

Pit Initiation on Partially Devitrified Glassy Alloys

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INTRODUCTION

A new class of amorphous and partially nanocrystalline-amorphous alloys has been recently produced over a broad range of alloy compositions.^{1,2,3} Many of these alloys devitrify at low temperatures by forming isolated spherical nanocrystals embedded in the remaining amorphous matrix. These nanocrystals are typically enriched in the major alloying element (here, aluminum), adopt the crystal structure of this alloying element, and reject the transition metal (TM) and rare earth metal (RE) solute. The rejected solute is concentrated in the remaining amorphous matrix and compositional gradients are formed at amorphous-nanocrystal interfaces under non-equilibrium conditions. The addition of nanocrystals enhances the mechanical properties of these alloys.^{4,5,6} However, it is likely that the nanocrystal heterogeneities affect corrosion properties, creating a possible “trade-off” in mechanical vs. corrosion properties. Moreover, it is likely that compositional gradients and the lack of grain boundaries and triple points affect the corrosion behavior of these partially amorphous materials in complex ways.

In order to understand the localized corrosion behavior of this new class of materials, the effects of devitrification on the pitting behavior of $\text{Al}_{90}\text{Fe}_5\text{Gd}_5$ have been studied by systematically varying the size of the isolated f.c.c. Al nanocrystals.^{7,8,9} Partially devitrified states in which both nanocrystals and ~500 nm f.c.c. Al or Al-TM-RE intermetallic “transitional phases” were embedded in a remaining amorphous matrix were also examined. These partially devitrified states retain the good macroscopic corrosion resistance of the fully amorphous alloy, which is lost upon complete crystallization. However, the mechanisms by which partially devitrified materials retain the μm -scale pitting corrosion resistance of the fully amorphous alloy are not understood.

OBJECTIVES

This paper examines the role of nanocrystals and transitional phases in pit initiation on the partially devitrified alloy. Investigations focused on individual pA scale metastable pitting events to determine whether a high density of nanocrystals and/or transitional phases increased the number of pit initiation events seen during exposure to NaCl solutions.

METHODS

Pit experiments were conducted on microelectrodes containing nanocrystals of controlled sizes using pA resolution methods to detect nm-scale diameter pits. These experiments examine whether pit initiation occurs with greater frequency or in a different manner in the presence of a large population of Al-rich f.c.c. nanocrystals or transitional phases. Results are compared to analogous studies on randomly cut surfaces through bulk f.c.c. Al single crystals (that simulate the random orientations of nanocrystals, as typically seen) to determine whether nanocrystals initiate pits as readily as bulk Al in the absence of grain boundaries and triple points. Localized corrosion morphology has also been characterized by high resolution scanning electron microscopy with secondary electron imaging.

RESULTS

Nanocrystals embedded in an amorphous Al-Fe-Gd alloy matrix do not promote pit initiation in halide solutions under the same electrochemical conditions where the bulk equivalent of Al-rich f.c.c. nanocrystals are expected to initiate pits. Although there is a high area density of surface nanocrystals, very few lead to pit initiation. The number, shape and size of pit initiation events is similar for the fully amorphous and amorphous-nanocrystalline alloy. However, the devitrified alloy containing transitional phases did exhibit pit initiation events at lower applied potentials. SEM observations indicate the presence of these small pits.

DISCUSSION

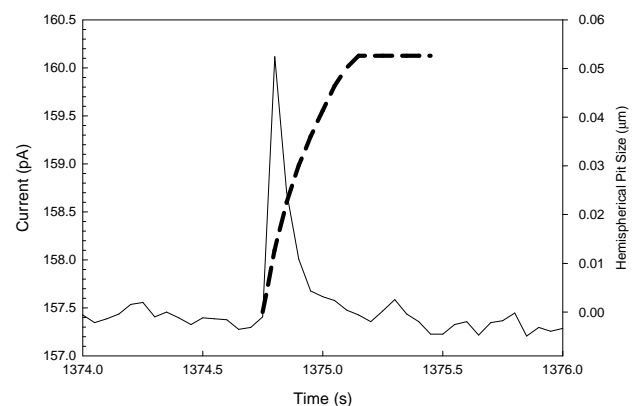
The results suggest that the mechanism by which amorphous-nanocrystalline alloys retain the improved localized corrosion resistance of the fully amorphous alloy is a combination of two factors. The first is reduced pit initiation, which may be due to a critical flaw size effect. These flaw size effects could be due to either oxide bridging over susceptible sites or other reasons. The other is that the growth of pits that do nucleate at nanocrystals or transitional phases is hindered at the nanocrystal/matrix interface due to the build-up of TM and RE solute. The TM solute is seen to increase resistance to pit propagation in certain Al-TM-RE alloys.

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Example of a pA-scale metastable pitting event on amorphous-transitional $\text{Al}_{90}\text{Fe}_5\text{Gd}_5$.