HYDROTHERMAL STABILITY OF TITANIUM/EPoxy ADHESIVE JOINTS

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γ-Aminopropyltriethoxysilane (γ-APS) was shown to be an extremely effective primer for improving the hydrothermal stability of titanium/epoxy adhesive joints when applied to the adherends by adsorption from dilute aqueous solutions prior to adhesive bonding. The breaking strength of lap joints prepared from unprimed adherends decreased slowly during immersion in water at 60°C and was only about 960 psi after 60 days. The breaking strength of joints prepared from adherends primed with γ-APS at pH 10.4 and 8.0 decreased very little during similar hydrothermal aging and was about 1750 psi after 60 days. Joints prepared from adherends primed with γ-APS at pH 5.5 were somewhat less durable and had a breaking strength of about 1180 psi after 60 days in water at 60°C. The performance of γ-APS as a primer was very different for titanium and iron adherends even though the molecular structures of the primer films formed on the two substrates were very similar. As a result, the performance of γ-APS primer films could not be related to the overall molecular structure of the films but was related to acid/base interactions between γ-APS and the oxidized surfaces of titanium and iron.

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INTRODUCTION

It is well known that proper pretreatment of metal surfaces is essential for the successful use of adhesive bonding for joining metals. Pretreatments for titanium adherends include a phosphate-fluoride conversion coating, a modified phosphate-fluoride process, an alkaline peroxide etch, and chromic acid-ammonium fluoride anodization\(^1\). The most useful pretreatments, the alkaline peroxide etch and the chromic acid anodization, produce a relatively thick, porous oxide\(^2\).

The use of organofunctional silanes as primers or coupling agents for improving the wet strength of glass fiber reinforced plastics is well known\(^3\). More recently it has been shown that certain organosilanes are extremely useful as primers for improving the hydrothermal stability of iron/epoxy\(^4\) and aluminum/epoxy\(^5,6\) adhesive joints. Comparatively little information is available regarding the use of silanes as primers for adhesive bonding of titanium. However, Schrader and Cardamone\(^7\) have considered the use of \(\gamma\)-aminopropyltriethoxysilane (\(\gamma\)-APS) as a primer for improving the hydrothermal stability of lap joints prepared from titanium-6Al, 4V adherends and an anhydride cured epoxy adhesive. The dry strength of lap joints prepared from adherends pretreated with 1\% aqueous solutions of \(\gamma\)-APS prior to adhesive bonding was always about 25\% greater than that of joints prepared from unprimed adherends. After 24 hours immersion in boiling water, the shear strength of joints prepared from primed adherends was about 50\% higher than that of joints prepared from unprimed adherends. The improved hydrothermal stability was attributed to possible covalent bonding between the silane and the adhesive and the oxide\(^7\).

The objectives of this research were to determine the molecular structure of films formed by \(\gamma\)-APS adsorbed onto titanium-6Al, 4V from dilute aqueous solutions and to determine the relationship between such structure and the performance of \(\gamma\)-APS as a primer for titanium/epoxy adhesive joints. The molecular structure of primer films formed by \(\gamma\)-APS adsorbed onto titanium was determined using reflection-absorption infrared spectroscopy (RAIR) and ellipsometry. RAIR is a technique for obtaining infrared spectra of thin films on metallic substrates by reflecting radiation polarized parallel to the plane of incidence from the substrate at a large, nearly grazing angle of incidence. Ellipsometry is a technique for determining the thickness and refractive index of a thin film on a metallic surface by reflecting plane polarized visible light from the surface and measuring the relative amplitude reduction and phase shift for components polarized parallel to and perpendicular to the plane of incidence. RAIR\(^8,9\) and ellipsometry\(^10\) have been thoroughly described in the literature and no further discussion will be given here.