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Influence of cooling rate on the microstructure and corrosion behavior of Al–Fe alloys

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ABSTRACT

The effect of Fe in Al is technologically important for commercial Al-alloys, and in recycled Al. This work explores the use of the novel rapid solidification technology, known as direct strip casting, to improve the recyclability of Al-alloys. We provide a comparison between the corrosion and microstructure of Al–Fe alloys prepared with wide-ranging cooling rates (0.1 °C/s to 500 °C/s). Rapid cooling was achieved via direct strip casting, while slow cooling was achieved using sand casting. Corrosion was studied via polarisation and immersion tests, followed by surface analysis using scanning electron microscopy and optical profilometry. It was shown that the corrosion resistance of Al–Fe alloys is improved with increased cooling rates, attributed to the reduced size and number of Fe-containing intermetallics.

1. Introduction

Aluminium and its alloys are prone to pitting corrosion due to the presence of secondary phases (constituents, precipitates, and dispersoids) formed during casting and subsequent thermo-mechanical processing [1–5]. The influence of secondary phases on the corrosion of Al alloys largely depends upon their morphology and chemical composition [4,6–13]. Fe is present as an impurity in Al-alloys and tends to form coarse intermetallics (e.g., Al_3Fe, AlFeMnSi, $Al7Cu_2Fe$, and $Al_2CuFeMn$) that are cathodic in nature and are known to cause severe pitting [2,14–21]. Fe cannot be avoided in commercial Al alloys, and its content increases during recycling [20]. Thus, Fe build-up limits the recyclability of high performance Al-alloys in which the Fe content is required to be less than 0.1 wt.% [22]. As a consequence, it is necessary to develop new technologies which could decrease the detrimental effect of Fe in Al-alloys [23], leading to the improved recyclability of these alloys [24].

Faster solidification is expected to result in smaller Fe-intermetallics and increased solid solubility in Al alloys [25] which is deemed to improve pitting susceptibility [8,26,27]. Any casting technology enabling a more rapid cooling rate is known to result in refined microstructure and therefore, a positive influence on the corrosion resistance is envisaged. Indeed, processing routes with high cooling rates are expected to offset the deleterious influence of Fe on corrosion of Al leading to an increase in tolerance limit of Fe in high performance Al alloys and consequently result in significantly increased recyclability of these alloys [28–30]. Various rapid solidification techniques such as melt spinning or splat quenching have been developed in the past, however such methods have limited potential for upscaling. In this paper, we investigate an industrial scale rapid solidification technique, direct strip casting (DSC), for Al alloys. Alloys were also produced with conventional casting techniques in order to provide a comparison of the effect of cooling rate on the alloys' microstructures/properties.

The DSC technology with a vertical twin-copper roll apparatus has been recently implemented in the steel industry and provides a practical, industrially applicable, means for rapid solidification [31]. In the present study, we used DSC to rapidly solidify Al–Fe sheet samples and characterise the impact of increasing cooling rate on the intermetallics and corrosion properties. In DSC, extremely high cooling rates in excess of 500 °C/s are encountered. In such rapid cooling condition, the morphology and volume fraction of intermetallics have been poorly investigated [23]. Two alloy compositions, Al-0.1 wt%Fe and Al-2 wt%Fe, have been tested in the present study. Both cooling rate and composition influenced the composition, morphology and number density of the intermetallics. The refined intermetallics after DSC caused a major

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improvement in the corrosion resistance. As a result, we propose that rapid solidification technologies, such as direct strip casting, could be used to increase the tolerance limit of Fe in high performance Al alloys, thus improving their recyclability.

2. Experimental

2.1. Alloy production

The two alloy compositions, Al-0.1 wt%Fe and Al-2 wt%Fe, were cast using three distinct casting routes:

1) The highest cooling rate (∼500 °C/s) was achieved using a strip casting simulator, known as a dip tester, which is designed to simulate the initial contact between the melt and the copper rolls during the twin-copper roll casting process [32]. This design resulted in 35 × 35 × 2 mm samples.
2) Small sand molds containing two steel plates separated by a 12 mm gap were used to achieve the intermediate cooling rate (∼1 °C/s). These molds resulted in samples with a diameter of 35 mm and a thickness of 12 mm.
3) A large rectangular sand mold was used to produce 3 kg alloy blocks. This final route provided the slowest cooling rate (∼0.1 °C/s), close to the conventional industrial processing.

2.2. Microstructural characterization

The microstructural characterization was carried out using secondary electron imaging with a Zeiss Supra 55VP scanning electron microscope equipped with a field electron gun (FEG) and energy dispersive X-ray spectroscopy (EDXS). The SEM samples were polished down to colloidal silica (∼0.01 μm).

2.3. Corrosion tests

Potentiodynamic polarisation tests were carried out in a conventional three-electrode electrochemical cell, consisting of a platinum mesh as counter electrode and a saturate calomel electrode (SCE) as the reference electrode. All the potentials, reported in this study are with respect to SCE. The tests were carried out at room temperature in 0.1 M NaCl using a VMP-3 potentiostat (BioLogic) under the control of EC-Lab software and with a scan rate of 1 mV/s. Prior to all experiments, the open circuit potential was monitored for 30 min to confirm its stability with time. The experiments were repeated at least five times to have a measure of reproducibility. The test specimens (Al–Fe alloys as produced by various methods) were mounted in epoxy and ground down to 1200-grit SiC paper, and cleaned with ethanol prior to the potentiodynamic polarisation tests.

The Al–Fe samples were immersed in 0.01 M NaCl solutions for 15 days. Prior to immersion, the specimens were successively polished to a colloidal silica finish (0.01 μm) followed by cleaning in ethanol in an ultrasonic bath for 5 min. Following the immersion tests, the specimens were cleaned in 15% HNO_3 to remove corrosion products. In order to quantify pitting that occurred following constant immersion, the sample surface was characterized using SEM and optical profilometry. Optical profilometry measurements (using a Veeco Wyko NT100 optical profilometer) were carried out at least in three distinct regions for each sample. The regions of analysis were 1.2 × 2 mm in size. The average pit depth was determined using Veeco Vision® analysis software.

3. Results

3.1. Thermal analysis

The cooling rates in the three casting techniques used herein were empirically measured, at a frequency of 10,000 Hz. The cooling rates were determined to be 0.1, 1, and 500 °C/s (over the range of 600 °C to 300 °C) for the three casting conditions used in this study. The solidification curves, for each casting condition, were measured during casting of Al-2 wt%Fe and are displayed in Fig. 1a. An exothermic event followed by a plateau at 642 °C can be identified in the slow cooling condition. These temperature effects can be attributed to the eutectic decomposition. The eutectic temperature (642 °C) is in a good agreement with what is reported in the literature [23,33]. The equilibrium eutectic results in the formation of the most common Fe-intermetallic of stoichiometry Al_3Fe [23,34], sometimes also referred as $Al_{13}Fe_4$ [35].

In the fast cooling condition, two exothermic events at 607 and 421 °C (highlighted with arrows) can also be observed. Part of the liquid decomposes into eutectic solid at 607 °C (high undercooling) but another metastable reaction seems also to occur at much lower temperature (421 °C). This low temperature reaction is most likely due to the formation of metastable Al_xFe ($3 < x < 6$) compounds [23,34,36,37]. The influence of cooling rate on Fe-intermetallic composition will be detailed in the discussion section.

The solidification curves for rapid cooling conditions for both Al-0.1 wt%Fe and Al-2 wt%Fe are represented together in Fig. 1b. No exothermic events are visible for the Al-0.1 wt%Fe.

3.2. Microstructural analysis

Representative SEM images of the as-cast microstructures of Al-0.1 wt%Fe and Al-2 wt%Fe, for the three cooling rates under investigation, are reported in Figs. 2 and 3 respectively. EDX elemental mapping for the Fe content are shown together with the micrographs. The influence of the composition and the cooling rate on the size and morphology of the intermetallics is evident from Figs. 2 and 3. In the case of Al-0.1 wt%Fe, the observed intermetallics are spherical in shape and their size is decreased by one order of magnitude when increasing the cooling rate from 0.1 °C/s to 500 °C/s. In the slowest cooling condition, Fig. 2c, coarser needle-like intermetallics aligned and interconnected (marked by yellow arrow in Fig. 2c) are also noticed.

In the case of Al-2 wt%Fe, the influence of cooling rate on the size and morphology of intermetallics becomes clearly visible (Fig. 3). For the fastest cooling rate, two morphologies are observed: (1) spherical and (2) needle-like aligned intermetallics. The size of the spherical intermetallics is similar to that for Al-0.1 wt% produced by conventional ingot casting (slowest cooling rate, Fig 3a). The two precipitate morphologies are linked to the two exothermic events reported in the solidification curve, Fig. 1. The literature indicated that these two populations are the stable Al_3Fe and metastable Al_xFe ($3 < x < 6$) compounds [23,34,36,37].

For the intermediate cooling of 1 °C/s, a clear change in morphology and number density of intermetallics is observed. The Fe-intermetallics are now arranged in a continuous network fashion. The presence of contrast differences between intermetallics (some are brighter than others) seem to highlight two distinct intermetallic compositions.

The slowest cooling rate, Fig. 2c, exhibits a continuous network of intermetallics of complex morphologies.

The average diameter of the spherical intermetallics, in the Al-0.1 wt%Fe, was measured from the SEM images and reported as a function of cooling rate in Fig. 4a. The average size of the spherical intermetallics in Al-2 wt%Fe cooled in DSC conditions was also measured and reported. For the slower cooling rate for Al-2 wt%Fe, the