

Understanding Corrosion Mechanisms of Impure Aluminum and Related Phenomena

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This paper reviews 50 years of research which has led to the present stage of understanding the surface structure and electrochemistry and the role of these properties on the corrosion behavior of aluminum alloys, specifically pitting and filiform corrosion. The emphasis is on 1000 (commercially-pure aluminum), 3000 (AlMn), 5000 (AlMg) and 6000 (AlMgSi) series alloys which have importance in the packaging, architectural and newly developing automotive applications.

Starting with the classical work of Aziz and Godard¹ in the 1950's on the effect of impurity and alloying elements on corrosion of 1000 and 3000 series alloys, significant effort has been put in understanding the microgalvanic interaction between the iron containing, aluminum-base intermetallic compounds. The classical work by Vosskühler and Zeiger demonstrated a correlation between the galvanic potential difference between the intermetallic particles, which typically exists in aluminum alloys, and their corrosion susceptibility. Zamin's study of 3000 series alloys established the significance of the Mn/Fe ratio in the alloy and the intermetallic particles on pitting resistance with reference to key Japanese work on the electrochemical properties of several types of Al-base intermetallics, which contain the alloying element Mn and the impurity elements Fe and Si.

Zamin's work had important ramifications in further development of corrosion resistant 3000 alloys, as well as Mg alloys in the AZ-series (MgAlZn). In subsequent work, the significance of anodic reaction rates on the surface chemistry and structure of different phases present in the alloy was demonstrated to give a better picture of the microgalvanic interaction, in addition to the differences in the corrosion potentials. The approach used was preparation and use of electrodes of synthetic intermetallic compounds and solid solution matrix alloys representing the different phases present in the commercial alloys. A significant amount of such data is now available in different environments.

Data for one-phase, one component model alloys in acidified chloride environments are relevant for the matrix alloy because electrochemically active matrix alloy is normally susceptible to localized corrosion, characterized by acidification of the local corrosive environment according to the classical electrochemical theory of localized corrosion. At the same time, the iron rich intermetallics act as the preferred cathodes, at which the reduction process leads to the local alkalization of the solution. Therefore, polarization data obtained for the synthetic intermetallic compounds in alkaline environments are relevant to understand the properties of these phases as cathodes in the actual corrosion process. It was shown that compositional changes are expected occur on all phases as a result of selective corrosion in respective environments. The intermetallic phases become stripped of the more active aluminum component in alkaline environment, which leads to enrichment of the particle surface in iron and thereby increased rate of the reduction reac-

tion. Enrichment of the particle surface by manganese reduces the deleterious effect of iron. However, enrichment of the matrix by manganese by a similar process leads to a reduced driving force for the microgalvanic coupling of the intermetallics and the matrix and also to increased pitting resistance of the matrix.

The foregoing summary of early work was largely focused on the bulk properties of the alloys, often exposed by deep etching, (electro)chemical polishing, or metallographic polishing before experiment. Recent investigation of the as-rolled aluminum sheet surface revealed the existence of a nanocrystalline layer of the order 1 μ m thick, characterized by grain sizes as small as 20 nm, *i.e.*, up to two orders of magnitude smaller than the bulk grains. The grains exhibit identical composition and structure to the bulk grains. The grain boundaries are contaminated by oxide particles incorporated during hot rolling and secondary intermetallic phases, which precipitate as a result of heat treatment during the thermomechanical processing of the sheet. The nanograins are quite stable against recrystallization during annealing due to Zener pinning by the grain boundary oxide and precipitates. The grain-boundary oxide is enriched in magnesium oxide even if magnesium is present as an impurity element in the alloy. Such surfaces have been shown to be especially susceptible to filiform corrosion, owing to the presence of fine distribution of intermetallic phases, which act as the local initiation sites and cathodes. Since precipitation of the phases deplete the nanograins of their heavy metal content, such as iron and manganese, the driving force for the microgalvanic action is locally enhanced. The nanograin structure has a secondary role in providing a large grain boundary area and an unstable, magnesium rich grain-boundary oxide which is chemically attacked by the acidified anolyte. A simple way of preventing filiform corrosion on rolled products is to remove the particle-rich surface layer by etching unless more than 0.5% of copper is present. The surfaces treated in this manner become highly resistant against filiform corrosion, such that conversion coatings become unnecessary except for improved adhesion of the organic coating.

A new discovery which is responsible for the dynamic electrochemical character of impure aluminum and has important consequences for localized corrosion is the effect of trace elements, particularly Pb. Lead is present in the bauxite, and it becomes incorporated in the metal also as a result of metal recycling. By exposure to temperatures above 400°C during thermomechanical processing of the material, Pb readily diffuses along the grain boundaries to the surface. Its enrichment in the metallic state at the oxide-metal interface causes a significant electrochemical activation of the surface when exposed to chloride solution. Even a few ppm of Pb content in the bulk may be detrimental. Lead enrichment contributes to the susceptibility of the painted surface to filiform corrosion. However, Pb enrichment may provide sacrificial protection of the bare surface against pitting corrosion. The phenomenon has practical significance in all high temperature processes, such as welding and brazing, especially insofar as galvanic corrosion at the activated zones. Clearly, the phenomenon can also be exploited to reduce or eliminate galvanic corrosion and in engineering the electrochemical properties of the surface in general by proper control of thermal processing.

¹ Please see related Proceedings article for list of references.

