The influence of Zn on the corrosion behaviour of amorphous and nanosized rapidly solidified (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} alloys and their crystalline analogues

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Abstract: The influence of Zn on the corrosion behavior of amorphous and nanosized rapidly solidified aluminum alloys (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} (x = 0; 1; 3) at. % and their crystalline analogues was studied. Data were obtained for resistance of basic and rapidly solidified aluminum alloys (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} (x = 0; 1; 3) at. % to uniform corrosion. It has been found that increasing the percentage of zinc increases the corrosion rate of both base alloys and rapidly solidified ribbons with similar composition. Pitting and intergranular corrosion tests have been performed. The parameters affected area, pitting density and pitting size were evaluated. An XRD analysis of the separated corrosion products was performed. It was found that the chemical composition, and not the amorphous microstructure of the ribbons, was of leading importance for the course of the corrosion process in the studied rapidly solidified ribbons (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} and base alloys.

Keywords: CORROSION, AMORPHOUS, RAPIDLY SOLIDIFIED, ALLOY, ALUMINUM, CUPRUM, MAGNESIUM, ZINC

1. Introduction

The amorphous structure is thermodynamically unstable. Nevertheless, it shows a chemically homogenous nature due to the absence of defects that act as chemically active sites: there are no structural inhomogeneities such as grain boundaries, duplicates and other defects of the metal crystal lattice; there are no inhomogeneities of the composition such as separations and inclusions. Therefore, it can be expected that the tendency to local corrosion of amorphous metals will be lower than that of their crystalline analogues [1].

On the other hand, unlike crystalline, amorphous metals have a complex composition. The high content of metalloid elements in complex amorphous compositions strongly influences their chemical properties. Amorphous materials are also resistant to corrosion due to the presence of useful minority solute in the solid solution [2, 3]. The beneficial role of minority alloying element (minority solute) is usually expressed in its ability to promote glass forming ability (GFA) [4].

The influence of minority solute on the corrosion resistance of metallic glasses has not been sufficiently studied. Although the role of supersaturated solutions in alkali-based alloys has been studied by characterizing binary solid solutions [5, 6], the influence of minority solute in multicomponent metallic glasses on corrosion resistance has not been well studied due to the difficulty of forming glass without minority solute. To study the role of minority solute requires at least two types of multicomponent metallic glasses, both with and without minority solute.

Data on the corrosion resistance of amorphous alloys in the Al-Cu-Mg system are missing or insignificant. It was found that the addition of more than 2 at.% Ni to the near-eutectic composition of the ternary alloy Al_{75}Cu_{17}Mg_{8} forms an amorphous structure by melt spinning [4]. In addition, these glass alloys (Al_{75}Cu_{17}Mg_{8})_{100-x}Ni_{x} showed an improvement in pitting corrosion resistance compared to their crystalline analogue (x > 2) [7].

The corrosion behavior of base alloys (b) and amorphous rapidly solidified ribbons (r) of the same composition (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} x=0; 1; 2.5; 3 at. % or (Al_{75}MgCu_{17})_{100-x}Zn_{x} x=0; 2; 7 mass. % was studied. The designations of (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} alloys and ribbons are presented in Table 1.

The synthesis of Al-Cu-Mg-Zn alloys was carried out in an installation, established at IMSETHAC-BAS. The rapidly solidified ribbons were obtained by planar flow casting (PFC) method on the laboratory installation. The synthesis of alloys and obtaining of the rapidly solidified ribbons are described in detail in [8, 9].

XRD and EDS analyzes of the ribbons showed that in ribbon 2r the amorphous part is 48 %, in 2r' - 45 %, in 2r'' - 63 % [9]. The ribbons microstructure is an amorphous matrix with nanosized crystals of several types of phases - Al, CuAl_{2}, Al_{3}CuMg, MgCuAl_{3}.

The test pieces were cut of the synthesized ingots and of the rapidly solidified ribbons.

Table 1 The designations of (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} alloys and ribbons

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2c</td>
<td>Al_{75}Cu_{17}Mg_{8}</td>
<td>3b</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2r</td>
<td>(Al_{75}Cu_{17}Mg_{8})<em>{100-x}Zn</em>{x}</td>
<td>2r'</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2r''</td>
<td>(Al_{75}Cu_{17}Mg_{8})<em>{100-x}Zn</em>{x}</td>
<td>2r''r</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

2.3 Test Methods

2.3.1 Uniform corrosion (UC)

The UC test was carried out gravimetrically by the method of continuous immersion of specimens for 15 days (360 hours) in environment of 3%NaCl + 0.1%H_{2}O_{2} at room temperature. One milliliter of 0.1%H_{2}O_{2} was added every three days to control the pH of the solution within the range 5.0-5.2. After the test completion, the corrosion products were removed in ultrasound bath using 30% HNO_{3} solution. The specimens were weighed prior to and after the testing on analytical scales with accuracy of 10^{-4} g.

The mass loss index Δm was determined as \( \Delta m = \frac{m_{n} - m_{f}}{S_{2}} \) [g/m²], where \( \Delta m \) was the mass of the specimen before the testing, and \( S_{2} \) the surface area of the specimen, and \( t \) [h] the test duration.

2.3.2 X-ray diffraction test

XRD analyses were performed to determine the composition of the corrosion products separated from the base (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} crystalline alloys and amorphous rapidly solidified (Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_{x} ribbons during the uniform corrosion test.
The products were collected, washed with distilled water and filtered.

XRD analyses were performed with Bruker D8 advance diffractometer with Cu Kα radiation and a LynxEye detector. Phase identification was performed with Diffracplus EVA using an ICDD-PDF2 database.

2.3.3 Pitting (PC) and intergranular corrosion (IGC)

Pitting corrosion tests were performed only on the base crystalline casting alloys (Al₃Cu₇Mg₆)₀ₓZnx (x = 0; 1; 3 at.%).

The PC and IGC tests were performed in full immersion conditions in a solution of 3%NaCl+1%HCl at room temperature.

After the corrosion test the surface of the samples was observed with SEM Hirox 5500 with EDS system BRUCKER.

The results of PC test were registered after the 2-nd, the 4-th, 6-th and 26-th hours of the testing. The affected areas of the testing specimens, pitting density and pitting size are calculated according to ISO 11463 by optical microscopy Jenavert.

The depth of IGC penetration after 48 hours exposure in the corrosion solution was measured on metallographic specimens, prepared according to the standard procedure normally to the corrosion exposed surface of specimens at a distance at least 5 mm from the edge of the test sample.

3 Results and discussion

3.1 Uniform corrosion tests results

The results of the uniform corrosion tests are presented in Table 2. The corrosion rates of each base alloy (Kb) and of the ribbons after rapidly solidification (Kr) were calculated. The parameter B shows how many times the corrosion rate of the base samples of each alloy Kb exceeds the corrosion rate Kr of rapidly solidified ribbon with the same composition.

Table 2 Corrosion rate of base alloy (Kb) and ribbons after rapidly solidification (Kr)

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Kb</th>
<th>Kr</th>
<th>B = Kb/Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.0508</td>
<td>0.0037</td>
<td>13.73</td>
</tr>
<tr>
<td>2'</td>
<td>0.0930</td>
<td>0.0114</td>
<td>8.16</td>
</tr>
<tr>
<td>2''</td>
<td>0.0975</td>
<td>0.0146</td>
<td>6.67</td>
</tr>
</tbody>
</table>

The obtained results show that, on the one hand, the corrosion rate in both basic and rapidly solidified ribbons increases with increasing Zn content. On the other hand, the Kr value of each of the investigated ribbons is several times lower than Kb for its corresponding base alloy. The highest value has the parameter B for the alloy not containing Zn, and the lowest is that with 7 wt.% Zn. These results can be explained by the results obtained from TEM and XRD studies of the microstructure of rapidly solidified ribbons.

In ribbon 2r (Zn-free), the degree of amorphousness is 48%, Kr is the lowest, and the parameter B has the highest value. In the ribbon 2', the degree of amorphousness is close to that of 2r, but Kb and Kr are significantly higher, and the parameter B is 40% lower than that of the zinc-free alloy. In ribbon 2''r the degree of amorphousness is almost 24% higher than in ribbon 2r, but Kb and Kr are even higher than those in ribbon 2', and the parameter B is 51% lower than in the alloy with 7mass. % Zn.

The corrosion rate of amorphous rapidly solidified ribbons is determined by two factors - chemical composition and microstructure of the alloys. The degree of amorphousness of 2''r is greater than that of 2''r, which means that it has fewer structural defects and inhomogeneities of composition, but the corrosion rate of 2''r is greater than that of 2' r. This is explained by the higher percentage of Zn in 2''r.

This gives us reason to believe that the leading role for the corrosion process in rapidly solidified ribbons (Al₃Cu₇Mg₆)₀ₓZnx with an amorphous part less than 100%, has the chemical composition and not the microstructure of the studied metal alloys.

3.2 Pitting and intergranular corrosion tests results

The results of the pitting corrosion test are presented in Tables 3, 4, 5 and Figures 1, 2, 3. The reported values are an instantaneous indication of the condition of the examined surface and the morphology of the pittings.

In the analysis of the results for the total affected area A of the samples after the 2-nd, 4-th, 6-th and 26-th hour of the test (Table 3) it was found that the relationship between the area affected by the pittings and the percentage of Zn in the test alloys. It is found that with the increasing the percentage contente of Zn in the alloys and the exposure time in corrosion medium, increases the affected corrosion area.

Table 3 Pitting corrosion - Affected area (A) [%]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>2nd</th>
<th>4-th</th>
<th>6-th</th>
<th>26-th</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>5.55</td>
<td>5.55</td>
<td>5.55</td>
<td>5.55</td>
</tr>
<tr>
<td>2'b</td>
<td>21.76</td>
<td>25.46</td>
<td>27.35</td>
<td>30.42</td>
</tr>
<tr>
<td>2''b</td>
<td>19.90</td>
<td>22.22</td>
<td>31.94</td>
<td>37.20</td>
</tr>
</tbody>
</table>

Fig. 1 Affected area of alloy 2b (Zn free) after 4-th hour exposition

Fig. 2 Affected area of alloy 2' b (2 mass. %. Zn) after 4-th hour exposition

The density of the pittings changes slightly with an increase in the percentage of Zn in the alloys (Al₃Cu₇Mg₆)₀ₓZnx (x = 0, 1, 3) (Table 4 and Fig. 1, 2, 3).
The pitting size (Table 5), where is possible to be observed, increases with the time of exposure of the samples to the corrosive medium and with the increase of the percentage of Zn (fig. 4).

Table 5 Pitting corrosion- Pitting size (S) [mm²]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>2-nd</th>
<th>4-th</th>
<th>6-th</th>
<th>26-th</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>2'b</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>8.0</td>
</tr>
<tr>
<td>2''b</td>
<td>2.0</td>
<td>2.0</td>
<td>8.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

The lack of strict dependence of the estimated indicators of pitting corrosion - affected area, pitting density and pitting size on the percentage of Zn in the alloys and the exposure time in a corrosive environment is explained by the model of developed pitting corrosion of Al-alloys containing Zn [10,11].

3.3 XRD results of corrosion products

The corrosion products separated from the base alloys (b) and rapidly solidified (Al_{75}Cu_{17}Mg_{8})_{100-x}Znx ribbons (r) are analyzed by XRD. The results obtained are presented in Table 6 and Fig. 6.

The basic component of the corrosion products separated from the aluminum alloys refers to a thin film of hydrated aluminum oxide. According to ref. [10] the aluminum hydroxide film consists of two sublayers: an internal one of boehmite AlO(OH) stuck to the metal surface, and an outer one of bayerite β-Al(OH)₃. Bayerite is more porous and, depending on the environmental conditions, its thickness slowly changes over time at the expense of boehmite. It is a crystalline phase which can turn to gibbsite depending on the environmental conditions.

Gibbsite is the main corrosion product of the test alloys (b) and ribbons (r). Bayerite dominates in the corrosion product of base alloys and in the ribbon without Zn. Because of the small amounts of corrosion products, it was not possible to determine exactly their crystallinity degree and the phases percentage composition.
4. Conclusions

- By increasing the percentage of zinc in the alloys (Al\textsubscript{75}Cu\textsubscript{17}Mg\textsubscript{8})\textsubscript{100-x}Zn\textsubscript{x}, x = 0; 1; 3 at.%, the corrosion rate of both base alloys and rapidly solidified ribbons with similar composition increases. The lowest is the rate of corrosion of the ribbons and the base analogue of the alloy, which does not contain zinc - Al\textsubscript{75}Cu\textsubscript{17}Mg\textsubscript{8}.

- The chemical composition, not the amorphous microstructure of the alloys, with an amorphous part less than 100%, is of leading importance for the course of the corrosion process in the rapidly solidified ribbons (Al\textsubscript{75}Cu\textsubscript{17}Mg\textsubscript{8})\textsubscript{100-x}Zn\textsubscript{x} studied.

- The development of pitting corrosion in Al-Cu-Mg-Zn base alloys is characterized by the initial formation of pittings, the density and width of which increase over time, but do not develop in depth.

- In the studied base alloys (Al\textsubscript{75}Cu\textsubscript{17}Mg\textsubscript{8})\textsubscript{100-x}Zn\textsubscript{x}, x = 0; 1; 3 at.%, no development of intergranular corrosion was observed.

- The study of the composition of the corrosion products showed the presence of the typical for aluminum alloys phases Bayerite Al(OH)\textsubscript{3} and Gibbsite Al(OH)\textsubscript{3}.

Acknowledgements

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5. References

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