Chromate-Free Pretreatment of AA6060 Aluminium for Adhesive Bonding

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Chromate based pretreatments have been successfully used for several decades to improve corrosion resistance and durability of adhesive bonded aluminium joints. However, due to health and environmental considerations recent legislation imposes strong limitations in future use of hexavalent Cr, *e.g.* in the automotive industry. There is consequently a need to develop alternative pretreatment processes. This is not an easy task since chromate conversion coatings are very effective in promoting both adhesion and corrosion protection.

The performance of chromate conversion coatings (CCC) has been attributed to several factors: The CCC provides barrier protection of the Al matrix due to its hydrophobic nature and stability over a wide pH range. Moreover, the coatings appear to be self-healing to some extent due to storage and release of Cr(VI) species that diffuse to the defect and interact with the bare metal and prevent pit initiation. Recent work [1,2] has shown that CCCs are also effective in reducing the activity of both anodic and cathodic sites on AA2024 aluminium. Inhibition of the oxygen reduction reaction at cathodic AlCuFeMn intermetallic particles is believed to be an important part of the corrosion inhibition mechanism [2].

The purpose of the present work is to study the role of substrate microstructure in corrosion and surface pretreatment of extruded AA6060-T6 used in adhesive bonded automotive spaceframes. The role of α-AlFeMnSi particles is specially addressed since these particles constitute the dominating cathodic phase in the material. Synthetically prepared α-AlFeMnSi phase electrodes and a particle-free 6060 matrix alloy were also made to separate the anode and cathode sites of the commercial 6060 material.

Among chromate-free pretreatments several fluorotitanate and/or fluorozirconate based processes are commercially available, mainly for powder coated products. Formation of Ti-Zr based conversion layers on alloy 6060 occurs preferentially on and around the α-AlFeMnSi particles as a result of local alkalisation at these sites [3,4]. Although fairly thick (>200 nm) layers may be formed on the particles under certain conditions, these conversion coatings are in the present work found to have only a slight effect on the cathode kinetics of α-AlFeMnSi during subsequent polarisation in aerated 0.1 M NaCl solution. In contrast, chromating in Alodine 6100 suppressed the cathode reaction on α-AlFeMnSi by two orders of magnitude under similar conditions.

An alternative to passivating the Fe-rich particles in commercial aluminium by use of conversion coatings is to etch the particles from the surface. Earlier work [5,6] has shown that removal of the cathodic particles significantly improves the corrosion resistance of bare aluminium alloys, at least until new particles are uncovered after extended exposure in aggressive environment [5,6].

On coated material, filiform corrosion (FFC) only takes place if there is microgalvanic coupling between the aluminium matrix and nobler second phase particles [7]. This is consistent with the present results on alloy 6060. Alloy 6060 specimens coated with an epoxy based structural adhesive suffered FFC during accelerated testing, indicating that FFC may be an important degradation mechanism for adhesive bonded joints. However, the particle-free (<0.001% Fe) AA6060 matrix alloy showed no evidence of FFC, irrespective of the pretreatment before coating.

Different methods of removing the α-AlFeMnSi particles from the surface of AA6060 were investigated, including cathodic etching in chloride solution [6], cathodic polarisation in nitric acid [8] and immersion in a HF/HNO_3 solution [9]. The methods exhibited a high efficiency according to SEM observations and electrochemical characterisation of the treated surfaces. The HF/HNO_3 etch (Figure 1) was superior in terms of simplicity and time consumption. Work in progress indicates that pretreatments involving removal of the cathodic particles improve the durability of epoxy bonded AA6060 joints.

References

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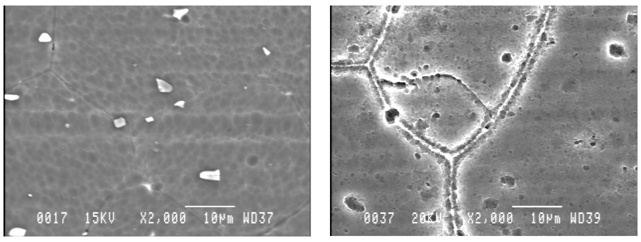

Figure 1. SEM images of AA6060 after NaOH etching, showing bright α-AlFeMnSi particles in the surface (left). Additional etching for 1 min in HF/HNO_3 solution caused removal of the particles and extensive corrosion along grain boundaries (right).