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Sample preparation methods for scanning electron microscopy of homogenized Al-Mg-Si billets: A comparative study

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ABSTRACT

Characterization of Mg-Si precipitates is crucial for optimizing the homogenization heat treatment of Al-Mg-Si alloys. Although sample preparation is key for high quality scanning electron microscopy imaging, most common methods lead to dealloying of Mg-Si precipitates. In this article we systematically evaluate different sample preparation methods: mechanical polishing, etching with various reagents, and electropolishing using different electrolytes. We demonstrate that the use of a nitric acid and methanol electrolyte for electropolishing a homogenized Al-Mg-Si alloy prevents the dissolution of Mg-Si precipitates, resulting in micrographs of higher quality. This preparation method is investigated in depth and the obtained scanning electron microscopy images are compared with transmission electron micrographs: the shape and size of Mg-Si precipitates appear very similar in either method. The scanning electron micrographs allow proper identification and measurement of the Mg-Si phases including needles with lengths of roughly 200 nm. These needles are β″ precipitates as confirmed by high resolution transmission electron microscopy.

1. Introduction

Al-Mg-Si alloys, also known as 6xxx series Al wrought alloys, are widely processed by extrusion and rolling. The billets or slabs for these processes are usually direct chill cast. Thereafter, the billets are homogenized which means that they are heated to a temperature in the range of roughly 450–600 °C and soaked at the elevated temperature for several hours [1].

The goals of homogenization of Al-Mg-Si alloys are to homogenize the distribution of alloying elements (remove segregation) [1] and to convert plate-like β-AlFeSi particles into more rounded α-Al(MnFe)Si particles [1,2]. These rounded particles are less detrimental to surface quality and mechanical properties of the end-product. Depending on the alloy composition, the precipitation of intra-granular dispersoids of α-Al(MnFe)Si, α-Al(MnFeCr)Si , or similar, with sizes usually below 500 nm, might also occur [3]. Below, the term dispersoids will only be used to denote this type of precipitate.

Furthermore, it is desired to dissolve coarse primary Mg_2Si particles during homogenization. Depending on the cooling rate from the homogenization temperature, Mg and Si remain in solid solution or are re-precipitated [4].

The extent of re-precipitation of Mg and Si and the size and type of the precipitates are of great importance for the subsequent forming processes. For extrusion, it is generally desired to re-precipitate most of Mg and Si to reduce the effect of solid solution hardening and, thereby, reduce breakthrough pressure. However, when the cooling rate is too low, the precipitates become too coarse. When this is the case, the coarse particles do not fully dissolve during extrusion leading to inferior surface finish and poor mechanical properties. See the review of Zhu et al. [4] for an overview on these phenomena and the research on the role of Mg-Si precipitates.

A possibility to assess all types of micro- and nanoscale precipitates prevalent in Al-Mg-Si alloys is transmission electron microscopy (TEM). Among the advantages of TEM are high resolution and the possibility to clearly identify phases, for example, by means of their selected area electron diffraction (SAED) patterns or high resolution TEM (HRTEM). However, sample preparation is complex, the analysis is very local due to the use of small samples and might thus not be

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representative, and the correct interpretation of the micrographs can be challenging [5]. Additionally, transmission electron microscopes are expensive and not always available at research institutions.

The use of scanning electron microscopy (SEM) can overcome some of these challenges. However, notwithstanding the industrial relevance of the homogenization of Al-Mg-Si alloys and the great amount of research that has been conducted in the field, the quality of SEM images obtained using many common sample preparation methods is improvable when it comes to secondary Mg-Si particles. It is generally possible to extract some information concerning the extent of precipitation, yet the type, size and number density of the particles cannot be precisely determined. The next section provides a brief description of these common methods as well as a literature review on a less-commonly used method – electropolishing with nitric acid and methanol.

1.1. Sample Preparation Methods for SEM of Al Alloys

Mechanical polishing is the simplest of the sample preparation methods discussed in this study. It is sufficient for imaging of large precipitates and, in some cases, for electron backscatter diffraction (EBSD) [6].

Another approach to the preparation of Al samples for SEM is chemical etching. A great variety of etchants can be found in textbooks on metallography [7,8], some of them suggested for micro-etching of Al-Mg-Si alloys.

Aside from solely mechanical polishing the most common procedure for the preparation of SEM samples of Al alloys is electrolytic polishing (electropolishing). A mechanism of electropolishing was proposed by Hoar and Mowat [9]. The theory suggests that a film of oxide is formed upon the onset of electropolishing, explaining the rise of potential usually observed for a constant current density. In contrast to electrolytic passivation of metals, during electropolishing this layer is rapidly dissolved by the concentrated acid solutions used as the electrolytes. The metallographic equipment manufacturer Struers suggests the use of its widely-used electrolyte A2 containing perchloric acid [10].

An electrolyte mixture of 30% (*v*/*v*) or 33.3% (*v*/*v*) of concentrated nitric acid with methanol is commonly reported for the preparation of thin foils of Al alloys for TEM investigations. Such an electrolyte is usually referred to as nital. This method was published by Tomlinson [11]. For the preparation of SEM samples of Al and its alloys, however, the use of this electrolyte is rarely reported. Hurley and Humphreys [12] use electropolishing with nital at −30 °C and a voltage of 12 V for sample preparation of an Al–0.1 Mg alloy for high resolution EBSD. Brunner et al. [13] use the same method to produce specimens of AA2024-T351 (an Al-Cu-Mg wrought alloy) for EBSD analysis. Murali et al. [14] describe the use of nital with 20% (*v*/*v*) glycerol for electropolishing of an Al-7 Si-0.3 Mg cast alloy at −33 °C and 25 °C; various voltages were tested. It was concluded that the use of nital gives acceptable results, yet the results using perchloric acid solutions yielded better results. Regarding Al-Mg-Si wrought alloys, Steele et al. [5] electropolished quenched samples of AA6111 with nital to quantify grain boundary precipitates and Fan et al. [15] investigated strengthening of an alloy called 6A02 in the hot forming-quenching process.

1.2. Aim of this Study

Using a homogenized Al-Mg-Si alloy, we compare different SEM sample preparation methods in order to identify the most suitable method to achieve high quality micrographs of the intragranular Mg-Si precipitates formed during homogenization. The studied methods are mechanical polishing, etching with different solutions, and electropolishing with perchloric acid or nital.

The samples were investigated by SEM; the most adequate sample preparation method is identified and thoroughly studied. Furthermore, the SEM images are compared to TEM micrographs for evaluation and the precipitates are identified by SAED and HRTEM; we also comment on sample preparation methods for TEM.

Given the commercial importance of the homogenization of Al-Mg-Si alloys, the results should be useful for material scientists and engineers at public and private institutions working on such alloys.

2. Experimental

2.1. Material and Methods

Samples of AA6082 were direct chill cast and then homogenized at 580 °C for 4 h and cooled at a rate of 300 °C h^{-1}; this heat treatment regimen was chosen because it yields relatively large intergranular precipitates. The alloy composition is Al—0.81% Si—0.70% Mg—0.44% Mn—0.22% Fe—0.05% Zn—0.02% Cr—0.02% Ti (all values in wt.%). Specimens from the billets were cut and mechanically polished using standard metallographic techniques.

For electropolishing, two different electrolytes were prepared. For the perchloric acid solution, 910 ml of a solution of 65–85% ethanol, 10–15% 2-butoxyethanol, and 5–15% water (Struers electrolyte A2-I) were mixed with 50 ml of 60% perchloric acid (Struers electrolyte A2-II). For the preparation of 30% (*v*/*v*) nital, 240 ml of nitric acid (65%, *p.a.*) were added very slowly to 560 ml of methanol (*p.a.*). The solution was magnetically stirred and cooled in a bath of ice and salt (−12 °C; see safety advice below).

A Struers LectroPol-5 electrolytic polishing and etching device was used with an electropolishing mask having a round opening of 0.5 cm^2. The respective electrolyte solution was filled into the plastics container of the electropolishing machine and cooled to a temperature of roughly −30 °C by immersing the container in liquid nitrogen. Then, the container was placed in the appliance and electropolishing started. By this procedure, an electrolyte temperature during polishing of −20 ± 5 °C was achieved. For the perchloric acid electrolyte, electropolishing at room temperature was also performed. Combinations of voltages of 9 V, 25 V, and 40 V with different flow rates (the device has arbitrary flow rate settings from 1 to 20) and electropolishing times were tested. Samples were then washed with methanol and dried.

Linear sweep voltammetry was performed using the built-in scanning function of the Struers LectroPol-5. Additionally, manual recordings of the current density at different voltages were performed. For this purpose, freshly mechanically polished surfaces were electropolished with the Struers LectroPol-5 under potentiostatic polarization and the current densities after 20 s of electropolishing were recorded.

As an alternative to electropolishing, samples were etched with diluted HF, Flick, Dix-Keller, and Keller solutions. The exact compositions and etching conditions are given in the supplementary information. The samples were subsequently washed with water, then washed with isopropanol and dried using a hair dryer.

SEM investigations were performed on a Zeiss Ultra Plus 55 field emission gun SEM equipped with a GEMINI in-lens detector for secondary electrons, referred to as the SE detector, an angle selective backscattered (AsB) electron detector, referred to as the BSE detector, and an energy dispersive X-ray (EDX) detector. The accelerating voltage was 15 kV and the working distance was between 5 and 10 mm.

TEM thin foils were either prepared by electropolishing at 8 V, −10 °C and a flow rate of 4 in a Struers Tenupol-5 using the nital electrolyte for 1-2 min, or thinned by ion-milling in a Precision Ion Polishing System (PIPS) at 4.5 V for about 10 h. TEM investigations were carried out on an FEI Tecnai F20, equipped with an X-FEG field emission gun with operation voltage at 200 kV. The characterization of the different precipitates was done by means of TEM bright field, high resolution TEM, SAED patterns, and EDX.