

## Order/Disorder in Electrodeposited Aluminum-Titanium Alloys

Gery R. Stafford<sup>a</sup>, Tetsuya Tsuda<sup>b</sup> and Charles L. Hussey<sup>b</sup>

<sup>a</sup>Materials Science and Engineering Laboratory  
National Institute of Standards and Technology  
Gaithersburg, Maryland 20899

<sup>b</sup>Department of Chemistry and Biochemistry  
The University of Mississippi  
University, Mississippi 38677, USA

Recently it has been shown that a variety of interesting aluminum-transition metal alloys can be deposited from the Lewis acidic  $\text{AlCl}_3$ -1-ethyl-3-methylimidazolium chloride ( $\text{AlCl}_3$ -EtMeImCl) molten salt, which is liquid at ambient temperature [1]. Similar to the higher temperature  $\text{AlCl}_3$ -NaCl system, several unique microstructural features such as extended solid solubility, metastable crystalline phases, and metallic glasses are observed. Based on the structural development of Al alloys deposited at high temperature, one would expect greater departures from equilibrium in deposits formed at ambient temperature. The aim of this study is to make a direct comparison of the electrodeposition process as well as the resultant crystal structure of several Al-Ti alloys electrodeposited from  $\text{AlCl}_3$ -NaCl at 150 °C and from  $\text{AlCl}_3$ -EtMeImCl at 80 °C.

Figure 1 is a graph showing the composition of alloys deposited onto copper substrates as a function of  $\text{Ti}^{2+}$  concentration and current density in 2:1  $\text{AlCl}_3$ -NaCl at 150 °C [2,3] and from 2:1  $\text{AlCl}_3$ -EtMeImCl at 80 °C [4] at a single  $\text{Ti}^{2+}$  concentration. In the high-temperature melt an alloy containing 25 % atomic fraction titanium is deposited at nearly all current densities once the  $\text{Ti}^{2+}$  concentration reaches 150  $\text{mmol L}^{-1}$ . Figure 1 also shows the alloy composition-current density relationship for deposits formed in  $\text{AlCl}_3$ -EtMeImCl at a  $\text{Ti}^{2+}$  concentration of 170  $\text{mmol L}^{-1}$ . There are two unusual aspects of the alloy composition data shown in Figure 1. The first is the apparent 25 % atomic fraction limit on the titanium concentration of the Ti-Al electrodeposits while the second is the independence of alloy composition on current density at the higher  $\text{Ti}^{2+}$  concentrations. Both of these can be explained if we introduce the concept of a single electroactive species having the structure and stoichiometry proposed by Seddon et al. [5,6], in this case  $[\text{Ti}(\text{AlCl}_4)_3]$ . This implies that  $\text{Al}_3\text{Ti}$  may form by the reductive decomposition of  $[\text{Ti}(\text{AlCl}_4)_3]$ .

Figure 2 shows electron diffraction patterns from an 18.4 % Ti alloy deposited from  $\text{AlCl}_3$ -EtMeImCl at 80 °C and a 16 % Ti alloy deposited from  $\text{AlCl}_3$ -NaCl at 150 °C. The pattern from the  $\text{AlCl}_3$ -EtMeImCl deposit is consistent with single phase fcc Al-Ti. No superlattice reflections were found in any of the diffraction patterns indicating that the detected phase has a random ordering of Al and Ti atoms. The alloys electrodeposited from the higher temperature  $\text{AlCl}_3$ -NaCl melt show the fcc reflections as well as the 100 and 110 reflections indicative of  $\text{L1}_2$  ordering. The presence of these superlattice reflections indicates that the crystal structure is not disordered fcc because the 100 and 110 reflections are forbidden in fcc. The  $\text{L1}_2$  structure, stoichiometrically  $\text{Al}_3\text{Ti}$ , is comprised of titanium atoms at the corners and aluminum atoms at the face-centers of an fcc unit cell. High resolution electron diffraction indicates that the  $\text{L1}_2$  domains measure 5 nm to 10 nm in size. It further shows that these domains appear to have grown through a first order nucleation and growth process, independent of the electrocrystallization process. This type of domain structure is quite common in rapidly solidified alloys wherein the disordered phase produced by the solidification process transforms to the equilibrium ordered phase quite rapidly during solid-state cooling to room temperature. The disordered fcc structure in the low-temperature alloys and the appearance of antiphase boundaries in the high-temperature alloys suggest that the deposit may be disordered initially and then orders in the solid state, subsequent to the charge transfer step and adatom incorporation into the lattice. The measured domain size is consistent with a mechanism of diffusion-controlled domain

growth at the examined deposition temperatures and times.

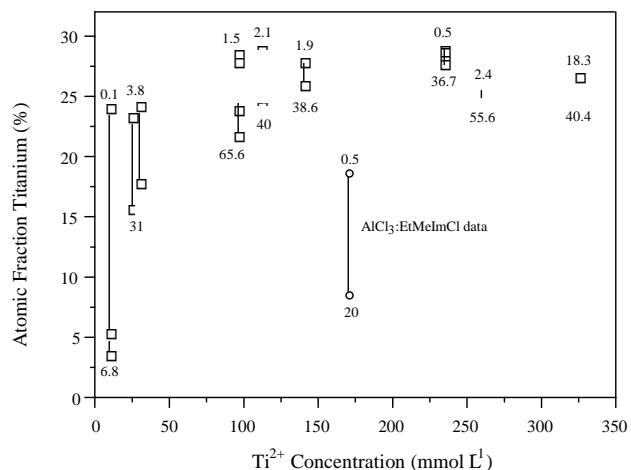


Figure 1. Alloy composition as a function of  $\text{Ti}^{2+}$  concentration in 2:1  $\text{AlCl}_3$ -NaCl at 150 °C (□), and from 2:1  $\text{AlCl}_3$ -EtMeImCl at 80 °C and a single  $\text{Ti}^{2+}$  concentration (○). The range of deposition current densities used at each  $\text{Ti}^{2+}$  concentration is also listed in  $\text{mA cm}^{-2}$ .

Figure 2. Selected area diffraction patterns of Ti-Al alloys taken on the [001] zone axis from as-deposited Ti-Al alloys containing: (a) 18.4 % Ti and deposited from  $\text{AlCl}_3$ -EtMeImCl at 80 °C and (b) 16 % Ti and deposited from  $\text{AlCl}_3$ -NaCl at 150 °C.

## References

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