

# Corrosion Of Aluminium Alloys

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**Abstract-** *The corrosion resistance of a series of aluminium alloys, comprising binary Al-Cu, Al-Si, Al-Mg, Al-Zn and ternary Al-Si-Cu alloys, was investigated. These alloys were respectively corroded in 60g<sup>l</sup><sup>-1</sup> NaOH (pH = 13.6) and their characteristics weight loss versus time responses correlated with alloying concentrations, inherent microstructural details and topographical features (corrosion profiles). It was found that corrosion rate progressively increased with increasing alloying concentration and the weight loss versus time responses followed an essentially linear behavior indicative of uniform rate of corrosion, except for Al - 5% Cu and Al – 5% Si alloys whose behaviour departed markedly from linearity and was anomalous. This deviation was attributed to serious segregation effects, owing to intensive grain-boundary precipitation of the second phase constituents (CuAl<sub>2</sub> or Si) and hence, the transition from general to localized corrosion. The situation was again reversed at very high silicon and copper concentrations (Al-20%Si, Al-20%Cu) owing to the relative predominance of the eutectic phase constituent*

## I. INTRODUCTION

Many different aluminium products are currently used for structural, industrial and domestic applications. In today's advanced technology steels have very high strength-to-weight ratios so that thinner sections can be used for most structural and engineering.

Construction. Yet aluminum continues to play an ever-increasing role in structural and engineering designs for reasons not unconnected with its relative strength, lightness, attractive appearance, high thermal and electrical conductivity, low temperature fracture toughness, non-sparkling characteristics, ease of fabrication and most importantly, excellent corrosion resistance. Weight reduction is an important factor in the automobile industry as automotive fuel efficiency

is markedly dependent upon weight. Although downsizing accounts for much of the average cars weight reduction, the so-called light –weighting has of recent become increasingly important and it is predicted that there would be an escalating demand for wrought aluminum products as automakers convert automotive body structures to aluminum (1-4)

The corrosion resistance of aluminum and indeed most engineering alloys, is not only dependent upon the impurity content but also on prior metallurgical treatment. These conjointly determine the nature and composition of the vital elements present, the crystalline structure adopted, the scope for mutual solid-state interaction and hence, the relative amounts and state of subdivision of the intermetallic constituents formed and their apparent distribution within the microstructure, with particular reference to the grain boundaries. Mechanical, corrosion and other properties are accordingly altered (5 and 6). Body structures require high formability and corrosion resistant with only modest strength. These needs must not only be met but alloy compositions must be tightly controlled to ensure consistent properties and effective performance of components. Solute impurities like Fe, Cd, Bi, Pb, Zn, Cu, Si, Ca and Mg are known to exhibit serious deleterious effects if used above tolerable limits. Each class of aluminum alloys tends to behave differently, with the composition and inherent microstructure dictating the service characteristics and subsequent properties that are developed. Often, mechanical properties are improved at the expense of corrosion resistance (6-8)

The present work aims to investigate the corrosion resistance of some binary and ternary aluminum alloys and to ascertain the relative influence of alloying content and inherent microstructure on the corrosion trend exhibition. The above results, it is hoped, will be used to correlate subsequent mechanical findings so as to effectively control, or possibly counteract, the injurious effects of some impurity elements.

II. MATERIALS AND METHOD

Casting of the aluminum alloys involved preparation of the so-called master alloys at a preliminary stage. These were subsequently remelted at a lower temperature, much closer to the melting point of pure aluminum. Surface oxidation and loss of aluminum was thereby minimized.

First, the master alloys (Al-20%Cu, Al-20%Si, Al-20%Mg and Al-20%Zn) were prepared by melting the respective alloying metals in a forced air furnace. Pieces of superpure (99.99%) aluminum were then added before pouring into steel moulds (vice versa for Al-20% and Al-20%Mg master alloys). Subsequently, fresh aluminum was melted and controlled quantities of the respective master alloys added. The mixture was rapidly stirred and allowed to briefly stand at about 700oc before casting to give a series of cylindrical specimens, 18cm long and 2cm in diameter. The composition of the alloy was varied by carefully controlling the relative proportion of master alloy and extra –aluminum added. Analysis of the cast specimen was effected a few hours after casting. A fine granular sample was taken form each specimen using a metal file and alloy composition determined spectrographically with the aid of an atomic absorption spectrophotometer, the respective specimen compositions being:

Al-20% Cu, Al-20%Si, Al-20%Mg, Al-20%Zn, Al-5%Cu, Al-5%Si, Al-5%Zn, Al-1.5%Cu, Al-1.5%Si, Al-12%Si, 4%Cu.

Specimens meant for corrosion were cut into smaller sections, 6cm long, the surfaces of which were partly masked off with Araldite adhesive to expose a constant specimen surface area of 15.7cm<sup>2</sup>. A narrow plastic handle was subsequently attached to each specimen via the araldite adhesive. Corrosion was carried out at a fixed temperature (25°c) in a 1L (100cm<sup>3</sup>) capacity glass vessel containing 60gl<sup>-1</sup> sodium hydroxide (NaOH) solution. The specimen was carefully weighed, clamped to a specimen holder and suspended vertically-downwards into the solution. A stop clock was used to monitor the time of corrosion which was for 15min, 30min, 1hr, 1.5hr, 2hr, 2.5hr, 3hr, and 3.5hr respectively. A fresh NaOH solution was prepared for each specimen. The corroded

specimen was rinsed (desmuted) with the distilled water, dried in a stream of cold air and again weighed. The weight loss was determine from the difference in weight before and after corrosion. Unless otherwise stated, all metals and reagents used were of analar grade. Specimen microstructures were effected by appropriate metallographic preparation (surface grinding) sequence. When necessary, an electron probe microanalyzer was used to monitor the presence of intermetallic constituents (incidence of segregation) and hence, the distribution map of alloying elements across the etched specimen surface.

III. RESULTS

Weight loss results

The weight loss versus time measurements for the respective aluminum alloy specimens were summarized (Tables I and II). Apparently, the lowest weight losses were recorded for the Al-20%Zn specimen, followed by the Al-20%Mg specimen and finally, the Al-20%Si and Al-20%Cu specimens both of which

Table 1, weight loss versus time measurements for Al-20%Cu, Al-20%Zn, Al-20%Si and Al-20%Mg master alloy specimens corroded in 60 gr-1 sodium hydroxide (NaOH) solution

Weight loss (g cm<sup>-2</sup>)

Time (hr)	Al-20%Cu	Al-20%Zn	Al-20%Si	Al-20%Mg
0.25	0.0084	0.0030	0.0070	0.0034
0.50	0.150	0.0050	0.0126	0.0075
1.00	0.0291	0.0116	0.0255	0.0182
1.50	0.0435	0.0190	0.0380	0.0306
2.00	0.0513	0.0260	0.0552	0.0428
2.50	0.0630	0.0322	0.0701	0.0550
3.00	0.0725	0.0412	-	0.0550
3.50	-	0.0516	-	-

Table II, weight loss versus time measurements for different aluminum alloy specimens corroded in 60 gl<sup>-1</sup> sodium hydroxide (NaOH) solution.

Time	Al-	Al-	Al-	Al-	Al-	Al-	Al-

(hr )	12 %Si 4% Cu	1.5 % Cu	1.5 % Si	5.0 % Cu	5.0 % Zn	5.0 % Si	5.0 % Mg
0.50	0.0030	0.0032	0.0020	0.0040	0.0030	0.0040	0.0030
1.00	0.0075	0.0069	0.0038	0.0091	0.0060	0.0091	0.0065
1.50	0.0125	0.0107	0.0057	0.0155	0.0085	0.0142	0.0107
2.00	0.0165	0.0140	0.0079	0.0245	0.0124	0.0180	0.0147
2.50	0.0195	0.0175	0.0097	0.0371	0.0155	0.0217	0.0180
3.00	0.0256	0.0215	0.0117		0.0190	0.0284	0.0235
3.50	0.0366	0.0245	0.0135		0.0235	0.0350	0.0280

recorded the highest corrosion rates although the specific corrosion trend seemingly alternated after 2 hr, a phenomenon not unconnected with a change in precipitation effects. For the more dilute aluminum alloys, a seemingly linear weight loss versus time curve was generally recorded, except for the Al-5%Cu, Al-5%Si and Al-12%Si, 4%Cu specimens whose characteristic weight loss versus time responses markedly departed from linearity, a deviation attributed to serious segregation effects (Table II). Apparently, this was caused by the preferential location of second phase constituents,  $\text{CuAl}_2$  and Si, at the grain boundaries. It is well known that the maximum solid solubility of copper, silicon magnesium and zinc in aluminum are 5.7%, 1.65%, 14.9% and 70%, respectively. Apparently, Al-1.5%Cu, Al-1.5%Si, Al-5%Mg and Al-5%Zn alloys were essentially homogeneous, moreso when rapidly cooled, thus, their characteristic linear response (uniform rate of corrosion)

- Influence Of Alloy Microstructure

The optical micrographs (microstructures) of etched aluminum alloy specimens are shown (plate 1). The as cast specimens were essentially characterized by cored widmanstatten and dendritic structures, plates 1a and 1b, owing to the uneven distribution of impurity

elements (microsegregation) in the aluminum matrix and hence, the selective manner of crystallization. The deformed or extruded specimens were, however, characterized by a network of deformation bands, the grains having been deformed into fibres parallel to the deformation axis. Finally, the microstructures of the annealed specimens, plates 1a – 1h, were relatively equiaxed grains with the magnitude of segregation (phase precipitation) increasing with alloying concentration, owing to the exclusive or conjoint presence of intermetallic constituents ( $\text{CuAl}_2$ ,  $\text{Mg}_5\text{Al}_8$ , Si, etc) at the grain boundaries. The Al-12% Si, 4% Cu specimen, plate 1(h), is of special interest. The said structure consists of primary aluminum solid solution crystals with  $\text{CuAl}_2$  particles at the grain boundaries and fine (Al+Si) eutectic.

Electron probe microanalysis of the etched specimen surfaces were shown (Figs 1-4). The Al-1.5%Cu and Al-1.5%Si alloys, Figs 1 and 2, showed clear evidence of segregation. In other words, the alloying elements Cu and Si were not evenly distributed but were rather preferentially located (concentration peaks) to certain areas of the surface, possibly the grain boundaries, as Cu-and Si-containing intermetallics. However, the effect of segregation is more pronounced in the Al-Si alloy with certain areas having a Si-content greater than 15% while other areas are virtually free of silicon, an indication that silicon may have been present not as a Si-rich intermetallic but rather as pure silicon particles. On the contrary, the electron probe microanalysis of the etched Al-0.1%Cu and Al-0.05%Si specimens showed a rather uniform distribution of both Si and Cu across the specimen surface which did not vary significantly from specified compositions, the respective alloys being homogeneous (Figs 3 and 4). A similar distribution pattern is anticipated for other alloys in the solid-solution state.

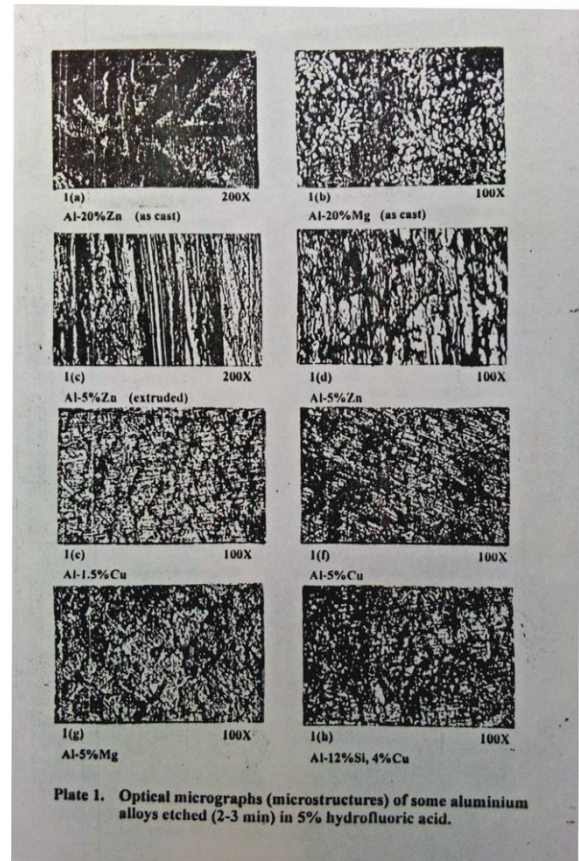
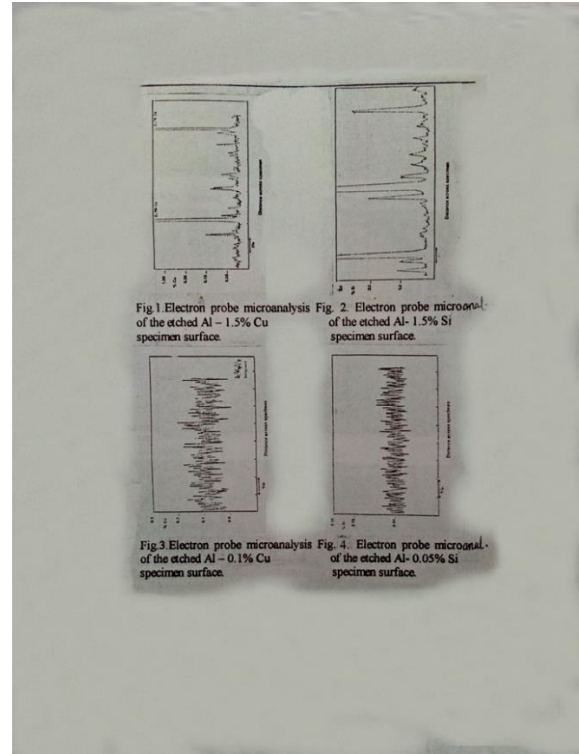
- Corrosion Profiles

Optical micrographs of the various alloys corroded in  $60\text{gl}^{-1}$  sodium hydroxide (NaOH) solution are shown (plate 2). Plate 2a provides valuable information about the corroded. Al.1. 5%Cu specimen with the corrosion film, i.e, the smut layer, intact while plate 2b displays the underlying surface details with the said smut layer completely removed (desmuted specimen). Smut comprises insoluble oxides, hydroxides, etc formed in

the course of metal dissolution. The undesmuted specimen was apparently covered by a thick, porous smut with a somewhat pasty or gel-like appearance. It was quite soluble in water and rinsed off easily. The desmuted specimens, plates 2b-2h, were characterized by numerous corrosion pits whose size and population density markedly increased with time, transforming the specimen surface into a heavily scalloped structure. The Al-Zn alloy, plate 2f, was the least corroded, followed by Al-Mg alloy, plate 2e, then, Al-Si-Cu alloy, plate 2g followed by Al-Si alloy, plates 2c and 2d and finally Al-Cu alloy, plates 2b and 2h. This is in good agreement with previous weight loss measurements.

#### IV. DISCUSSION

The corrosion resistance of a series of aluminum alloys comprising Al-Cu, Al-Mg, Al-Zn, Al-Si and Al-Si-Cu alloys was investigated in  $60\text{g l}^{-1}$  sodium hydroxide (NaOH) solution (pH=13.6). Theoretically, aluminum is a very active metal with a standard electrode potential of 1.66V (vs S.H.E). In aqueous media, aluminum is thermodynamically stable over the PH range 4-9, and relatively unstable in highly acidic and alkaline environments. The high incidence of pitting in aluminum alloys is thus, not unconnected with increased conductivity (pore migration) through the  $\text{Al}_2\text{O}_3$  or  $\text{Al}(\text{OH})_3$  film which, ironically, is markedly dependent upon alloying concentration (11). It was observed that the corrosion rate of aluminum alloys progressively increased with increasing alloying concentration as well as period of immersion. The characteristics weight loss versus time curves followed a typically linear response except for the Al-5%Cu and Al-5%Si specimens whose behavior markedly departed from linearity, a deviation attributed to serious segregation effects. Apparently, a second phase constituent ( $\text{CuAl}_2$ , or Si) was preferentially located at the grain boundaries, the effect of which is less pronounced of the Al-5%Si alloy owing to the relative predominance of the eutectic silicon phase. It is worth emphasizing that for said Al-5%Cu and Al-5% alloys, the maximum solid solubilities of copper and silicon in aluminum are





materials selection and strict compositional control (alloy tailoring) to emphasize optimum composite properties (14-17)

### CONCLUSION

1. The corrosion resistance of a series of aluminum alloys comprising binary Al-Cu, Al-Si, Al-Mg, Al-Zn and ternary Al-Si-Cu alloy specimens has been investigated in  $60\text{g l}^{-1}$  sodium hydroxide (NaOH) solution, the characteristics weight loss versus time responses of which were effectively correlated with spectrographic, microstructural and topographical details.
2. It was duly established that whenever the alloying element existed purely in solid solution, dissolution of the alloy proceeded rather uniformly. Above solid solubility concentrations, the excess solute impurities were often precipitated as intermetallic compounds ( $\text{CuAl}_2$ ,  $\text{Mg}_5\text{Al}_8$ , Si, etc) and were selectively attacked by the corrosive medium since they tended to exhibit different

solution potentials from the aluminum (solid-solution) matrix.

3. Evidently, the very dilute alloys suffered uniform or general corrosion, a behavior essentially characterized by a linear weight loss versus time response while the more concentrated alloys suffered severe intergranular attack, the characteristic weight loss versus time response of which markedly departed from linearity and was anomalous.
4. This deviation was attributed to severe segregation effects (alloy heterogeneity) owing to the exclusive presence of second phase constituents at the grain boundaries and hence the transition from uniform to intergranular corrosion. The situation was, however, reversed at higher alloying concentrations owing to a change in precipitation effects. A semblance of alloy homogeneity (decline in segregation) was seemingly restored with substantial presence of the eutectic phase constituent in addition to the equilibrium grain-boundary precipitate and hence the possible reversion from intergranular to general corrosion.
5. The wider spread or increased delocalization of intermetallic constituents within the crystalline matrix apparently minimized or evened-out the interfacial potential-cum-concentration gradients, a phenomenon equally enhanced by progressive grain refinement which is a direct consequence of increasing alloying concentration.

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