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Pre-electrodeposition process for improving tensile ductility of Al electrodeposited from a dimethylsulfone bath

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ABSTRACT

Al was electrodeposited from a dimethylsulfone ($DMSO_2$) bath using a new pre-electrodeposition process to investigate the effect of sulfur and chlorine on the tensile ductility. Al electrodeposited from a $DMSO_2$ bath contains sulfur and chlorine, which are impurities are incorporated into the electrodeposits as sulfide and chloride, respectively. By pre-electrodeposition, the sulfur and chlorine contents of electrodeposited Al decreased from approximately 0.64 and 0.71 at% to 0.15 and 0.17 at%, respectively. This reduction in the sulfur and chlorine contents affects the microstructure, hardness, and ductility of the electrodeposits. The grain size increased from approximately 200 nm to 4 μm, and the microhardness decreased from 1.67 to 0.24 GPa. In tensile tests, electrodeposited Al before pre-electrodeposition exhibited failure even in the elastic regime, while electrodeposited Al after pre-electrodeposition exhibited good tensile ductility of approximately 30%.

1. Introduction

Recently, electrodeposition from nonaqueous solutions, such as ionic liquids [1,2] and an organic solvent [3], has been expected as a fabrication process for bulk nanocrystalline Al and Al alloys. Ionic liquids can be used at room temperatures [4–6]. Organic solvents that consist of dimethylsulfone and aluminum chloride ($DMSO_2$ bath) have some features, including low cost, high current efficiency, and good thermal stability [7–15]. In fact, synthesis of nanocrystalline Al and Al alloys with high hardness has been achieved using a $DMSO_2$ and ionic liquid electrolyte [3,16,17]. However, previous studies have not established that the resulting materials have high strength and ductility [17].

Electrodeposits from a $DMSO_2$ bath typically contain sulfur and chlorine as impurities [3,15]. Miyake et al. [15] noted that these impurities make the electrodeposits brittle. They also reported that the amount of impurities could be reduced by adding trimethylamine hydrochloride (TMA) to $DMSO_2$ bath. However, through a tensile test, Okamoto et al. [18] reported that the electrodeposited Al obtained from a $DMSO_2$ bath with TMA exhibits a plastic deformability. It is not clear whether the improvement in tensile ductility of electrodeposited Al obtained from a $DMSO_2$ bath occurs because of decrease in sulfur and chlorine contents or addition of TMA. In this study, we report a new pre-electrodeposition technique for decreasing the amount of impurities in electrodeposits without using additives. We investigate the effect of reductions in sulfur and chlorine contents on microstructure and tensile properties of electrodeposits after pre-electrodeposition and determine whether the reduction improves the tensile ductility of electrodeposited Al prepared from a $DMSO_2$ bath.

2. Experimental procedure

All samples were prepared using the $DMSO_2$ bath as described in our previous study [3]. The electrolyte consisted of $AlCl_3$ and $DMSO_2$ with a molar ratio of 3:10. To prevent co-deposition of iron, chromium, and manganese, a polytetrafluoroethylene-coated thermocouple was used for temperature control. All samples were electrodeposited onto a copper sheet at a current density of 30 mA/cm^2 and a bath temperature of 110 ± 1.0 °C. Sulfur and chlorine contents of electrodeposits were measured by energy-dispersive X-ray spectrometry using a scanning electron microscope (HITACHI S-4800). To determine structures, X-ray diffraction (XRD, RIGAKU Ultima IV) analyses were conducted using Cu Kα radiation. To prepare transmission electron microscopy (TEM) specimens, thin foil specimens of 3 mm diameter were fabricated by a twin-jet polishing technique using a nitric acid–methanol solution (20% by volume of HNO_3) at −30 °C and 15 V. The TEM specimens were examined using a JEOL JEM-2100F, operated at 200 kV. To evaluate the hardness of the electrodeposits, micro

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Vickers tests were conducted with a load of 300 g for 10 s. Each reported data point represents an average of at least 12 impressions. Dog-bone specimens with 11 mm gauge length, 4.0 mm width, and ~0.3 mm thickness were machined for tensile tests by electrical discharge machining from the as-deposited plates, and the copper substrate was removed by mechanical polishing. Tensile tests were performed at a strain rate of $1 \times 10^{-3}\ s^{-1}$ and room temperature. Plastic deformation of a specimen after fracture was measured by the gauge length change.

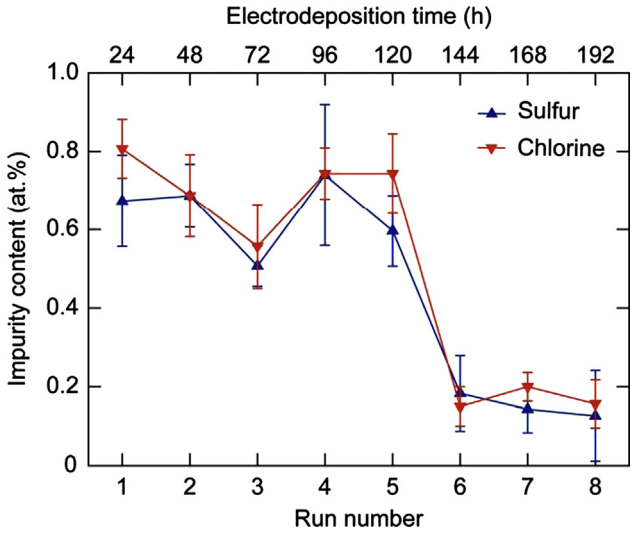

Fig. 1. Effects of run number on sulfur and chlorine contents in Al electrodeposited from a $DMSO_2$ bath.

3. Results and discussion

In our pre-electrodeposition process, electrodeposition from a $DMSO_2$ bath for 24 h was performed eight times consecutively. High current efficiencies (> 90%) were obtained for electrodeposition of all samples. Sulfur and chlorine contents of the electrodeposits obtained from pre-electrodeposition are shown in Fig. 1. From the first to fifth electrodeposition, sulfur and chlorine contents of electrodeposited Al were ~0.64 and ~0.71 at%, respectively. Although each electrodeposition was performed under identical conditions, after the sixth electrodeposition, the sulfur and chlorine contents decreased to ~0.15 and ~0.17 at%, respectively.

Fig. 1 shows that the impurities content in the electrodeposits can be reduced by consecutive electrodepositions. It has been reported that sulfur and chlorine impurities are incorporated into electrodeposits as sulfide and chloride [15]. These results also

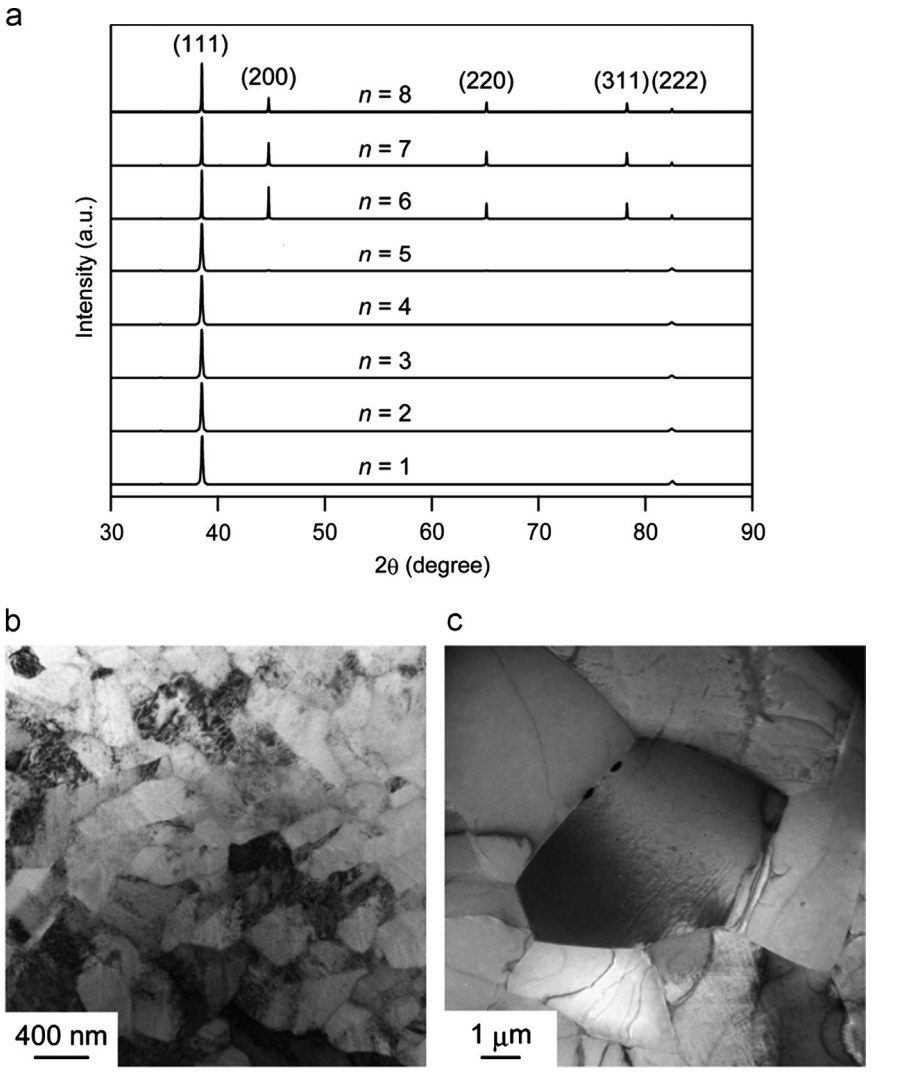

Fig. 2. (a) XRD patterns of Al electrodeposited from a $DMSO_2$ bath. (*n* represents the run number.) Bright-field TEM images of Al electrodeposited from a $DMSO_2$ bath (b) before and (c) after pre-electrodeposition processes.