Critical Issues for Chrome-free Pretreatment of Aluminium Alloys

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Successful chrome-free pretreatment of aluminium alloys depends on a number of critical factors ranging from alloy and process route selection through to appropriate surface cleaning and corrosion or durability testing. Corrosion susceptibility, in most instances, is controlled by active surface layers that have been studied in detail only for the past few years [1-6]. The following summarises the main issues.

Alloy Selection

Over the years there have been several requests for "stainless" aluminium, that is aluminium with a low propensity to corrode. If this is considered for painted sheet applications then recent results have shown that the severity of corrosion under a paint film is directly related to the manganese content of the alloy. This means that alloys like AA3003, AA3103, AA3004, AA3104, AA3005 are all inherently susceptible to corrosion and strong consideration should be given, where possible, to using alloys with a lower manganese level, like AA3105, or to using alloys like AA5050, AA5251, AA5754 etc. It is quite difficult to make most AA5xxx alloys susceptible to corrosion under paint films. In this context, such alloys can almost be considered to be "stainless" aluminium.

Generally, the corrosion susceptibility of painted aluminium is due to the development of active surface layers. These arise from the high level of surface shear induced during rolling that transforms the near surface microstructure (figure 1). Deformed surfaces are characterised by an ultra-fine grain size that can be stabilised by magnesium oxide pinning in magnesium containing alloys [7]. However, it is not the fine grain size that is responsible for the corrosion susceptibility of the surface layer. This susceptibility is promoted by the preferential precipitation of manganese rich dispersoids during annealing treatments (figure 2). Susceptibility is directly related to density of precipitated dispersoids that, in turn, depends on the manganese solid solution level and the temperature and time of annealing (figure 3). This is why manganese has such a strong influence on corrosion susceptibility [8-11].

Alloy Processing

Deformed surface layers on aluminium alloys are produced most readily by hot rolling and generally the layer thickness of sheet and plate after hot rolling is of the order of a micron. The deformed layer thickness is progressively reduced by cold rolling so alloys that have been extensively cold rolled have thinner deformed layers that can more readily be removed by conventional etch cleaning operations. This means that resistance to corrosion can be improved by increasing the transfer gauge thickness so that after cold rolling the amount of surface to be removed at final gauge is 0.2µm or less.

Another route to reduce susceptibility is to homogenise rolling blocks before hot rolling to precipitate out the manganese from solid solution. This is equivalent to using a lower manganese containing alloy (figure 4). A further possibility is to eliminate hot rolling by using either roll cast or thin belt cast production routes. This is particularly effective when used in combination with appropriate alloy selection.

Cleaning

This is the most critical process step to provide alloys surfaces that can be successfully pretreated with a chrome or chrome-free pre-treatment (figure 5). Basically, the corrosion active surface layer must be removed using either an acidic or alkaline treatment. The amount of metal to be removed depends directly on the layer thickness and this means that cleaning is facilitated where there has been significant cold rolling to reduce layer thickness. In low magnesium alloys the ultra-fine grains are usually annealed out but there is still a preferential precipitation of dispersoids compared to the bulk microstructure. The entire corrosion sensitive layer must be removed. For most AA5xxx alloys the only requirement is to remove magnesium oxide from the surface as this can reduce adhesion particularly for bonding applications. This means that cleaning of AA5xxx alloys is much more straightforward than cleaning AA3xxx alloys particularly those with high manganese content.

To date we have not found an alloy that does not become immune to underfilm corrosion following effective cleaning to remove any corrosion susceptible layers. However, it is very important to avoid accumulation of copper on the alloy surface during the cleaning operation and/or to ensure that any copper enrichment is removed by a suitable desmutting treatment (figure 6). Copper is readily enriched on the surface of aluminium alloys in both acid and alkaline etching solutions. Generally it is important that surfaces are not over cleaned and that the cleaning operation is calibrated such that the end of cleaning coincides with active layer removal. Copper enrichment during cleaning can be measured on alloys where the nominal copper level in the alloy is less than 0.1%.

Chrome-free Pretreatment

The principal function of pretreatment or conversion treatment after cleaning is to provide good adhesion (figure 7). This can be achieved by using a treatment to enhance the natural oxide layer like anodising or hydrothermal treatment in water or steam. Anodising pretreatments have been used very effectively for many years although they are not in widespread use as coil line treatments. Coil line treatments are based on fast anodising in either sulphuric acid or phosphoric acid. These types of preteatment have the advantages of speed, control and uniformity compared to most chemical conversion treatments. They are much under utilised as chrome-free pretreatments.

Fluorotitanic and fluorozirconic acid based pretreatments are in fairly widespread use as chrome-free alternatives. Such pretreatments can certainly be effective but are more difficult to monitor in production compared to traditional chrome-based systems. This is particularly an issue where polymeric additions are made to the formulation to improve performance. For such systems good adhesion is achieved through good surface coverage of a uniform film of either zirconium and/or titanium oxide. However adhesion is severely compromised if the film is too thick and this can lead to coating failure in service that is unrelated to corrosion sensitivity.

Pretreatment systems based on the use of adhesion promoters such as silanes, phosphonates and polyacrylic acids have been extensively researched. These pretreatments can certainly be very effective especially when applied as monolayers rather than thick films. They are probably most useful when used in combination with a thin anodising treatment or similar treatment to increase barrier film thickness and to develop a micro-surface roughness to enhance adhesion.

Corrosion Testing

There is very little systematic information on field performance of painted aluminium products. Most useful information has come from the carefully monitored exposure of sets of test panels on exposure sites. The results of these studies correlate extremely well with filiform corrosion tests and with certain cyclic corrosion tests like the TNO test. There is generally poor correlation with the results of acidified salt spray tests either in terms of performance ranking or in the observed mode of corrosion. It is certainly entirely inappropriate to use corrosion tests designed for steel substrates for aluminium, as the conditions that promote corrosion are quite different. Corrosion of painted aluminium requires the presence of chloride and a high humidity. Corrosion of aluminium under conditions of total immersion or at humidity levels of more than 95% does not show the filamental corrosion mode that is seen on exposure sites or in service. It is interesting to note that corrosion of panels removed from an acidified salt spray test often occurs once the panels have been removed from the test cabinet. A simple form of filiform corrosion testing has been developed that can be used to optimise alloy and process route selection and to tune cleaning treatments to ensure that active surface layers are removed [12].

Corrosion on painted panels occurs most readily on marine sites when panels are exposed vertically, facing north and the panel is protected by an overhang so that accumulated chloride is not removed by rain. Such conditions are not reproduced in most cabinet based corrosion tests. There is certainly scope to develop an improved test method that reproduces the important exposure site conditions that promote corrosion.

Grinding and Machining

Although the surface of wrought aluminium products can be made corrosion resistant by cleaning to remove active surface layers it is important that such surfaces are not damaged by subsequent high shear processes like grinding or machining operations. This is particularly important for aluminium automotive alloys, like AA6111 and AA6016 that are used in external closure panel applications. Mechanical grinding during processes such as rectification can readily produce an ultra-fine grain sized surface layer. This layer is not removed during cleaning and phosphating as part of the body-in-white finishing operation. The layer can become more corrosion active than the underlying bulk metal following paint baking. This is due to preferential precipitation of the ageing precipitate in the surface layers compared to the bulk microstructure (figure 8).

The situation for aluminium external closure panels is similar to using galvanised steel in that rectification must be minimised in areas that are susceptible to stone chip damage. For galvanised steel surface grinding removes the protective zinc layer whereas for aluminium a corrosion active layer is created by the grinding and finishing operation. However, corrosion in service can only occur if the paint film is damaged to expose bare metal.

Although as-cast surfaces have not been found to be susceptible to filiform corrosion it is possible to develop active layers on castings by grinding or machining and subsequent thermal treatment. This is probably the main influence on the corrosion of cast aluminium wheels. The surface of extruded aluminium has been studied extensively although ultra-fine grain microstructures have not been reported. However, transformed surface microstructures particularly those with coarse grain structures are well documented. Resistance to filiform corrosion is also significantly improved by deep surface etching. Cutting, grinding and machining operations following cleaning and pretreatment either before or especially after painting are probably highly significant in promoting corrosion in service.

Recycling and Secondary Metal

Secondary metal generally contains higher levels of impurities compared to primary metal. This can lead to higher levels of elements like iron, silicon and copper and also to contamination by elements like lead, bismuth, zinc and tin. There is also the problem of manganese from the large tonnage of high manganese alloys in use in many building product and packaging applications.

Aluminium alloys made from secondary metal can be highly resistant to corrosion using chrome free pretreatments provided that alloy compositions are optimised such that deliberate manganese additions are minimised. In addition, continuous casting production routes should be chosen to minimise active layer development by eliminating hot rolling. Effective cleaning is critical and surface enrichment of elements like copper, lead, bismuth, zinc and tin must be avoided or such enriched layers must be removed. After such cleaning continuously cast alloys made from secondary metal can be shown to be highly resistant to corrosion using a simple chrome-free pretreatment like a silane to promote good adhesion.

Summary

Chrome-free pretreatment of aluminium is not difficult to achieve. It can be facilitated by appropriate alloy and process route selection. The most important finishing process is surface cleaning to remove corrosion active surface layers. Following effective cleaning a wide range of chrome-free pretreatments can be used successfully provided good adhesion is achieved. The most effective pretreatments are those base on anodisation although hydrothermal treatments should also be considered. One of the major hurdles to chrome-free pretreatment is the use of overly aggressive corrosion test methods that do not relater to service performance.

Acknowledgements
The author is indebted to his friends and colleagues within the FICARP project, Innoval, Alcan and UMIST for making this work possible, interesting and enjoyable.

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