Investigation of mechanical properties of secondary AlSi7Mg0.3 cast alloys before and after corrosion

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Abstract. The casting industry currently use about 35% of secondary (recycled) aluminum and about 65% of primary aluminum to meet their needs. The manufacturer wants to use the secondary aluminum alloys more and more, but these materials have the higher amount of the undesirable elements. The most negative element in such alloys is Fe. Although the corrosion current increased due to the presence of alloying elements in the matrix of aluminum alloys, the higher content of Fe (which led to increasing amount of Fe-rich phases) could affect the corrosion resistance. The basic metallography assessment of experimental materials microstructure confirm the higher amount of Fe-rich phases in secondary alloys. The results of mechanical properties shows that the higher content of Fe (also Fe-rich phases) does not lead to decreasing the mechanical properties. The similar results of mechanical properties were reached after corrosion attack with 3.5 wt. % NaCl. The assessment of corrosion attack confirmed the presence of pitting corrosion on experimental samples, which increase with increasing Fe content.

Keywords: aluminum alloys; recycling; iron; corrosion behavior; mechanical properties;

1 Introduction
Eutectic and near eutectic Al-Si alloys are widely used in casting industry due to superior abrasion and corrosion resistance, low thermal expansion coefficient and high strength/weight ratio [1]. The AlSi7Mg0.3 cast alloys belongs to near eutectic alloys which are used for engine constructions, vehicle and aero plane constructions, shipbuilding, electrical engineering and engine constructions, car wheels and so on [2]. Automotive and aerospace industries have interest in decreasing weight, costs and CO₂ emissions. However, most of aluminum alloy scrap for recycling is generated from the automotive and beverage industries, the application of aluminum alloys especially recycled is required. The main impurities that exist in recycled Al-Si cast alloys are Fe, Mn, Cu and Zn [1,3]. Iron is most critical because Al has limited solubility of iron and hence forms intermetallic compounds during solidification of the alloy. Also iron leads to formation of casting defects and eventually deteriorates the mechanical properties of alloys [1,4]. The main Fe-rich intermetallic phases formed in Al-Si alloys are α-Al₁₅(Mn,Fe)₃Si₂ (Chinese script type structure), α- Al₅Fe₃Si (phase is hexagonal shaped) and β-Al₃FeSi (phase has a monoclinic/orthorhombic structure [4-6]. The other β phases identified in Al-Si alloys are Al₅FeSi₂, Al₅FeSi, Al₅Fe₂Si₂, b-Al₅FeSi, b-A₄.₅FeSi and Fe₂SiAl₅ [4]. All of β phases formation in plate like form (needles in 2D) decreasing mechanical properties of materials especially
ductility. Their formation can be affected with cooling rate but also with neutralizers (Mn, Be, V, Mo, etc.) [7-9]. The Mn is the best neutralizers which transforms coarse Al2FeSi needles to a finely dispersed constituent Al2(Mn,Fe)2Si2 exhibiting a Chinese script type structure in the present [10]. The condition is the Mn/ Fe ratio of 0.5 [6]. Also was researched that if an iron amount exceeds a value of the mass fraction \( w = 0.45 \% \), the recommended addition of Mn should not be lower than half of the iron content [11-13]. The critical iron content (in wt. \%) for an alloy can be calculated using the following relationship (1) [8,9]:

\[
Fe_{crit} \approx 0.075 \cdot [\text{wt. \% Si}] - 0.05. *
\]

*at 5 wt. \% of Si, the critical iron content is ~0.35%, at 7 wt. \% of Si it rises to ~0.5, at 9 wt. \% it is ~0.6 and by 11 wt. \% it reaches ~0.75% [14].

Previous works shows that mechanical properties of commonly used Al-Si casting alloys do not only depend on the chemical composition. However, dendritic \( \alpha \)-Al(Si) morphology and other intermetallic in the microstructures have important effects on the microstructural properties [1,4,5,8,14-16]. The Ambant [17] in their work state that the presence of Fe-rich intermetallic particles has a detrimental effect on corrosion resistance. Iron rich phases are catalytic sites for cathodic reactions, and at the same time are sites for nucleation of pits [17]. One can see that aluminum is stable in the pH range from 4 to approximately 9 due to the presence of aluminum oxide film, which makes its use possible for many applications where corrosion resistance is required. However, in acidic and alkali environments, the aluminum corrodes with the formation of \( Al^{3+} \) and \( AlO_2^- \) ionic species, respectively. It should also be noted that the passivity of aluminum in neutral solutions could be overruled, if in the solution there are species like chlorides that can cause the breakdown of the oxide film and promote corrosion [16]. Also the phase \( Mg_2Si \) phase is seen to be ‘active’ compared to the Al-alloy matrix [18].

From these reasons were examined mechanical properties of secondary (recycled) AlSi7Mg0.3 cast alloys considerably affected from microstructure and corrosion attack in this study. The materials were casted into the sand mold in Uneko Ltd. company, Zátor, Czech Republic in form of bars 20 x 300 mm.

## 2 Experimental methods

The experimental materials were casted as primary (set marking P3 with 0.123 wt. \% of Fe) and secondary (sets marking as S4 with 0.454 wt. \% of Fe and S5 with 0.655 wt. \% of Fe) in order to reflect the effect of secondary aluminum alloys chemical composition to mechanical properties (table 1). Since the material is used for casting, which are exposed to corrosive environment the effect of corrosion to mechanical properties, were also studied.

### Table 1 The chemical compositions of experimental materials (in wt. \%).

| Material | No. of set | Si  | Fe   | Cu  | Mn  | Mg  | Zn  | Ti  | Al  |
|----------|-----------|-----|------|-----|-----|-----|-----|-----|-----|
| primary  | P3        | 7.028 | **0.123** | 0.013 | 0.009 | 0.354 | 0.036 | 0.123 | 92.253 |
| secondary| S4        | 7.340 | **0.454** | 0.021 | 0.009 | 0.302 | 0.020 | 0.118 | 91.673 |
| secondary| S5        | 7.315 | **0.655** | 0.030 | 0.010 | 0.292 | 0.028 | 0.120 | 91.486 |

The samples for measurements of mechanical characteristic were prepared with turning and milling operation. The sets of experimental materials were divided to half in order to examine properties before and after corrosion attack. According to the fact [16] that presence the chlorides in solution can cause the breakdown of the oxide film (promote corrosion) and that Fe rich phases are catalytic sites for cathodic reactions, and at the same time are sites for nucleation of pits [17] the 3.5 wt.% NaCl solution was used as corrosion environment. The corrosion tests were performed according to
rules of immersion tests. The temperature during testing was 20 °C for three weeks. The solution of 3.5 % was used because these content correlate to the average salinity level of the sea and these results could by compared to results of potentiodynamics tests. The mechanical tests were performed immediately after degreasing samples in ethanol and drying. The equipment INSTRON Model 5985 was used for tensile tests, which took place according to the standard ISO 6892-1:2009. Test rates and control were set according to Method A recommended range. The calculated results include ultimate tensile strength (UTS) and ductility (A). Hardness measurement was performed by a Brinell hardness tester with a load of 2451.66 N (250 Kp), 5 mm diameter ball and a dwell time of 15s. The bending impact test was performed on Charphy tested hammer with nominal energy 300 J. The results of such tests include resistance of the material to impact stress (Impact energy in J). The mechanical characteristic value at each state was obtained by an average of at least six measurements. The observation of corrosion attack of specimens for tensile tests was performed on the stereo microscope. The assessment of the effect of higher content of the Fe to microstructure was evaluated with using an optical microscope Neophot 32 and quantitative analysis software NIS Elements. Samples were prepared by standards metallographic procedures (wet ground, DP polished with diamond pastes and etched by Dix-Keller). The assessment of corrosion attack were performed on mechanical specimens before testing (stereo microscopy study) and on metallography samples prepared after testing (non-etched).

3 Research results and discussions

3.1 The basic microstructure of experimental materials

The microstructure of primary alloys (P3) correlate with binary diagram and knowledge about basic microstructural features [5,6,8,14] and consist of the: matrix (α = Al(Si)), eutectic (mechanical mixture of eutectic Si and matrix), Mg-rich intermetallic phases (Mg2Si) and Fe-rich intermetallic phases (Al5FeSi, Al15(FeMg)2Si2) (figure 1). The other set`s (secondary alloys S4 and S5) microstructure is creating from the same microstructural features, but the percentage of the Fe-rich phases - Al5FeSi grows and the Fe-rich phases Al15(FeMg)2Si2 is not formed (in very small volume) and Mg2Si is also in small volume (figure 2).

The calculation (1) was used for assessment of Fecri according to Taylor [14]. The results are: for set P3 = 0.4771, for set S4 = 0.5005 and for set S5 = 0.498625. Experimental materials has fulfilled the condition at 7 wt. % of Si is the Fecri ~ 0.5. Therefore, were confirmed the ratios Mn/Fe for each material. The results show that in primary experimental alloy is ratio 0.07, for set S4 is 0.0198 and for set S5 is 0.0153. The results demonstrated that ratios Mn/Fe [11-13] are not fulfilled. These results point to the fact that even if the content of Fe does not reach the Fecri is important to observe the specified content of Mn for the lower formation of the Al5FeSi Fe-rich phases. When it is no so the formation of such phases increase (figure 2). The quantitative analysis shows that the average length of the Fe-rich phases increase (for set P3 = 30.44 µm², for set S4 = 59.77 µm² and for set S5 = 52.57
and correlate with results of the ratio, because the highest was on samples S4. Moreover, Esquivel [20] reported that increasing the Mn/Fe ratio would result in increased corrosion resistance in various cast alloys containing Mn, Fe, Si and minor additions of Mg. Therefore, there is assumptions that secondary experimental alloys will have lower corrosion resistance, which caused decreasing of the mechanical properties.

![Figure 2](image1)

**Figure 2** The changes in microstructure caused with higher the Fe content, etch. Dix-Keller

a) set P3; b) set S4; c) set S5.

3.2 *The corrosion attack*

The assessment of corrosion attack shows presence the pitting corrosion on each experimental samples. The presence of such corrosion correlate with corrosion environment and also with chemical composition [16,17]. With increasing Fe content has been observed increasing density and scale of corrosion pit (figure 3). These changes correlate with research work of Samuel [19], that the higher content of Fe lead to the increasing pitting corrosion of Al-alloys. Also, Esquivel [20] and Ambant [17] demonstrated that the chemical composition, size, number and distribution of the intermetallics in the matrix govern the corrosion of Al alloys.

![Figure 3](image2)

**Figure 3** The pitting corrosion of experimental alloys a) set P3; b) set S4, c) set S5.

3.3 *The changes in mechanical properties after and before corrosion*

The results of mechanical properties of experimental materials shows that combination of the corrosion in 3.5 % NaCl and Fe content influence these properties (figure 4). The basic mechanical properties in materials before corrosion attack are more or less the same. The differences were very small (table 2, figure 4). These results confirm the knowledge [1,4,14-16] that the chemical composition affecting the mechanical properties, but also confirm that the presence of higher amount of Al5FeSi Fe-rich phases make these materials cleavages.
The results of basic mechanical properties after corrosion shows that the Fe content have a great influence on the properties, because the UTS and HBW increase with the Fe content. The impact energy and ductility decreasing with increasing Fe content in experimental materials after corrosion (table 2, figure 4). The corrosion effect on the mechanical properties is not clearly, because the results are not according to knowledge’s in research works of [16-19]. The important is the note that with increasing content of Fe increase strength properties but decreasing tension properties in samples after corrosion.

Table 2 The mechanical properties of experimental materials

| N° of experimental sets | Before corrosion | After corrosion |
|-------------------------|------------------|-----------------|
|                         | P3   | S4   | S5   | P3   | S4   | S5   |
| UTS [MPa]               | 144  | 150  | 142  | 130  | 140  | 144  |
| HBW 5/250/15            | 52   | 55   | 54   | 58   | 59   | 59   |
| Ductility [%]           | 1.45 | 1.91 | 1.58 | 1.7  | 1.5  | 1.3  |
| Impact energy [J]       | 14   | 12   | 10.5 | 10.5 | 8    | 7.8  |

Figure 4 The results of mechanical properties of each experimental material before and after corrosion.

4 Conclusions

The secondary experimental materials (S4 and A5) have increasing amount of the Al3FeSi Fe-rich phases, because the ration Mn/Fe is not sufficient. The negative effect of the Al3FeSi phases on to basic mechanical properties was also not confirmed (the primary alloy have similar properties as secondary). It supposes that these phases have not the critical length (more than 500 µm [14]) and their amount can act as barriers to the propagation of the fracture. The negative effect of the corrosion on the properties was also not confirmed. Decreasing only UTS and Impact energy. Moreover, the properties of secondary alloys after corrosion have similar, small, or less high value as primary alloys. These results lead to creating new research works for declaration that secondary alloys with higher content of Fe have not so negative properties and are completely useful for casting the automotive casts.
Acknowledgement
This work has been supported by the grant projects N° 016ŽU-4/2020, N° 1/0398/19, N° 012ŽU-4/2019. The authors also thank for cooperation with casting samples to Uneko Ltd. Company.

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