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Grain size-dependent Sc microalloying effect on the yield strength-pitting corrosion correlation in Al-Cu alloys

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ABSTRACT

Coarse-grained (CG), fine-grained (FG), and ultrafine-grained (UFG) Al-2.5 wt% Cu (Al-Cu) alloys were respectively prepared, with and without 0.3 wt% Sc addition, for comparison. The influences of minor Sc addition on the microstructural evolution, tensile mechanical properties and pitting corrosion resistance were systematically studied at different grain scales. A significant Sc microalloying effect on the precipitation was observed that the minor Sc addition promoted the dispersion of finer θ'-Al_2Cu precipitates in the CG alloy and favored the intragranular θ'-Al_2Cu precipitation in the FG and UFG alloys, with the smaller grain size leading to a stronger Sc microalloying effect. The Sc addition induced convincing increases in the yield strength at all the three grain scales, and improved (in the CG and UFG Al-Cu alloys) or retained (in the FG Al-Cu alloy) the pitting corrosion resistance at the same time. This indicates that the inverse strength-pitting corrosion correlation as usually observed can be broken by minor Sc addition. The strengthening mechanisms were discussed and the grain size-dependent pitting corrosion resistance mediated by the Sc addition was rationalized in terms of a competition between the positive influence derived from the interfacial Sc segregation and the negative influence come from the deformation-induced dislocations. The present findings provide a possible approach to break the inverse strength-pitting resistance correlation in heat-treatable Al alloys by modifying the precipitate/matrix interfaces through the suitable microalloying atom segregation.

1. Introduction

The low density combined with the high strength have made aluminum (Al) alloys the primary material of choice for applications such as in aircraft, where specific strength (strength-to-weight ratio) is a major design consideration [1,2]. Besides the high strength, the excellent corrosion resistance is also a prerequisite for the Al alloys used in practice services [3]. Improving the mechanical properties and simultaneously retaining the excellent corrosion resistance is a relentless pursuit in the Al community to develop advanced Al alloys with enhanced performances.

Both the strength and the corrosion resistance of Al alloys are closely dependent on the microstructures. The high strength of Al alloys is predominantly derived from the fine hardening second phase particles that, precipitated from the supersaturated solid solution, act as obstacles to moving dislocations [4]. Other strengthening mechanisms mainly include solid solution strengthening, cluster strengthening, grain boundary strengthening, and dislocation hardening [5–8]. From an electrochemical perspective, the presence of the hardening precipitates causes the microstructure heterogeneous and renders the heat-treatable Al alloys susceptible to localized corrosion [9]. Effects of the grain size on the corrosion resistance are relatively complex and some other influencing factors should be considered at the same time [10–13]. Summarizing pertinent literatures mainly on pure metals (including pure Al), Ralston et al. claimed [10] that there exists a relationship between the corrosion rate and the grain size, *i.e.*, the corrosion rate is proportional to the grain size. The underlying mechanism was proposed that the increasing grain boundary density enhances the formation of the protective oxide films on surfaces [10], which hints that fine grain structures are more corrosion resistant. However, this relationship is confined to the case where an oxide/passivity exists. Without the oxide films on surfaces, such as when the current densities are high up to greater than about $10\,\mu A\,cm^{-2}$, the increased grain boundary densities will likely enhance the overall surface reactivity and concomitantly raise the corrosion rate [10,11,13]. In the fine- and ultrafine-grained metals or alloys prepared by the severe plastic deformation, the dislocation density increases accompanied by the refinement in the grain size [7,12,14–16], which promotes the pitting corrosion due to their disorder characteristic [13,14]. Thus a competition exists between the dislocation effect and the grain size effect on

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the corrosion susceptibility, especially in the grain-refined pure Al and non-heat-treatable Al alloys. In the heat-treatable Al alloys with precipitates dispersed, however, the corrosion susceptibility was found to be generally dominated by the precipitates [9,17,18].

Pitting is the most common form of localized corrosion in Al alloys, difficult to predict and prevent due to its random occurrences [19]. Pitting corrosion can be the origin of other types of corrosion, including intergranular corrosion, exfoliation corrosion and stress corrosion cracking [20]. It is commonly believed that the approaches to improve the strength of Al alloys through the microstructural modification generally cause detrimental changes to the pitting corrosion resistance [21]. This inverse correlation between the two important engineering properties of the strength and the pitting corrosion resistance substantially limits the practice services of Al alloys. How to break this inverse correlation attracts increasing attentions [22–24]. Pioneer work by Hutchinson *et al.* [22] was devoted to understanding the effect of the precipitate size and state on the combination of the yield strength and the pitting corrosion susceptibility of an Al-2.5 wt% Cu-1.5 wt% Mg alloy by controlling the aging time. They found that the formation of small coherent atomic solute clusters within the matrix at early aging time did not appear to cause the alloy to become susceptible to the pitting corrosion, but they did increase the yield strength substantially [22]. In addition, the microstructures containing S-phase precipitates with the thickness less than ~ 10 nm were also observed to have similar pitting resistance to the as-quenched solid solution [22,25]. It appears that a critical precipitate size exists in the Al-Cu-Mg alloy, below which the second-phase precipitates cease to act as distinct electrochemical entities. These experimental results highlight the strategy of tailoring the precipitates to break the inverse yield strength-pitting corrosion resistance correlation in Al alloys.

Microalloying is an effective approach to tailor the precipitation in Al alloys, in which the addition of minor microalloying elements will remarkably change the precipitate size and distribution [26]. Two microalloying mechanisms have been generally proposed [27–30]: (i) the one is that the microalloying atoms facilitate the heterogeneous nucleation of precipitates, and (ii) the other is that the microalloying atoms segregate to the precipitate/matrix interface, decreasing the interfacial energy and concomitantly reducing the precipitate size. The first mechanism has been experimentally confirmed in the Sn (In or Cd)-microalloyed Al–Cu alloys and (Si, Ge)-coadded Al-Cu alloys by using Atom Probe Tomography (APT) and High-resolution TEM [27,28]. While the second mechanism was evident in the Ag-doped Al-Cu-Mg [29] and Al-Cu [30] alloys. The precipitate evolution and resultant hardening/strengthening response related to the microalloying effect have been extensively investigated in Al alloys [31–33]. However, the microalloying effect on the corrosion resistance of Al alloys was much less studied. In particular, the microalloying with the second mechanism modifies not only the precipitate size/distribution but also the precipitate interface, which may impact on the corrosion resistance [34]. The microalloying possibly becomes another strategy to break the inverse yield strength-corrosion resistance correlation, for which systematical researches are required.

In this paper, we illustrate that minor Sc addition into a model Al-Cu alloy increases the yield strength and simultaneously improves the pitting corrosion resistance. More interestingly, the Sc microalloying effect displays a significant grain size-dependence within the three length scales studied, *i.e.*, the coarse-grained (CG), fine-grained (FG), and ultrafine-grained (UFG) sizes. The choice of the Sc-microalloyed Al-Cu alloys with different grain sizes as the studied materials in present study is because: (i) our primary experimental results have shown [35,36] that the Sc microalloying in coarse-grained Al-Cu alloys is mainly the Sc segregation at the θ'-Al_2Cu/matrix interfaces, which, enhancing the precipitate hardening, may also affect the corrosion resistance positively; (ii) the refinement of the grain size is in accompany with marked changes in the disorder density and the grain boundary characteristics that may highly influence the precipitation thermodynamic/kinetics and lead to the precipitation behaviors much different from those in the CG counterparts [37–41]. Since the precipitates are the predominant factors in determining the pitting corrosion susceptibility, the strength-corrosion correlation is expected to be sensitive to the grain size.

2. Experimental procedures

2.1. Material preparation and heat treatments

Two kinds of alloys with the compositions of Al-2.5 wt% Cu (abbreviated as Al-Cu alloys) and Al-2.5 wt% Cu-0.3 wt% Sc (abbreviated as Al-Cu-Sc alloys) were respectively cast by using 99.99 wt% pure Al, 99.99 wt% pure Cu and Al-2.0 wt% Sc master alloys. All cast ingots were homogenized at 723 K for 5 h. Billets with the size of 100 mm × ∅10 mm were machined from the cast ingots for Equal-channel angular pressing (ECAP) to prepare the FG and UFG samples. After being solution-treated in vacuum for 3 h at 873 K and quenched in cold water, the billets were subjected to 4 and 12 ECAP passes by route Bc [12,15,42] at room temperature, respectively. After ECAP processing, the samples were immediately aged at 398 K for 6 h, 10 h, 20 h, and 30 h, respectively. For comparison, the CG samples were prepared by hot extruding the cast ingots into plates with 14 mm in thickness and 60 mm in width at 723 K. The plates were subsequently solution-treated at 873 K for 3 h, quenched in cold water (defined as CG), and finally aged at 523 K for a series of time. The maximum error of all temperature measurements in the present experiments was ± 1 K.

2.2. Microstructural characterization

Microstructural analyses were carried out by using scanning electron microscopy/electron backscattered diffraction (SEM/EBSD), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). SEM-EBSD specimens of the post-ECAP samples were cut from the cross-sectional center of the ECAP billets, and then electropolished by using an electrolyte of 25% nitric acid and 75% methanol at 253 K (− 20 °C) with an operation voltage of 15 V. 3 mm TEM foils were twin-jet electropolished using the same solution. Statistical results on the number density and size of precipitates were obtained from more than 300 measurements. The volume fraction of precipitates was evaluated following the methods in references [43–45]. The precipitate diameter was determined after correction for the truncation effects based on a method by Crompton et al. [46]. The reader can refer to our previous publications [35,36,47] for more measurement details.

The dislocation density was measured by performing X-ray diffraction (XRD) experiments. Each sample was tested at least six times to obtain a set of diffraction profiles. The evaluation of these profiles was done following the Multiple Whole Profile (MWP)-fit method developed by Ungár and co-workers [48–50], where simulated profiles are fitted to the recorded profiles. This is done for all reflections simultaneously with *ab initio* theoretical functions for the strain- and size-induced profile broadening. The reader can refer to reference [51] for experimental details.

Three-dimensional atom probe (3DAP) experiments were performed using a Cameca LEAP 3000 HR instrument. Needle-like ATP samples were prepared from blanks with the size of $300 \times 300\ \mu m^2 \times 1$ cm by combining the mechanical grinding and a two-step electropolishing [52,53], which consists of the coarse polishing using a solution of 10.0 vol% perchloric acid in methanol and the final polishing using a solution of 2.0 vol% perchloric acid in butoxyethanol. 3DAP experiments were performed using a pulse repetition rate of 200 kHz, with a background gauge pressure of $< 6.7 \times 10^{-8}$ Pa (5×10^{-10} Torr). The specimen temperature was controlled at 30 ± 0.3 K.