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Simultaneous improvement in the strength and corrosion resistance of Al via high-energy ball milling and Cr alloying

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ABSTRACT

The corrosion resistance and mechanical properties of nanocrystalline aluminium (Al) and Al–20 wt.%Cr alloys, synthesized by high-energy ball milling followed by spark plasma sintering, were investigated. Both alloys exhibited an excellent combination of corrosion resistance and compressive yield strength, which was attributed to the nanocrystalline structure, extended solubility, uniformly distributed fine particles, and homogenous microstructure induced by high-energy ball milling. This work demonstrates the possibilities of developing ultra-high strength Al alloys with excellent corrosion resistance, exploiting conventionally insoluble elements or alloying additions via suitable processing routes.

1. Introduction

Most aluminium (Al) alloys possess a comparatively high specific strength, making them suitable for a wide range of engineering applications. However, their use often remains limited in many applications due to: 1) a deterioration of the corrosion properties with any effort made to increase the strength [1,2], and 2) the maximum ultimate tensile strength of conventional commercial Al alloys is limited to ~600 MPa [2,3], whilst higher strengths have been shown to be possible via methods such as severe plastic deformation [4]. In an era of light weighting and metals entering extreme environments, any effort to improve the mechanical properties together with the corrosion resistance of Al alloys is of significance. Whilst there are well-documented examples of improving either the corrosion resistance or the mechanical properties separately, there is a paucity of reports which reveal improvement of both properties simultaneously.

It has been shown that the corrosion resistance of sputter deposited thin films of Al–M alloys (M: Cr, Mo, Ti, Ce, Nb, W, Mn, Ta) exhibited significantly improved corrosion resistance due to the extended solid solubilities of M (which is possible via the sputtering process), and the formation of a passive film enriched in these alloying elements [5,6]. Such metals, typically the transition metals, have negligible solid solubility in Al (for example maximum solubility of Cr is 0.77 wt.%), in addition to highly differing melting points (usually >1000 °C). Both of these factors mean that conventional additions of transitional metals to Al results in the formation of coarse intermetallics, rendering these alloys prone to pitting corrosion. Recent studies have validated that the level of corrosion damage depends upon the size, distribution, and electrochemical characteristics of second phases in the Al matrix [7–9]. In this study, we examined the possibility of implementing high-energy ball milling (HEBM) as a way to extend the solubility of Cr in Al alloys in an attempt to produce a homogenous microstructure that would result in improved corrosion performance, which has been suggested on the basis of previous studies on the corrosion of Al–Cr thin films [5,6]. In this present study however, 'bulk' specimens were prepared to allow the determination of bulk mechanical properties and corrosion performance.

HEBM followed by consolidation has previously been successful in synthesizing Al, Al–Fe, Al–Ti, Al–Mn, Al–Mg alloys [10–17] and ferrous alloys [18–20], exhibiting significantly improved properties, including strength [10–17,21] and corrosion resistance [22]. Furthermore, HEBM has been reported to impart a significant increase in the room temperature solubility of many elements [16,23–25]. For instance, the solubility of Fe in a HEBM Al–Fe alloy powder at room temperature was reported to be ~4.4 at.% [23], which is ~150 times higher than the equilibrium solubility (0.03 at.%).

Based on the above background, we hypothesize that the HEBM of Al with a suitable alloying element (in this case, Cr) will result in alloys with improved strength (due to the nanocrystalline structure and

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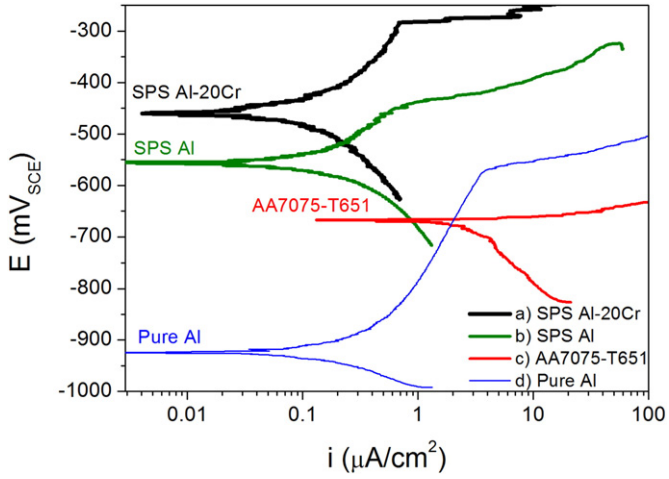

Fig. 1. Representative potentiodynamic polarization curves for spark plasma sintered a) Al–20 wt.% Cr and b) Al alloys along with c) AA7075-T651 and d) pure wrought Al in 0.01 M NaCl.

solution strengthening) and corrosion resistance (owing to the extended solid solubility of Cr in Al). Herein, powder produced by HEBM was consolidated by spark plasma sintering (SPS). The mechanical properties, microstructural characteristics and corrosion resistance of HEBM/SPS bulk alloys of Al and Al–20 wt.%Cr are compared to the wrought pure Al and commercial Al alloys.

2. Materials and methods

Al and Al–20 wt.%Cr alloy powders were prepared via HEBM. High purity powders of Al (99.99% purity and particle size ~300 μm) and Cr (99.95% and particle size <50 μm) with hardened stainless steel balls (10 mm in diameter) were loaded into a hardened stainless steel vial in a high purity nitrogen atmosphere. HEBM was carried out at room temperature for 60 h in Fritsch planetary (Pulverisette 5) ball mill. The ball-to-powder weight ratio was kept at 20:1 and the HEBM was operated at 280 rpm. Stearic acid (1.5% of powder weight) was used as a processing controlling agent. Produced alloy powders were consolidated into 20 mm diameter discs using SPS at 450 °C under an applied pressure of 600 MPa. A heating rate of 100 °C/s was used with an isothermal hold at 450 °C for 5 min. The Al and Al–20 wt.%Cr alloys produced for this study are termed as SPS alloys in the rest of the paper, and for comparison high-purity wrought Al (99.99% pure) and commercial AA7075-T651 (composition and characteristics reported in [1]) were included in the study.

Compression test samples were electro-discharge machined into cylinders of 4 mm diameter and 6 mm height. Compression tests were performed with a strain rate of 10^{-3}/s using an INSTRON universal test machine equipped with a 30 kN load cell. At least three compression tests were performed for each alloy composition.

Potentiodynamic polarization was used to characterise the electrochemical corrosion of these alloys, via a conventional three-electrode electrochemical cell. Tests were carried out at room temperature in 0.01 M NaCl at a scan rate of 0.5 mV/s following 30 min stabilisation of open circuit potential. All experiments were repeated at least four times.

X-ray diffraction (XRD) analysis was performed on the as-milled alloys with a Cu K_α radiation ($\lambda = 0.1541$ nm) to estimate the grain size and formation of intermetallics. Grain size was determined from the X-ray peak broadening (after eliminating the instrumental peak broadening) using the Scherrer equation [26,27]. Microstructural characterisation of Al alloys was carried out using high-resolution scanning electron microscope (Zeiss Supra 55VP FEG SEM) equipped with energy dispersive X-ray spectroscopy (EDXS). Alloy samples were polished to 0.01 micron colloidal silica for microstructural analysis using scanning electron microscope (SEM). Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy (EDXS) were also used for microstructural characterisation, employing a JEOL 2100 F for studying 50 μm thick foils subsequently thinned to approximately 50 nm using PIPS (Gatan precision ion polisher).

3. Results

3.1. Potentiodynamic polarization

The potentiodynamic polarization curves for the SPS Al and Al–20 wt.%Cr alloys along with AA7075-T651 and wrought pure Al (Fig. 1) reveal the influence of extended Cr additions from HEBM + SPS on the resultant corrosion behaviour. The cathodic current density for SPS alloys was higher than that for the pure Al, on the basis of the Cr additions. Whereas the anodic current densities for SPS alloys were significantly lower than those for pure Al and AA7075-T651. The latter effect provided a significant passive region (a much more noble pitting potential) and reduced corrosion rates overall; significantly lower than that of both pure Al and AA7075-T651. The decreased anodic activity of SPS Al and SPS Al–20 wt.%Cr alloys can be attributed to the improved passivation abilities caused by the changes imparted by HEBM and high Cr content in solid solution [5,6], potentially further aided by the incorporation of elements like O and N from processing media [28], and by the nanocrystalline structure [22].

Table 1 presents corrosion current density (i_{corr}) and pitting potential (E_{pit}) of the SPS Al and Al–20 wt.%Cr alloy, determined using potentiodynamic polarization. The pitting potential of SPS Al and Al–20%Cr was significantly higher than that for pure Al and AA70775-T651 indicating significantly improved corrosion resistance due to the HEBM and Cr addition. The corrosion current densities for both SPS Al and Al–20 wt.%Cr were ~20 times lower than that for AA7075-T651.

3.2. Compression tests

Fig. 2 shows a typical true stress–strain curve of the SPS Al and Al–20 wt.%Cr alloy. Both SPS alloys exhibited high yield strength (0.2% proof stress) of 1104 (±30) MPa for SPS Al–20 wt.%Cr and 394 (±7) MPa for SPS Al. The compressive yield strength for SPS Al–20 wt.%Cr was revealed to be much higher than that of high-strength Al alloys (e.g. AA7075-T651, 557 MPa [2,3]) and is comparable with the strength exhibited by amorphous or nanocrystalline Al alloys [10,17,29]. SPS Al exhibited good ductility which supports the idea that the lack of ductility usually exhibited by nanocrystalline materials is not their inherent property [15,30]. Comparatively the Al–20 wt.%Cr alloy exhibited limited ductility, which could be attributed to the dominant influence of intermetallics. A comparison between the specific compressive strengths of the various investigated alloys together with engineering alloys for other alloy classes (Fig. 2b, including data sourced from [2,3]) demonstrates that SPS Al and SPS Al–20 wt.%Cr alloys exhibit significantly

Table 1
Corrosion current density and pitting potential values as calculated from the potentiodynamic polarization in 0.01 M NaCl.

	SPS Al	SPS Al–20 wt.%Cr	Pure Al	AA7075-T651
i_{corr} (μA/cm^2)	0.37 (±0.16)	0. 26 (±0.08)	0.56 (±0.12)	6.18 (±1.5)
E_{pit} (mV$_{SCE}$)	−460 (±17)	−290 (±29)	−550 (±18)	−680 (±16)