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The role of corrosion/oxidation in the failure of aluminum adhesive joints under hot, wet conditions

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Abstract

Wedge tests were performed on a variety of adhesively bonded aluminum joints at two different temperatures. At both temperatures, one specimen was submerged in water and a second specimen, cut from the same panel, was submerged in a dilute sulfite solution. Separate tests indicated that the sulfite solution reduced the free oxygen content to less than 0.5 ppm and reduced the corrosion rate to a third of its value in pure water. In each case, no difference was observed in the amount of apparent adhesive failure over one day. These tests were supplemented by a reflection–absorption infra-red spectroscopy (RAIRS) study of silane-coated and uncoated surfaces aged under similar conditions. The results indicate that corrosion is not the limiting factor in the failure of these bonds. On the very thin air-formed oxides employed, this also suggests that conversion of the oxide to a trihydrate is not cause of the apparent adhesive failure.

Keywords: Adhesive bonding; B. Aluminum and alloys; B. Surface treatment; D. Durability

1. Introduction

It is well known that aluminum joints have a tendency to fail "adhesively" when subjected to hot, moist conditions. A great deal of effort has been expended over the years to find surface preparations that prevent or at least significantly reduce this problem. This has resulted in a wide variety of treatments being developed. These include anodization treatments, such as phosphoric acid anodization [1], etches such as FPL etch [1] or those involving strong alkalis [2], and chromate conversion coat treatments such as Alodine [3]. More recently there has been a growth in interest in techniques that are more environmentally benign, including boiling water treatments [4,5] and the use of silane coupling agents [6–8]. This paper examines the failure mode involved when silanes are used to improve the environmental resistance of aluminum joints.

Early on there appeared to be a correlation between the susceptibility of an aluminum alloy to corrosion and adhesive bond durability [9]. Davis et al. [10] studied the hydration of the aluminum oxide layer created using phosphoric acid anodization and demonstrated morphological and compositional changes which indicated the conversion of the oxide to pseudoboehmite and then to bayerite. In addition to this information, Venables noted that when aluminum substrates with different pretreatments were submerged in hot water, there was a correlation between the incubation time to rapid hydrogen evolution (corrosion) and performance in the wedge test. This led him to suggest that oxide hydration resulted in a cohesively weak oxide layer that failed under load [11].

Rider and Arnott [12,13] noted that aluminum oxide appeared on the adhesive side of failed wedge test specimens prepared using pretreatments based on grit-blasting with alumina and silane coupling agents. On the

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basis of the apparent failure within the surface oxide, they suggested that the same hydration/corrosion mechanism proposed by Venables was at work in this system. This has led some authors to investigate the corrosion resistance imparted by various silane coupling agents [14,15]. However, improvements in the moisture resistance imparted by different silanes, as measured by the wedge test [16], have been modest, despite significant differences in the observed corrosion resistance imparted by different silanes to the aluminum surfaces.

Other authors have suggested that hydroxide growth occurs after fracture [17–19] and is unrelated to the critical failure process itself. The conversion of oxide to hydroxide is thought to involve the dissolution of aluminum oxide followed rapidly by its reprecipitation. While this can occur on a free surface in water or solution, it is not clear that the same mechanism can occur when the oxide is completely wetted by a polymeric layer. Clearly, in order to effectively develop techniques that improve the hydrolytic stability of an adhesive bond to aluminum, it would be very useful to have a clear understanding of exactly how moisture causes these joints to fail. In this paper, the role of corrosion in the adhesive failure of aluminum joints is examined by subjecting the joints to different environments whose corrosivity relative to the aluminum used, can be directly measured. The adhesive failure in these joints can be quantitatively measured and compared to the differences in environment to determine if corrosion is important to the adhesive failure process.

2. Experimental

A series of wedge test samples was prepared by bonding 6″ × 3″ panels of AL2024 T3 unclad using FM73. Prior to bonding, the panels were degreased using soap and water, rinsed with water, dried, and grit-blasted using 50 μm alumina propelled with dry N_2 at 30 psi. Residual grit was removed by rinsing with deionized water and drying the panels in hot air. Some panels were further processed by applying a 1% solution of either 3-glycidoxypropyltrimethoxy silane (GPS) or 3-mercaptopropyltrimethoxy silane (MPS). The silane solutions were hydrolyzed for half an hour in deionized water that had been acidified to a pH of 2.2 by the addition of a drop of nitric acid. Each set of bonded panels was cut to give two 1″ × 6″ samples.

Both samples were wedged using a wedge as specified in ASTM D3762. One of the samples was then placed in a jar containing deionized water which had been fully aerated. The other was placed in a jar containing a sulfite solution which is described below. This jar was topped up with solution to exclude any air and a lid was screwed on tightly. Both jars were then placed in a temperature-controlled bath and left overnight. The next day the samples were extracted and split so that the growth of the adhesive failure zone could be measured.

The sulfite solution was created by adding 0.1 g of Na_2SO_3 to 1 L of deionized water (resistance > 4 MΩ). This reduced the dissolved oxygen in the water from 8 ppm (typical) to less than 0.5 ppm as measured using a YSI Model 57 dissolved oxygen meter. Unfortunately, it also shifted the pH of the solution from 5.7 (typical for deionized water) to 8.5. Hence, while the reduction of dissolved O_2 would be expected to decrease the corrosion rate, the shift in pH would tend to increase it [20]. The dissolved oxygen content in the jars was measured when the samples were removed. It had not changed by more than 0.1 ppm.

In order to quantitatively determine the change in corrosion rate, an electrochemical cell was set up in which the current was passed from a graphite cathode to an aluminum (2024) anode. The current was measured using a zero resistance ammeter, while the potential of the aluminum sample was monitored using a saturated calomel electrode. The two electrodes were immersed in 200 mL of a 0.03% (wt) Na_2SO_4 solution and allowed to stand for 1 h to come to equilibrium. A mass of 0.056 g of Na_2SO_3 was then added to the solution and the reduction in current was measured. The corrosion current fell by just over a factor of three indicating a significant reduction in the corrosion rate.

A Nicolet Impact 410 FTIR using a Thunderdome Attenuated Total Reflection (ATR) attachment was used to perform an IR analysis of the adhesive side of the failure surface. This device gives useful information about the infra-red adsorption spectrum in the range 650 cm^{-1} to approximately 3000 cm^{-1} with a resolution of 4 cm^{-1}.

In order to examine the chemical changes that occur at aluminum surfaces under conditions similar to those used in this test a further series of experiments was conducted. In these, a series of 5 cm × 7.5 cm slides were prepared either by abrading the surface of the samples with a Scotch-Brite pad or by using an FPL etch. Half of each of these surfaces was then coated with the mercapto silane as described above. The coated and uncoated surfaces of these slides were then examined with RAIRS, using a grazing-angle bench set to an average angle of incidence of 85° from the surface normal. The bench was attached to the external port of a Nicolet 510P FTIR. Spectra were accumulated at 4 cm^{-1} resolution for 128 scans. One FPL etched and one abraded slide were then immersed in room temperature deionized water and a second pair of slides was placed in an environment chamber set to 50 °C and 95%RH After 1 day the slides were removed and the surfaces examined again using the grazing-angle FTIR bench to detect changes in the surface chemistry. It should be noted that wedge test specimens prepared using the FPL etch and silane treatment show no crack growth at 50 °C and