution of the problem of difficult brazeability of stainless steels in reduction controlled atmospheres.
### TABLE 2

<table>
<thead>
<tr>
<th>No of sample</th>
<th>Brazing alloy</th>
<th>Temperature of spreading test °C</th>
<th>Spreading test</th>
<th>Parameter $K_p$</th>
<th>Layer height of braze alloy mm</th>
<th>Parameter $K_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Spreading surface area $\text{mm}^2$</td>
<td>$P_{sp}$</td>
<td>$S_{sp}$</td>
<td>$H_{sp}$</td>
</tr>
<tr>
<td>1</td>
<td>Ag 272</td>
<td>850</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>900</td>
<td>44.8</td>
<td>9.3</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>950</td>
<td>63.0</td>
<td>7.6</td>
<td>2.3</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>1000</td>
<td>92.0</td>
<td>8.4</td>
<td>3.8</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>BAg-8a</td>
<td>850</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>900</td>
<td>53.4</td>
<td>8.5</td>
<td>1.8</td>
<td>2.3</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>950</td>
<td>72.0</td>
<td>10.4</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>1000</td>
<td>108.0</td>
<td>13.0</td>
<td>4.6</td>
<td>1.2</td>
</tr>
<tr>
<td>9</td>
<td>BAg-19</td>
<td>850</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>900</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.6</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>950</td>
<td>76.0</td>
<td>7.4</td>
<td>2.9</td>
<td>1.5</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>1000</td>
<td>114.0</td>
<td>13.4</td>
<td>4.9</td>
<td>1.0</td>
</tr>
<tr>
<td>13</td>
<td>AgLi</td>
<td>850</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>900</td>
<td>67.7</td>
<td>2.1</td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>950</td>
<td>100.0</td>
<td>20.0</td>
<td>4.2</td>
<td>1.0</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>1000</td>
<td>126.7</td>
<td>15.3</td>
<td>5.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

### 4. Strength tests and metallographic studies

Brazed joints due to lower strength of the filler metal in comparison with the brazed material are typically designed as a shear joints working for example in: lap joints and overlay sheets, socket connections and telescopic tubes. Therefore, a fundamental feature of endurance of these connections is the shear strength. This study was conducted using the samples prepared by brazing two elements like it is shown in Fig. 2 [2, 12]. The sample consisted of two cylindrical brazed elements (Fig. 2), subjected to shear perpendicular to the axis. Such samples were also used for qualitative metallographic examination.

Brazing the samples of austenitic stainless steel, (grade X2CrNi 18-9 according to PN-EN 10088:1998) were conducted in a vacuum furnace of type S-16 (TORVAC), $1.33 \times 10^{-3} \div 1.33 \times 10^{-4}$ mbar in the case of BAg-8a and BAg-19 filler metal. For brazing with AgLi, the resistance furnace working in the atmosphere of high purity argon was applied. The brazing temperature in both cases was $1000^\circ$C and the heating time was 5 min. Such conditions were applied because good properties of brazing alloy were observed in the studies of spreading.

![Fig. 2. The scheme of configuration of stainless steel brazed samples for the shear strength test (arrow indicates braze)](image-url)
Before the shear tests the samples were first visually examined. It showed complete spreading of the brazing alloy and fulfilling the gap between the joined elements.

The shear tests of cylindrical samples were conducted using special jaws, eliminating the effect of specimen bending during shear. The studies were performed using an INSTRON testing machine. The results of studies based on Student’s t-distribution are shown in Table 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>No of sample</th>
<th>Brazed material</th>
<th>Brazing alloy</th>
<th>Shear strength of joints MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X2CrNi18-9</td>
<td>Ag 272</td>
<td>X = 285, S = 19.1, PU = 258.5÷311.5</td>
</tr>
<tr>
<td>2</td>
<td>BAg-8a</td>
<td>293</td>
<td>10.3, 278.7÷307.3</td>
</tr>
<tr>
<td>3</td>
<td>BAg-19</td>
<td>288</td>
<td>15.9, 265.9÷310.0</td>
</tr>
<tr>
<td>4</td>
<td>AgLi</td>
<td>295</td>
<td>16.0, 272.8÷317.2</td>
</tr>
</tbody>
</table>

X – average value from 5 measurements; S – standard deviation; PU – confidence interval for α = 0.95

The values of the shear strength of joints were fairly similar and they differed between 285 and 295 MPa. Comparing the strength of the joints with the use of silver filler metal Ag 272 without lithium (with a composition similar to the eutectic) with those containing lithium designated as BAg-8a and AgLi, one can conclude that the addition of lithium to the brazing alloys of Ag-Cu type increased somewhat the shear strength of joints and reduced the scatter of results. This can be explained by higher wetting properties of the brazing alloy and more accurate surface de-oxidation of the joined materials, as a result of the higher active surface properties of lithium. The qualitative observations of the joints were carried out using an optical microscope Leica MEF4M. The metallographic structures of joints are shown in Figures 2÷4. All samples were etched with FeCl₃.

The metallographic examinations of samples showed good quality of the joint. Only in the case of AgLi braze alloy characterized by relatively high content of Li, the occurrence of larger spheroidal inclusions of reaction products of relatively low melt lithium compounds with metal oxides such as Li₂CrO₄ were observed. They originated from the effect of intense lithium de-oxidation of the surface of the materials to be joined. The formation of such precipitates, which moved into the liquid brazing
alloy were also reported in [4, 6, 10]. That separation did not significantly affect the mechanical properties of the joints, but they could reduce its resistance to corrosion. Therefore, the maximum lithium content does not normally exceed 0.5% (wt.). The braze structures showed in the middle part of joints made of Ag 272, BAg-8a and AgLi filler metals (Fig. 3, 4 and 6), respectively the eutectic mixture of limit solid solutions $\alpha$ (solution of Cu in Ag) and $\beta$ (solution of Ag in Cu), and in the joints brazed with BAg-19 (Fig. 5) a small separation of the $\beta$ secondary solid solution crystals in the solid solution $\alpha$ (according to the Ag-Cu phase equilibrium) [1, 5]. The exact structural analysis of phases present in the brazes was not performed because such studies were not predicted in the research program of the project.

3. The metallographic examination confirmed the good quality of brazed joints in spite of the presence of spheroidal reaction products in the solid braze, whose amount increased with the Li content in the brazing alloy.

4. The slug inclusions occurred in the structure of the solid braze, identified in the literature as a low melting lithium compounds with the oxides of materials assembled, did not reduce the strength properties of joints, but because they might decrease their corrosion resistance, the lithium content in the brazing filler metal should not exceed the 0.5 wt.%.

REFERENCES

Fig. 6. Microstructure of the stainless steel (X2CrNi 18-9) joint brazed with AgLi brazing alloy (70.34% Ag, 0.67% Li, Cu), braze – middle part

5. Conclusions
1. Investigations of brazing alloys containing lithium: BAg-8a (72.32% Ag, 0.37% Li, Cu), AgLi (70.34% Ag, 0.67% Li) and BAg-19 (92.27% Ag, 0.27% Li, Cu), showed their higher wetting properties compared with a silver brazing alloy without lithium: Ag 272 (B-Ag72Cu-780). This conclusion was yielded based on the spreading tests of brazing alloys on the surface of X2CrNi 18-9 stainless steel performed in vacuum and the atmosphere of high purity argon.
2. Studies of the strength properties of X2CrNi 18-9 stainless steel joints brazed with the silver filler metals containing lithium (BAg-8a and BAg-19) and the one marked as AgLi showed similar results of shear strength of 288±295 MPa. In the case of joints which were prepared using the silver brazing alloys of the composition similar to the binary Ag-Cu eutectic Ag 272 (B-Ag72Cu-780) and those with the addition of lithium (BAg-8a and AgLi) it was found that it increased the strength of joints by about 4%. This effect can be explained by better de-oxidation and wetting of brazed elements surfaces.

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