CHARACTERIZATION OF PHASES IN SECONDARY AlZn10Si8Mg CAST ALLOY

Eva Tillová1,*, Emília Ďuriníková1, Mária Chalupová1
1Department of Materials Engineering, Faculty of Mechanical Engineering, University of Žilina, Univerzitná 1, 010 26 Žilina, Slovak Republic.
* corresponding author: Tel: +421 41 513 2613, Fax: -, e-mail: eva.tillova@fstroj.uniza.sk

Resume
Using recycled aluminium cast alloys is profitable in many aspects. Requiring only 5% of the energy to produce secondary metal as compared to primary metal and generates only 5% of the greenhouse gas emissions, the recycling of aluminium is therefore beneficial of both environmental and economical point of view. Secondary AlZn10Si8Mg (UNIFONT® - 90) cast alloy are used for engine and vehicle constructions, hydraulic unit and mouldmaking without heat treatment. Properties include good castability, very good mechanical strength and elongation, light weight, good wear resistance, low thermal expansion and very good machining. Improved mechanical properties are strongly dependent upon the morphologies, type and distribution of the secondary phases, which are in turn a function of alloy composition and cooling rate. The presence of additional elements as Mg, Mn, Fe, or Cu allows many complex intermetallic phases to form, which make characterisation non-trivial. These include, for example, Mg2Si, Al2CuMg and AlFeMn phases, all of which may have some solubility for additional elements. Phase’s identification in aluminium alloys is often non-trivial due to the fact that some of the phases have either similar crystal structures or only subtle changes in their chemistries. A combination different analytical techniques (light microscopy upon black-white and colour etching, scanning electron microscopy (SEM) upon deep etching, energy dispersive X-ray analysis (EDX) and HV 0.01 microhardness measurement) were therefore been used for the identification of the various phase.

1. Introduction
Among the light metal family, aluminium has been acquiring increasing significance for the past few decades due to its excellent properties and diversified range of applications. Aluminium has been recognized as one of the best candidate materials for various applications by different sectors such as automotive, construction, aerospace, etc. The increasing demand for aluminium-based products and further globalization of the aluminium industry have contributed significantly to the higher consumption of aluminium scrap for reproduction of aluminium alloys [1].

The increase in recycled metal becoming available is a positive trend, as secondary aluminium produced from recycled metal requires only about 2.8 kWh/kg of metal produced while primary aluminium production requires about 45 kWh/kg produced. It is to the aluminium industry’s advantage to maximize the amount of recycled metal, for both the energy-savings and the reduction of dependence upon overseas sources.

The remelting of recycled metal saves almost 95% of the energy needed to produce prime aluminium from ore, and, thus, triggers associated reductions in pollution and greenhouse emissions from mining, ore refining, and melting. Increasing the use of recycled metal is also quite important from an ecological standpoint, since producing aluminium by recycling creates only about 5% as much CO2 as by primary production [2, 3, 4].
Today, a large amount of new aluminium products are made by recycled (secondary) alloys. This represents a growing ‘energy bank’ of aluminium available for recycling at the end of components’ lives, and thus recycling has become a major issue. The future growth offers an opportunity for new recycling technologies and practices to maximize scrap quality; improve efficiency and reduce cost.

Aluminium cast alloys are extensively used in the automotive industry due to their excellent castability, good mechanical properties, machinability and wear resistance. Recycled Al-Si-Zn casting alloys can often be used directly in new cast products for mechanical engineering, in hydraulic castings, textile machinery parts, cable car components, mould construction or big parts without heat treatment [5].

One major hurdle in the direct use of recycled aluminium for new applications is the level of impurities present in the recycled (secondary) alloy; which is considered to impair the overall properties of Al-Zn-Si based casting alloys. By implementing adaptable alloying- and process technology, the mechanical properties will therefore be radically enhanced, leading to larger application fields of complex cast aluminium components such as safety details. Generally, the mechanical and microstructural properties of aluminium cast alloys are dependent on the composition; melt treatment conditions, solidification rate, casting process and the applied thermal treatment. The mechanical properties of Al-Si and Al-Zn-Si alloys depend, besides the Si, Zn, Mg and Fe-content, more on the distribution and the shape of the silicon particles [6]. The presence of additional elements in the Al-Si or Al-Zn alloys allows many complex intermetallic phases to form, such as binary phases (e.g. Mg2Si, Al3Cu), ternary phases (e.g. Al3CuMg, Al5FeSi, AlFeMn, Al7Cu3Ni and AlFeNi) and quaternary phases (e.g. cubic α-Al15(FeMn)3Si2 and Al5Cu2Mg5Si6) [7-10], all of which may have some solubility for additional elements.

The present study is a part of larger research project, which was conducted to investigate and to provide a better understanding morphology and composition of complex microstructures containing intermetallic phases formed in the secondary (recycled) aluminium cast alloy.

2. Experimental procedure

As an experimental material was used secondary (scrap-based - recycled) unmodified AlZn10Si8Mg cast alloy (UNIFONT® - 90) with very good casting properties, good wear resistance, low thermal expansion and very good machining [5, 11]. Alloy contains relatively high Si, and their impurity limits tend to be relatively loose. Test bars (ø 20 mm with length of 300 mm) were produced by process sand casting in foundry Zátor, Ltd. Czech Republic. Sand casting is the simplest and most widely used casting method. The melt was not modified or refined. Chemical composition of the alloy is given in Table 1.

The only intentional and controlled additions of Zn to Al-casting alloys are in the 7XXX series, and those are not yet suitable for die casting or any of its variations. Otherwise, zinc is present merely as an acceptable impurity element in many secondary (scrap-based) die casting alloys. As such, zinc is quite neutral; it neither enhances nor detracts from an alloy’s properties. It should be recognized that zinc is a relatively dense (heavy) element, and as such it

| Chemical composition of AlZn10Si8Mg alloy (wt.%) |
|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|
| Zn   | Si    | Cu   | Fe   | Mn   | Mg   | Ti   | Ni   |
| 9.6  | 8.64  | 0.005| 0.1143| 0.181 | 0.452 | 0.0622 | 0.0022 |
| Cr   | Hg    | Ca   | Cd   | Bi   | P    | Sb   | Al   |
| 0.0014 | 0.0006 | 0.0002 | 0.0001 | 0.0003 | 0.0001 | 0.0007 | rest |

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increases an alloy’s mass density. High-zinc secondary alloys usually seem attractive because they cost somewhat less than low-zinc versions. However, that attractiveness can be deceiving if the cost differential is too small; it can make little sense to purchase lower cost alloys if doing so means shipping a higher weight of material with each casting [5, 11].

AlZn10Si8Mg cast alloy is a self-hardening alloy that is particularly used when good strength values are required without the need for heat treatment. With these alloy types, the mechanical properties are achieved after storage of approximately 7 to 10 days at room temperature. Particular attention should be paid to the high 0.2% yield strength. The low iron content has a particularly beneficial effect on the mechanical properties, which can also be traced to good fatigue strength.

The sand casting alloy AlZn10Si8Mg achieves high values for tensile strength (220 - 250 MPa), offset 0.2% yield stress (190 - 230 MPa), however the low ductility limits (1 - 2%), Brinell hardness 90 - 100 and fatigue resistance (80 - 100 MPa) [5, 11, 12].

Cast samples (1.5 cm x 1.5 cm) were sectioned from the test bars (in transversal and longitudinal direction), standard prepared for metallographic observations (wet ground on SiC papers, DP polished with 3 µm diamond pastes followed by Struers Op-S) and etched first by standard reagents (HF, Fuss, Dix-Keller, and H2SO4) and next by colour reagent (MA, Weck-Al and Murakami) [13-15]. The microstructures were studied using an optical microscope (Neophot 32) under 100x, 500x and 1 000x magnification. Some samples were also deep-etched for 30 s in HCl solution in order to reveal the three-dimensional morphology of the silicon phase [13, 16-18]. The specimen preparation procedure for deep-etching consists of dissolving the aluminium matrix in a reagent [13] that will not attack the eutectic components or intermetallic phases. The residuals of the etching products should be removed by intensive rinsing in alcohol. The preliminary preparation of the specimen is not necessary, but removing the superficial deformed or contaminated layer can shorten the process.

The various phases reported in this work were identified using scanning electron microscope VEGA LMU II linked to the energy dispersive X-ray spectroscopy (EDX analyser Brucker Quantax). All phases were analysed by EDX technique.

The phases Vickers microhardness was measured in HTW Dresden using a MHT-1 microhardness tester under a 1 g load for 10 s (HV 0.01). Twenty measurements were taken per sample and the median microhardness was determined.

3. Results and discussion

Typical microstructures of the as-cast alloy are shown in Fig. 1. The microstructure of recycled AlZn10Si8Mg cast alloy consists of a primary phase, α-solid solution, an eutectic mixture of α-matrix and fine spherical phases (probably silicon) and variously type’s intermetallic phases (Fig. 1a). The α-matrix precipitates from the liquid as the primary phase in the form of dendrites and is nominally comprised of Al and Zn.

In the commercial 7XXX aluminium alloys a wide range of intermetallic particles formed during solidification - in the interdendritic regions and at the grain boundaries. In these aluminium alloys besides the intentional additions, metals such as Mg, Fe, Mn and Cu are always present. Even not large amount of these impurities causes the formation of a new phase component. The exact composition of the alloy and the casting condition will directly influence the selection and volume fraction of intermetallic phases.

Figures 1b and 1c show tree types of intermetallic compounds. These intermetallic particles had different morphologies, such as: platelet or needles, skeleton- or script-like or “Chinese script” too and oval.
Optical microscopy and SEM observation with EDX analysis (combination of identification chemical data of each phase with mapping) have been combined to produce a simple method for phase identification. Figure 2 shows a SEM image and X-ray mapping of the microstructure of phases in AlZn10Si8 alloy. Iron is the most common impurity in aluminium alloys. The low solubility of iron in aluminium alloy allows for the easy combination of Al, Si, or Mg to form various Fe-rich phases during solidification. Fe-containing intermetallics, such as AlFeMn phases, are formed between the α-dendrites. The morphology of this Fe-rich phase is plate-like (thin grey needles in Fig. 1b and Fig. 1c) with a thickness of a few tenths of a micrometer and other dimensions of the order of 10 μm. It is these plate-shaped precipitates that are considered most deleterious to mechanical properties (particularly ductility), Fe-needles also reported to reduce the castability, the corrosion resistance, and the machinability of Al-casting alloys.

Besides the Fe-needles were observed Fe-rich phases (AlFeMnSiNi or AlFeNi) in the form sharp-edged coarse particles. Platelets act as potential nucleation sites for porosity (Fig. 1d) and sites for crack initiation that, consequently, results in decohesion failure [13, 19, 20]. Thus, control of these phases (e.g. quantitative analysis [21-22]) is of considerable technological importance.
Addition of Mg to Al-Zn-Si alloys leads to formation strengthening Mg-rich intermetallic compounds. Mg-phases can in Al-Zn-Si alloy solidify in two different forms: Mg$_2$Si and Al$_2$CuMg. The Mg$_2$Si phase was identified by EDX analysis as individual skeleton-like or script-like so called “Chinese script” morphology (blue or black phase) - Figures 1c and 2. Oval round-like particles was detected as S-phase (Al$_2$CuMg - light grey phase).

Phases AlFeMn, AlFeMnSiNi, AlFeNi and Mg$_2$Si are formed by impurities during solidification and can also be found, which are detrimental to the mechanical properties, as they act as stress-raisers. Next intermetallic phases besides these few phases were neither by using colour contrast in optical microscopy not observed.

The EDX analysis revealed, that the spherical phases in eutecticum ones (Figures 1 and 2) are really the eutectic silicon. The silicon precipitates, present in commercial Al-cast alloys, are almost pure, faceted crystals. Figure 3 shows the three-dimensional morphology of eutectic silicon observed by SEM on the deep-etched samples. The silicon phase exhibits a typical fine and rosette-like, rather than plate-like form. The centre of a rosette could be the centre of a eutectic cell/grain, indicating the nucleation of the eutectic phases could be independent to the surrounding primary α-aluminium dendrites. This result about Si morphology is in accordance with previous reports for unmodified Al-Si alloys [13, 16, 23].
The phases Vickers microhardness was measured in HTW Dresden using a MHT-1 microhardness tester under a 1g load (HV 0.01) for 10 s. Twenty measurements were taken per sample and the median microhardness was determined. The results of the Vickers microhardness values of the phases are shown in Table 2. It is evident that the microhardness of the eutectic silicon is highest (1124 HV 0.01). This phase with plate-like morphology is very brittle. Fe-particles break during polishing in slurry of alumina.

<table>
<thead>
<tr>
<th>Phase Description</th>
<th>HV 0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-matrix</td>
<td>92</td>
</tr>
<tr>
<td>eutectic phase (α-matrix + Si)</td>
<td>155</td>
</tr>
<tr>
<td>Si-particles</td>
<td>1124</td>
</tr>
<tr>
<td>Al$_2$CuMg - oval round-like particles</td>
<td>426</td>
</tr>
<tr>
<td>Mg$_2$Si - Chinese script</td>
<td>548</td>
</tr>
<tr>
<td>AlFeMn - needle-like phase</td>
<td>950</td>
</tr>
<tr>
<td>Fe-phase (AlFeNi or AlFeMnSiNi) - sharp-edged particles</td>
<td>727</td>
</tr>
</tbody>
</table>

Fig. 3. Morphology of Si particles, deep-etch. HCl, SEM
4. Conclusion

Understanding of metal quality is of superior importance for control and prediction of casting characteristics. The results are summarized as follows:

The secondary AlZn10Si8Mg cast alloy used in this study possessed a complex as-cast microstructure. By using various instruments (light microscopy, SEM) and techniques (black-white, colour and deep etching, EDX) a wide range of intermetallics phases were identified.

The microstructural analyses show that all the alloying element studied form intermetallic phases. Zn is present in solid solution \( \alpha \). Fe enters the intermetallic phases regardless of its concentration in the alloy. Mn and Ni usually are present in the Fe-containing phases and often substitutes part of Fe. Mg forms intermetallic phases with Si or Cu. Cu makes the intermetallic phases form more compact, Mg skeleton-like and Fe needle-like.

Si is present a typical fine rosette-, rather than plate-like brittle form with highest microhardness. Just very hard and brittle are all Fe-rich phases independently of their morphology.

Acknowledgements

This work has been supported by Scientific Grant Agency of Ministry of Education of Slovak republic No 1/0249/09, No 1/0841/11 and SK-CZ-0086-09.

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