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Why do Fe–Al Alloys Show Good Passivation Behavior in Acids Compared to Elemental Al?

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We present some general concepts and pose questions connected to the difference between the ambient temperature passive film formed on elemental aluminum in acid vs that which forms on iron-aluminum alloys containing less than about 35–40 at % Al. Data is presented which demonstrates that the non-protective oxide that forms on aluminum is not related to impurity effects, either in the matrix or in grain boundaries.We argue that the ability of aluminum to form a protective passive film in a single-phase solid solution alloy is connected to atomic-scale size effects that vanish once the aluminum concentration increases to about 60 at%.

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Although elemental Al readily forms an oxide in an acid such as H_2SO_4, the oxide undergoes combined electrochemical and chemical dissolution and does not protect the underlying aluminum.[1] Nevertheless, at ambient temperature single-phase Fe–Al alloys containing 15–25 at% Al are well known to develop a protective passive film.[1–4] This behavior is differentiated from that of Fe–Cr alloys, since elemental Cr forms excellent passive films in acids.[5] Importantly, the oxide that forms on Al can show a tendency toward pitting behavior which may be connected to the fact that anodic porous alumina forms in H_2SO_4 at large enough voltage.[6]

In a series of papers, the passive films formed, in pH 2.5–13.8 electrolytes, on Fe–Al alloys containing 8, 15 and 22 at% Al were characterized using a variety of surface science techniques.[2,3] While these results clearly revealed an enrichment of Al (compared to the bulk Al metal concentration) within the passive layer, and the formation of a mixed FeAl oxide/(oxy)hydroxide, they were not informative with respect to understanding the alloy concentration effects that our communication addresses.

Previous work on Fe–Cr and Ni–Cr alloys in sulfuric acid demonstrated that chronoamperometry can be used to determine the quality of the passive film formed as a function of the Cr content in the alloy.[7] The charge density obtained from these experiments was used to ascertain the required number of dissolved monolayers for passivation. Unlike the situation for Cr, the air-formed oxide on elemental Al cannot be fully reduced even in strong acid.[2,3] However, repassivation experiments, using a scratching electrode method, have been performed in 0.25 M H_2SO_4 on elemental Al, elemental Fe and a Fe-28 at% Al alloy at a potential of 1.24 V (SHE).[8] In such a test a key parameter that one examines is the charge density required for the repassivation process. This charge density results from both the quantity of metal actually dissolved into the electrolyte and that required to form the passive film. Unless separate measurements are performed to establish the thickness of the passive film and/or the ion concentration in the electrolyte, the total charge density required for passivation cannot be partitioned without making some drastic assumptions. We note that in such experiments the surface area of the scratch often represents the parameter with the greatest uncertainty and in the worst case, could be in error by a factor of two. Accordingly, we reanalyzed the results in Ref. 8 as shown in Fig. 1. In terms of the number of Al monolayers dissolved or oxidized a good number to use is about 500 μCcm^{-2} per monolayer. We obtain about 1000, 35 and 6 monolayers for Fe, Al and Fe-28 at% Al, respectively. Earlier scratching experiments reported charge densities for repassivation of about 70,000, 3000 and 280 μCcm^{-2} for Fe–Al alloys containing 10, 27 and 41 at% Al, respectively.[9] Since the 41 at% Al alloy is close to the two-dimensional site percolation threshold, we would expect that only a few dissolved monolayers are required for the passivation process.[7] Good passivation behavior requires that the charge to repassivate is about 10 monolayers or less, otherwise too much material can be lost limiting the life span of a component in service.[7]

We suggest that there are three possible explanations for the passivation behavior of Fe–Al alloys in sulfuric acid as a function of the Al concentration: (i) impurity effects in elemental Al, (ii) sulfate/bi-sulfate anion adsorption and (iii) the selective dissolution of Fe, the formation of a mixed FeAl oxide/(oxy)hydroxide and percolation.[7]

In order to characterize the behavior of elemental Al, with respect to whether impurities play a role in passivation behavior, we employed linear sweep voltammetry (LSV) on three different sets of samples: 5–9's pure polycrystalline Al, 3–9's pure single crystal Al (001) and 6–9's pure single crystal Al (001). LSV was performed on the three sets of samples in 0.1 M H_2SO_4, 0.1 M $HClO_4$, and 0.1 M HNO_3 to search for qualitative differences in the current voltage behaviors. For each case samples were held at −1.36 V SHE for 2 min after which the samples were held at the corrosion potential for 1 h prior to initiating LSV at a 1 mVs^{-1} sweep rate from near the corrosion potential to 800 mV SHE. A standard three-electrode cell was used, that employed a Pt-mesh counter electrode and a Mercury-mercurous sulfate reference electrode. All potentials are reported with respect to the standard hydrogen electrode (SHE).

Figure 2 shows our results and demonstrates that the LSV in the sulfuric and nitric acids is similar while the behavior in perchloric acid shows about 10 times higher current densities as a result of pitting. Scanning electron microscopy of the corroded surfaces showed that a high density of pits only evolved on the sample surfaces tested in perchloric acid. Figure 3 shows the behavior of the three sets of samples in 0.1 M H_2SO_4 and 0.1 M HNO_3 with 0.6 M NaCl added and reveals results similar to that observed in the neat 0.1 M $HClO_4$. Even though we used ultra-high purity perchloric acid, we can't rule out the presence of micro-molar quantities of the Cl^- anion.

When Al is the solute in a single-phase binary alloy, it is partitioned on atomic length scales. In a random BCC lattice, at a composition of 0.20 mole fraction, the average Al cluster size including 1st and 2nd nearest neighbors is a trimer[7] that will form an oxide cluster as a result of the oxyphilic nature of Al. During the active dissolution portion of the passivation process, Fe is selectively dissolved resulting in an increased density of these nanoscale oxide clusters that incorporate Fe cations. As a result of the small number

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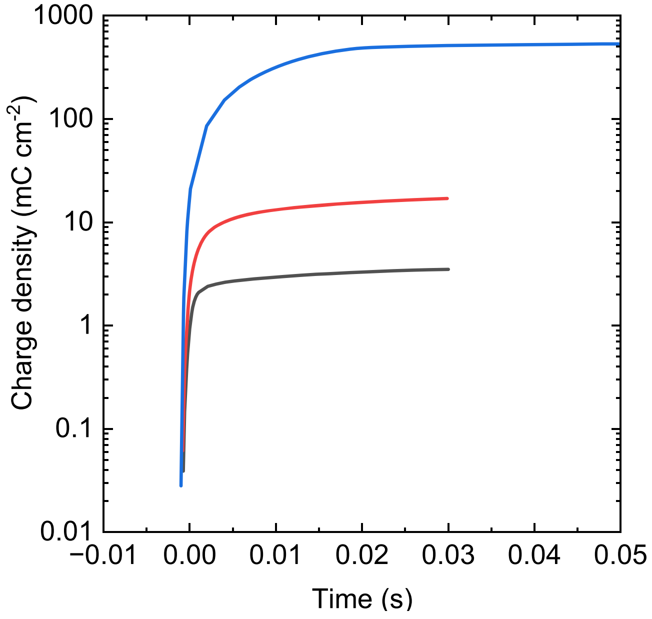

Figure 1. Scratch test integrated chronoamperometry taken at 1.24 V (SHE) for elemental Fe (blue), elemental Al (red) and Fe-28 at% Al (black). The accumulated charge densities are 535, 18 and 3 mC cm^2. Data adapted from Ref. 8.

of Al atoms in the cluster, the oxide must nucleate as an amorphous structure, but as the oxide clusters merge and growth continues across the surface, the amorphous structure may transform to one of its crystalline polymorphs.[10]

From a theoretical viewpoint, the small oxide clusters are likely susceptible to undercutting as Fe selectively dissolves prior to the point at which the oxide percolates across the surface of the alloy.[7] While the percolating oxide is susceptible to dissolution; the rate at which this occurs is likely mediated by both the ramified fractal structure of the percolating network and the Fe-cations incorporated within the oxide surrounding the Al^{3+} cations.

In order to illuminate our discussion of Al cluster size and passivation consider that one has a powerful microscope which makes it possible to distinguish between Fe and Al atoms. In a dilute alloy (<5 at% Al) most of the Al will be partitioned as monomers. If we now slightly de-focus the microscope such that the spatial resolution is of order 1 nm, the surface of the alloy would appear to contain only Fe. This *coarse graining* of the atomic-scale structure is a useful way to think about how, as a function of composition, a single-phase alloy will respond to both an electro-adsorption process and passivation.[7,11] Generalizing this argument, when Al is the solute in the alloy, Al will become "visible" to the passivation process when there are 1 nm-scale Al islands within a sea of solvent Fe. Now consider the inverse situation, for which Al is the solvent. In this case, nanoscale Fe islands would be surrounded by a sea of Al and our expectation is that such an alloy would show passivation behaviors in H_2SO_4 similar to that of elemental Al.

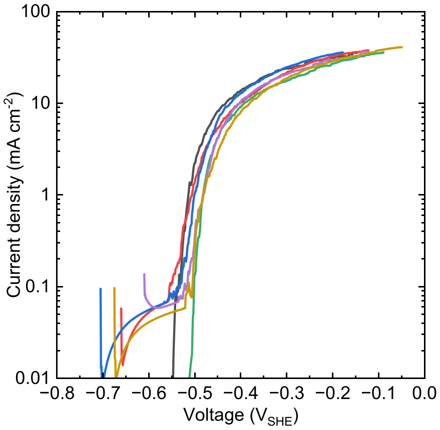

Figure 3. LSV in 0.1 M HNO_3 + 0.6 M NaCl: polycrystalline Al (gold), 3–9's Al (001) (green), 6–9's Al (001)(violet): in 0.1 M H_2SO_4 + 0.6 M NaCl: polycrystalline Al (blue), 3–9's Al (001) (black); and 6–9's Al (001) (red).

The considerations outlined above naturally lead to the following questions: are there atomic size-scale effects on the dissolution behavior and pitting tendencies of aluminum in alloys? At what composition will Al in an Fe alloy behave like elemental aluminum in terms of passivation behavior? This question is best posed from the view of a percolation problem: at what composition will the aluminum nearest-neighbor coordination resemble that in elemental aluminum? We suggest that this is a high-density percolation problem which has been previously discussed[12] and addressed in the literature for a random solid-solution FCC alloy.[13] Kinetic Monte-Carlo simulations demonstrated that dissolution occurs for atoms coordinated by 9 and fewer nearest-neighbors.[13,14] The high-density site percolation threshold for this is about 60 at%.[13]

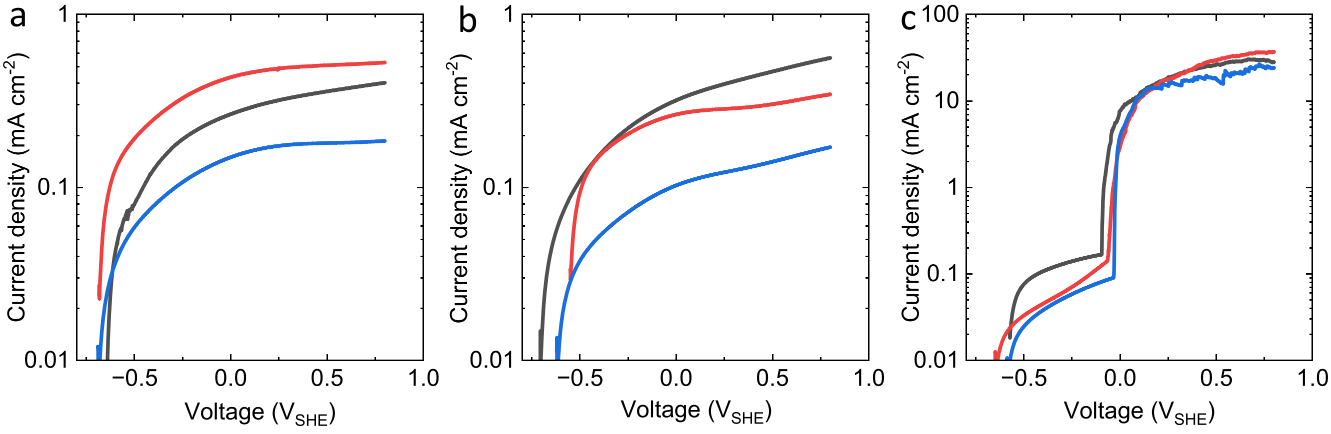

Figure 2. LSV of polycrystalline Al (black), 3–9's Al (001) (red) and 6–9's Al (001), (blue) single crystals in (a) 0.1 M HNO_3, (b) 0.1 M H_2SO_4, and (c) 0.1 M $HClO_4$.

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