Corrosion-Resistant Zeolite Coatings by *In Situ* Crystallization

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A new class of inorganic corrosion-resistant coating, zeolite coating, was prepared on aluminum alloys and shown to be highly corrosion resistant even in strong acid and pitting aggressive media. The coating also has good adhesion, wear- resistance, and paint compatibility. The *in situ* crystallization coating deposition process is clean and can coat surfaces of complex shapes and in confined space. Therefore, it can potentially serve as an environmentally friendly, alternative corrosion-resistant coating for aluminum alloys. The coating also appears to be generally applicable to other metals, including steel.
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Metal corrosion is a ubiquitous problem and generally costs an industrialized country several percent of its annual gross domestic product (GDP).[1-3] For combating corrosion of aluminum and its alloys,[4] chromic acid anodization and chromate conversion have thus far proved most effective.[5-7] Both processes, however, use and release hexavalent chromium, a proven human carcinogen, causing serious environmental and worker health and safety concerns.[5,8] A chromium-free alternative with equivalent or superior corrosion performance has long been desired.[5-10] Here we show that a dense polycrystalline as-synthesized high-silica zeolite coating on aluminum alloys offers remarkable corrosion and abrasion resistance and paint compatibility. We also show that an *in situ* crystallization coating process is intrinsically simple and clean, and can selectively coat surfaces of complex geometry and in confined spaces, and therefore can potentially serve as an environmentally friendly alternative coating technology for aluminum alloys. Further, zeolite coatings by *in situ* crystallization appear to offer a general corrosion protection strategy for other metals including steels.

Zeolites are a class of microporous crystalline aluminosilicates, and have been most commonly used in powder composite form as catalysts and separation media.[11] Recently, zeolite thin films on porous ceramic and metal substrates have been developed for membrane and membrane reactor applications.[12-15] While all present applications of zeolites, either in the form of a particle or a film, exploit their uniform microporosity, in this study we show that as-synthesized high-silica zeolite coatings can be nonporous and extremely corrosion resistant. The model system we chose in this study was high-silica ZSM-5 coatings on aluminum alloy 2024-T3 (Al-2024-T3). First, high-silica or pure silica zeolites are known for their high thermal, mechanical and chemical stability.[11] For example, pure-silica ZSM-5 does not lose its crystallinity up to 1100°C and does not react with any mineral acids but hydrofluoric acid.[16] Second, Al-2024-T3 is an important alloy widely used in aerospace and defense applications, and has serious corrosion problems because of its high copper content.[3-7]

Figures 1a and b show the top and cross-sectional views of as-synthesized high-silica ZSM-5 coating on Al-2024-T3 (ZSM-5 structure was confirmed by X-ray diffraction). The coating is dense, polycrystalline, and ~35 μm thick. The thickness of the coating is uniform over large surfaces (*e.g.*, 15 in. long tubes) and can be readily varied by adjustment of the synthesis composition (*e.g.*, 0.5-50 μm). The cross-sectional sample was prepared by etching away part of the film with hydrofluoric acid. To be corrosion resistant, a polycrystalline zeolite coating must be dense with no intercrystal porosity and no intracrystal porosity. While good intergrowth can eliminate intercrystal porosity,[12-15] intracrystal porosity can be avoided by leaving trapped structure-directing-agent (SDA) mol-

ecules inside the zeolite.[17] Bulky organic molecules are often used as SDA for synthesis of high-silica zeolite and are left trapped inside the crystal.[11] As shown in Fig. 1c, each tetrapropylammonium (TPA) molecule (SDA in ZSM-5 system) is located at the intersection of straight and zigzag channels with each of its four propyl groups pointing into one channel, completely blocking the channel.[17] Note that the carbon and nitrogen atoms in TPA molecule were not drawn to scale and a space-filling model showed clearly that trapped TPA molecules tightly fit in the channel (ZSM-5 has a channel size 5.5 Å).[17] As-synthesized ZSM-5 film has been proved to be impermeable to all gases suggesting absence of both inter and intracrystal porosity.[12-15] These trapped molecules are fairly stable, and normally removed by calcination in air or oxygen at 350°C or higher.[11-15]

Figure 2 shows dc polarization results of as-synthesized ZSM-5 coating in several corrosive media. In all cases, the polarization current of zeolite coating (curve 1) approaches the detection limit of the potentiostat (10^{-10} A) and consequently the signal is noisy. For corrosion in sulfuric acid (Fig. 2a), zeolite coating shows much lower polarization current than anodization coating (curve 2), bare Al-2024 (curve 3), and chromate conversion coating (curve 4), suggesting its superior corrosion protection. The superior performance of zeolite coating is even more pronounced when the immersion time in sulfuric acid is increased from 2 h to 10 days (Fig. 2b). Anodization coating was severely damaged and offered little corrosion protection (*i.e.*, curve 2 moves very close to curve 3), while zeolite coating was hardly affected confirming its excellent acid stability. To test the performance of zeolite coating against pitting corrosion, polarization tests were carried out in the presence of chloride ions (Fig. 2c) and a mixture of chloride and cupric ions (Fig. 2d) as chloride and cupric ions are known to facilitate pitting corrosion.[3] Again zeolite coating performs better in both cases. By comparing Fig. 2c and d with Fig. 2a, it is clear that both anodization and conversion coatings suffer serious pitting corrosion, but zeolite coatings are not affected. The superior corrosion performance of zeolite coatings is also found in basic solutions (0.1 M NaOH, data not shown) in which zeolite coating's polarization current increased only slightly after 24 h of immersion, while anodization coating was severely damaged within 20 min. The high polarization current of stand-alone chromate conversion coating is expected because conversion coating is usually used as a primer for more corrosion-resistant polymer paints.[3,5] Painted chromate conversion coating (STOPSRUST, Navy 7723, Rust-Oleum Corp., Vernon Hills, IL) was examined and showed much lower polarization current in sulfuric acid (about 10^{-8} A/cm^2, data not shown). But its performance deteriorates with immersion time. The corrosion performance of zeolite coatings was also examined by ac impedance method. As shown in Fig. 3, in all corrosion media, zeolite coating showed remarkably higher impedance than anodization and conversion coatings consistent with our previous findings in polarization tests. We

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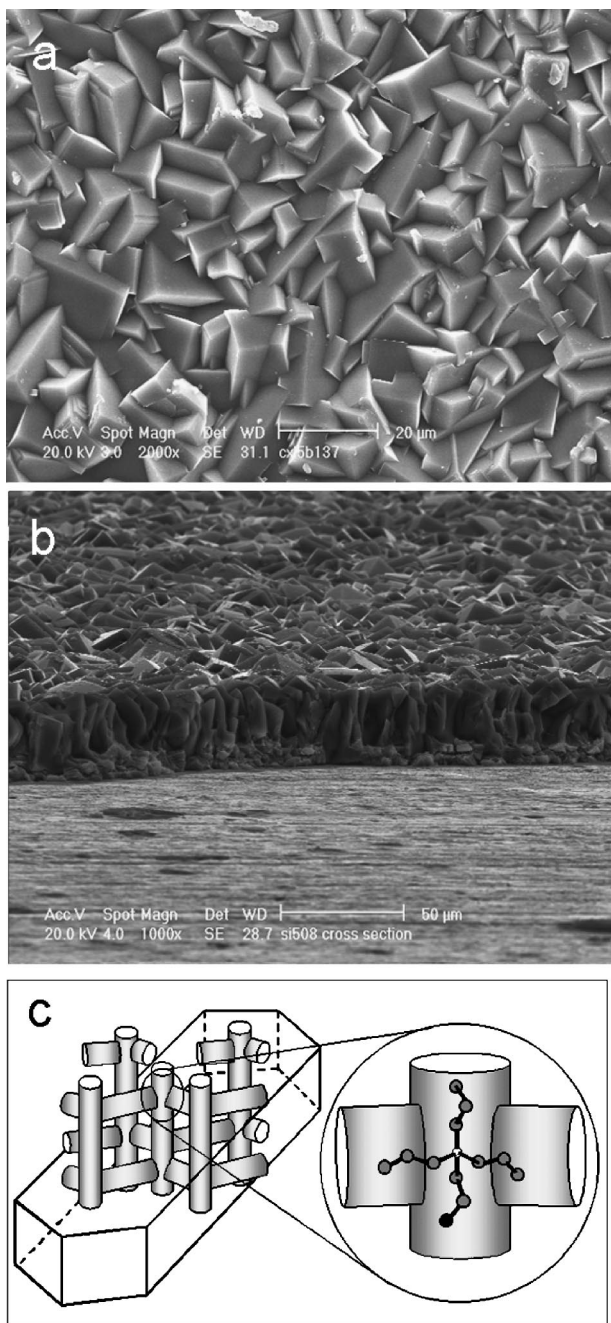z E-mail: yushan.yan@ucr.edu

Figure 1. SEMs of an as-synthesized zeolite coating on Al-2024-T3. (a) Top view and (b) cross-sectional view. (c) Schematic of ZSM-5 pore system and location of the trapped structure-directing-agent (SDA)-tetrapropyl-ammonium (TPA) molecule. (○) nitrogen atom and (●) for carbon atom. Hydrogen atoms are not shown.

Figure 2. DC polarization curves of several coatings in different corrosive media. (1) zeolite coating on Al-2024-T3, (2) anodization coating on Al-5005 (sulfuric acid anodized and sealed by hot water, 18 μm thick, provided by Southern Aluminum Finishing, Atlanta, GA), (3) bare Al-2024-T3, (4) chromate conversion coating on Al-2024-T3 (submicrometer thick provided by Triple AAA Plating, Inc. Bells, TX); (a) 0.5 mol/L H_2SO_4 after immersion for 2 h, (b) 0.5 mol/L H_2SO_4 after immersion for 10 days, (c) 0.5 mol/L NaCl/HCl (pH 1) after immersion for 2 h, (d) 0.5 mol/L NaCl + 0.26 g/L $CuCl_2$ + HAc (pH 3) after immersion for 1 day. All tests at 25°C with sweep rate of 1 mV/s, saturated calomel electrode (SCE), and Solartron 1287 potentiostat.

have also examined the polarization current of a thin pure silica ZSM-5 film and 10^{-7} to 10^{-8} A/cm^2 was usually obtained. Some of our 35 μm thick zeolite coating samples showed polarization currents as high as 10^{-8} A/cm^2, and are believed to have minor intercrystal porosity. These samples were, however, still very stable in all aforementioned corrosive media (*e.g.*, little change of polarization current for a few days of immersion), and performed better than anodization and conversion coatings.

The ZSM-5 coating reported here was prepared by *in situ* crystallization using a clear synthesis solution. The term *in situ* crystallization originates from the fact that no preformed zeolite crystals were used in the synthesis, and the polycrystalline coating was crys-
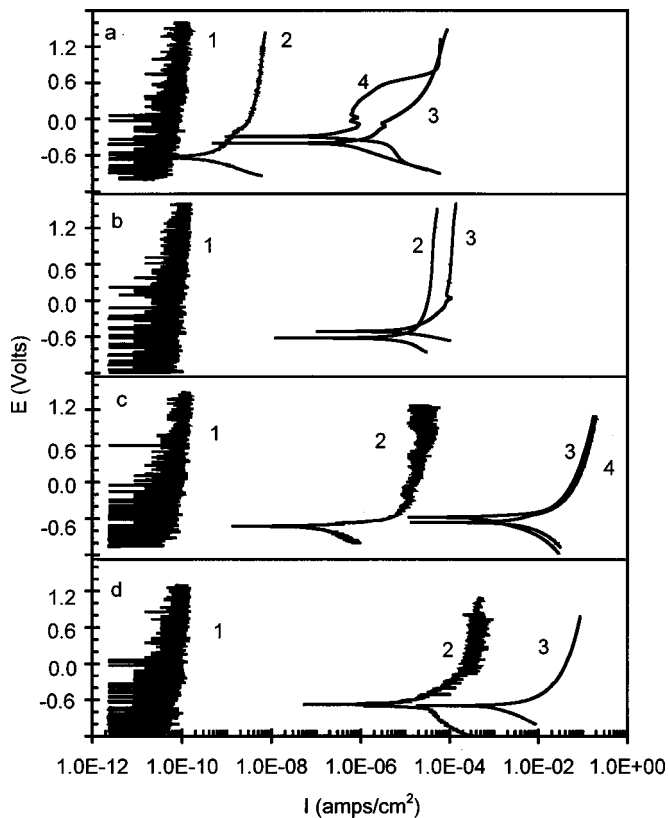
tallized directly at the solid-liquid interface. Coating deposition steps are as follows. A clear synthesis solution with molar composition 0.16TPAOH:0.64NaOH:TEOS:92H$_2$O:0.0018Al was obtained by dissolving aluminum foil (Aldrich) in sodium hydroxide (Aldrich) solution followed by dropwise addition of tetrapropylammonium hydroxide (SACHEM) and tetraethylorthosilicate (TEOS) (Aldrich) under stirring. The clear solution was aged at room temperature for about 4 h under stirring before use. A Teflon-lined Parr autoclave was used as the synthesis vessel. Metal substrates (normally 2.5 × 5 cm plates) were fixed vertically inside the synthesis solution (Fig. 4a). Similar coatings were obtained when substrates were positioned horizontally or tilted. Crystallization was carried out in a convection oven preset at 175°C for about 16 h. Then the autoclave was removed from the oven and quenched with tap water. The coated sample was water rinsed and dried in ambient room air before characterization. The coating thickness produced by the above procedure is about 35 μm and it can be adjusted by change of synthesis composition. For example, a 0.5 μm pure silica ZSM-5 film can be obtained by using a solution of molar composition 0.32TPAOH:TEOS:165H$_2$O. The synthesis solutions used thus far had a pH of 9-11, and no corrosion of the aluminum alloy was observed. It is believed that a gel layer was quickly formed at the beginning of the coating process,[12] protecting the substrate from corrosion by the alkaline solution. The optimal thickness has not been identified and it is believed that it will be application dependent.
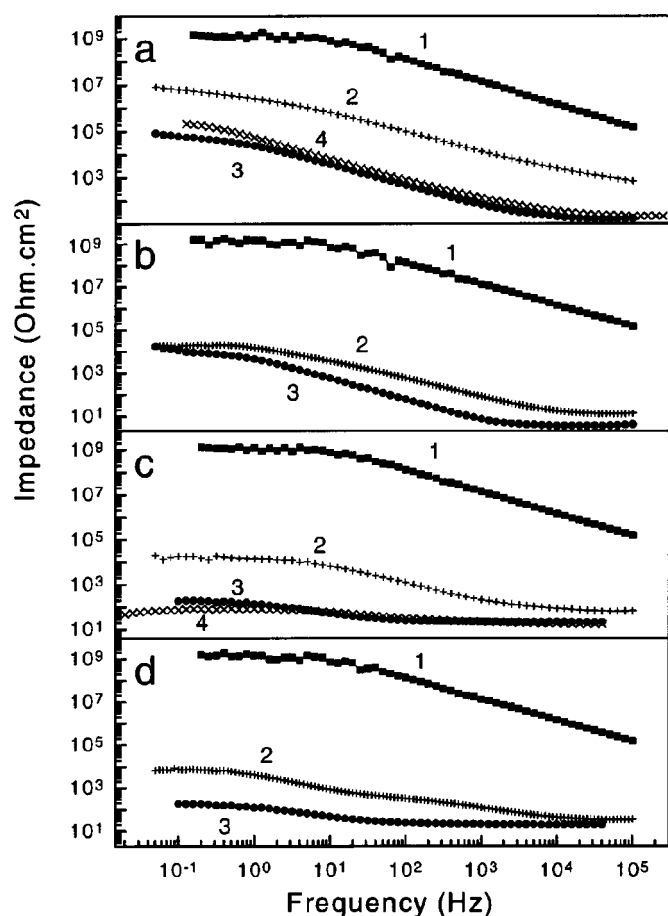
Figure 3. AC impedance of several coatings in different corrosive media. (1) zeolite coating on Al-2024-T3, (2) anodization coating on Al-5005 (sulfuric acid anodized and sealed by hot water, 18 μm thick, provided by Southern Aluminum Finishing, Atlanta, GA), (3) bare Al-2024-T3, (4) chromate conversion coating on Al-2024-T3 (submicrometer thick provided by Triple AAA Plating, Inc. Bells, TX); (a) 0.5 mol/L H_2SO_4 after immersion for 2 h, (b) 0.5 mol/L H_2SO_4 after immersion for 10 days, (c) 0.5 mol/L NaCl/HCl (pH 1) after immersion for 2 h, (d) 0.5 mol/L NaCl + 0.26 g/L $CuCl_2$ + HAc (pH 3) after immersion for 1 day. All tests at 25°C and open-circuit condition with ac amplitude of 10 mV, SCE, Solartron 1260 impedance analyzer, and Solartron 1287 potentiostat.

In situ crystallization can coat surfaces with complex geometries and in confined spaces, and can also coat surfaces selectively; forming coating where desired and leaving other surfaces coating-free. Figure 4a shows a schematic of the *in situ* crystallization process with a flat sheet substrate. Basically, any surface that is in contact with the synthesis solution during crystallization is uniformly coated. The synthesis solution was always clear after synthesis, indicating that little bulk phase crystallization was produced. Excess bulk phase crystallization is undesirable because it tends to clog very small channels. Because the solution used was a dilute aqueous aluminosilicate solution and had very low viscosity (similar to that of water), the *in situ* crystallization process is inexpensive and can readily coat surfaces with complex geometries and in confined spaces. Figure 4b shows some of the geometries we examined, flat surface, inside and/or outside surface of a small tube, and a curved narrow channel. The smallest tube and the narrowest channel attempted were 3 mm i.d. and 3 mm wide, respectively, and in both cases good zeolite coatings were obtained. Selective coating can also be readily achieved. For example, selective coating of the inner surface of a tube can be achieved by plugging the bottom end of the tube, fixing the tube vertically, and providing synthesis solution only to the inside of the tube. To avoid loss of synthesis solution from
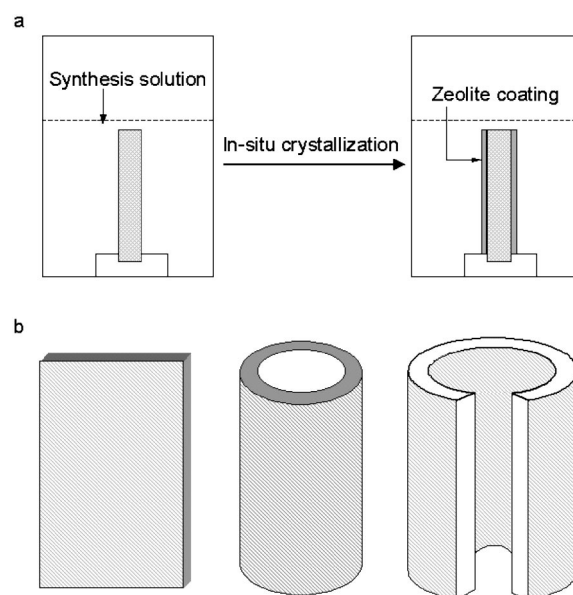

Figure 4. Schematics of an *in situ* crystallization process and substrate geometries successfully coated. (a) *In situ* crystallization process. (b) Substrates geometries: flat surface and inside and/or outside surfaces of a tube and a curved narrow channel.

inside the tube during synthesis, extra solution was provided outside the tube substrate, but not in contact with the tube. The ability to coat small curved channels without clogging distinguishes *in situ* crystallization from the conventional coating technologies such as dip or wash coating where straight channels are usually required.[18]

Zeolites themselves are nontoxic materials and have recently been studied as an oral contrast agent for magnetic resonance imaging (MRI),[19] although the toxicity of the organic SDA (TPA in this case) is not known. Oil-based polyurethane type paint, a widely used corrosion resistant paint,[3] was successfully applied on the zeolite coating with excellent adhesion consistent with previous findings that zeolites could be incorporated into polymer membranes.[20] Abrasion experiments showed that the abrasion rate was ~6.5 μm/h for zeolite coating and ~26 μm/h for anodization coating (automatic Buehler polisher with 2 μm diam alumina paste, 150 cm/s linear velocity, and 13.1 kPa load). Although not a standard (*e.g.*, ASTM) test, this shows clearly that zeolite coating is more wear-resistant. No film cracking or delamination was observed during thermal cycling to 240°C and to −70°C from room temperature and during polishing with abrasive paper (1200 grit silicon carbide from Norton) indicating zeolite coatings' excellent adhesion. The corrosion resistance of zeolite coating did not decrease after the coated sample was heated in an oven at 240°C for 1 day, indicating that the zeolite coating has fairly good thermal stability, which is better than chromate-conversion coating (60°C) and anodization coating (200°C).[3] Note that although zeolite shows good thermal stability the long-term stability of zeolite coating still requires further study.

Metals successfully coated to date include Al-2024-T3, Al-6061, carbon steel A-36, and stainless steel 304 and 316, and high-silica zeolite ZSM-12 coatings also showed good corrosion resistance. We believe that the coating strategy demonstrated here is general and could be directly extended to other metals and other micro- and nanocomposite materials. Work is in progress to reduce coating application temperature and time.

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