Corrosion Behaviour of Al-based Metal Matrix Composites - A Review

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Abstract— Metal matrix composites have entered in industry with extreme interest from the automobile and aerospace sectors due to their superior mechanical properties and applications. From several studies it is concluded that there are different types of MMCs available. During last few years, researchers have uncovered many secrets relating to these advanced materials. This paper briefly reviews the turning operations carried on MMCs using uncoated carbide tool and coated tool. Due to the abrasive nature of the reinforcements, MMC is considered as a difficult to cut material. Turning test were performed at various speed, feed rate, depth of cut and percentage of alumina inclusion in MMCs. From most of the studies it has been concluded that poor machinability is due to abrasive nature of the reinforcements and hardness of MMC material. It is also concluded that with increase in the hardness and volume fraction of particle machinability decreases.

Keywords- MMC; turning, chip formation; tool wear; surface roughness; metal removal rate; cutting forces.

I. INTRODUCTION

Aluminium alloys have been used successfully in a variety of applications for many years, often in aggressive environments. They obtain their corrosion resistance from a stable oxide surface film which forms when the bare metal surface is exposed to an oxidizing environment. Aluminium surfaces suffer from various types of corrosion in many urban, rural and industrial situations as shown in figure 1.



Figure 1. Corrosion of Al products.

If in metal matrix composites (MMCs) the protective film is affected by the incorporation of a reinforcing phase, the general corrosion resistance may be compromised. Where MMCs are considered as a structural component for use in an aggressive environment, the susceptibility to stress corrosion and corrosion fatigue may cause concern as the resistance to these modes of failure has yet to be characterized. This paper provides a b review of the mechanisms of corrosion characteristic of Al-based metal matrix composites.

II. CORROSION CHARACTERISTICS OF AL-BASED MATRIX ALLOYS

when a metal is placed in an aqueous environment it can behave in three ways: corrode, show immunity or passive. If corrosion was occurred metal dissolution would result. Under conditions of immunity the potential of the metal is lowered sufficiently to prevent metal dissolution. Under passivation the potential of the metal is raised as the metal becomes covered with a protective film which removes it from direct contact with the environment.

The usefulness of this graphical representation of thermodynamic data for corrosion studies was discussed by Pourbaix who showed three possible states of a metallic material:

Immunity region: In the conditions of potential and pH of that region a metal is considered to be totally immune from corrosion attack and safe to use.

Passive region: In such region a metal tends to become coated with an oxide or hydroxide that may form on the metal either as a compact and adherent film practically preventing all direct contact between the metal itself and the environment, or as a porous deposit which only partially prevents contact between the metal and the environment.

Corrosion region: Thermodynamic calculations indicate that, in such region of an E-pH diagram,



a metal is stable as an ionic (soluble) product and therefore susceptible to corrosion attack. Experience is required to find out the extent and form of the corrosion attack that may occur in the corrosion region(s) of a Pourbaix diagram (figure 2).



Figure 2. E-pH corrosion diagram of aluminum at 25°C [p26].

Environmental factors such as temperature and solution turbulence can have a profound effect on the corrosion resistance of aluminium. Factors dictated by the aluminium alloy itself include the surface-to-volume ratio, heat capacity of the surface, surface finish, alloying additions and the presence of surface defects. The composition, volume, location and potential of microconstituents relative to aluminium solid solutions also have a direct influence on the amount, form and distribution of corrosion attack.

Wrought alloys in the 3XXX (Al-Mn), 5XXX (Al-Mg) and 6XXX (Al-Mg-Si) series are resistant to corrosion. In these alloys, the alloying elements tend to form second phases. In the 3XXX series manganese forms $Al_6(Mn.Fe)$ and $Al_{12}(Mn.Fe)_3Si$ precipitates. In the 5XXX series magnesium forms Al_8Mg_5 precipitates which are evenly dispersed throughout the matrix. In the 6XXX series magnesium and silicon together form Mg₂Si phase which provides the basis for precipitation hardening.

III. FORMS OF CORROSION

Corrosion is the chemical reaction of a metal, in this case aluminum, with its environment. Different forms of corrosion are as follows:

• Pitting corrosion

- Intergranular corrosion
- Exfoliation
- Stress corrosion
- Corrosion fatigue
- Corrosion protection

A. Pitting Corrosion

Pitting Corrosion is the localized corrosion of a metal surface confined to a point or small area, that takes the form of cavities as shown in figure 3. Pitting of aluminum alloys occurs if the electrolyte contains a low level of chloride anions, and if the alloy is at a potential above the "pitting potential." Pitting initiates at defects on the surface of the aluminum, such as at second phase particles or on grain boundaries.



Figure 3. Pit corrosion.

Mechanism of pitting corrosion includes dissolution of the passivating film and gradual acidification of the electrolyte caused by its insufficient aeration (Oxygen penetration). Stages of pitting corrosion are as follows:

1. Pit initiation. An initial pit may form on the surface covered by a passive oxide film as a result of the following:

- Mechanical damage of the passive film caused by scratches. Anodic reaction starts on the metal surface exposed to the electrolyte. The passivated surrounding surface act as the cathode.
- Particles of a second phase (non-metallic inclusions, intermetallic inclusions, metallic particles, Micro-segregation) emerging on the metal surface. These particles precipitating along the grain boundaries may function as local anodes causing localized galvanic corrosion and formation of initial pits.
- Localized stresses in form of dislocations emerging on the surface may become anodes and initiate pits.



• Non-homogeneous environment may dissolve the passive film at certain locations where initial pits form.

2. Pit growth. In presence of chloride ions pits are growing by autocatalytic mechanism. Pitting corrosion of a stainless steel is illustrated in the figure.

The pitting density is defined as the number of pit units formed per cm^2 of test piece surface. The pitting corrosion of commercial grade aluminium exposed to ethanol is shown in figure 4.



Figure 4. Pitting corrosion of commercial grade aluminium exposed to ethanol.

B. Intergranular Corrosion

Aluminium alloys are subject to intergranular corrosion where precipitation or formation of more anodic or cathodic phases, with respect to the matrix, occurs at the grain boundaries. Depending on the alloy system, this results in selective corrosion at the grain boundaries or any precipitate- free zones (PFZs) adjacent to them, with the bulk matrix remaining relatively unaffected. Intergranular corrosion is caused by potential differences between the grain-boundary region and the adjacent grain bodies.

In 2XXX Al alloys Al₂Cu, Al₂CuMg precipitations may occur at the grain boundaries. In the case of AA2024-T3 alloy, second-phase particles function in initiation of intergranular corrosion. Copper content is low in the vicinity of secondphase particles, making these regions vulnerable to corrosion. As soon as dissolution is accelerated in such regions, damage nucleated at a grain boundary in contact with the vicinity of the second-phase particle. Copper-depleted region is present along grain boundaries. Figure 5 shows SEM image of clustered intermetallic particles. EDX analysis was carried out at two positions in the cluster, as shown in Figures 5 (b)-(c). Interestingly, the spectrum from point 1 exhibits a higher Mg peak than that from point 2 with both spectra showing similar intensity at Al and Cu. Thus, point 1 is rich in aluminium, copper and magnesium, indicating S-phase (Al₂CuMg); point 2 is only rich in aluminium and copper, indicating θ -phase (Al₂Cu). This suggests variation in composition at different parts of the cluster.



Figure 5. (a) Scanning electron micrograph of a cluster of S-phase and θ -phase particles; and (b)-(c) EDX spectra of the cluster.



Figure 6. 5056 as-cast ingot showing (Fe, Cr)₃SiAl₁₂ (gray), Mg₂Si (dark), and Mg₂Al₃ (mottled, outlined) in dendrite interstices.

When magnesium content exceeds about 3.5%, Mg₂Al₃, or metastable Mg₂Al₃ may precipitate in grain boundaries of 5XXX Al alloys as shown in figure 6. In 6XXX Al alloys Mg₂Si constituent forms at the grain boundaries. Figure 7(a) depicts a large grain boundary phase (~ 2 µm length) in a sample that was air-cooled after the solution heat



treatment and subsequently aged for 23 h at 160 °C. Extensive grain boundary precipitate nucleation and growth then already occur during the slow cooling process. The structure at all parts of the particle was found to be hexagonal with a = 10.4 Å and c = 4.1 Å. The chemical other hand, composition, on the varies significantly, as can be seen from figure 7 (b). Here, the relative Mg-, Si- and Cu-concentrations are plotted for different equidistant locations on the particle, which are given in figure 7(a). Especially the relative Mg- and Si-concentration can be seen to vary significantly along the grain boundary phase.



Figure 7. (a) TEM-micrograph of grain boundary phase in air-cooled AA6061; (b) Relative concentrations of solute elements at different spots on the grain boundary phase.

 Mg_2Al_3 constituent and $CuAl_2$ constituent form in Cu-free 7XXX and Cu-bearing 7XXX Al alloys. For 7XXX Al alloy, the scan was carried out across a selected GBP with a step of 1 nm along the path, marked with a red line in figure 8a. The

curves shown in figure 8b demonstrate the concentration profiles of solutes obtained from the scan. The intensity ratio (Ci/CAl) reveals the relative content of each solute in GBs and PFZs. Zn concentration in GBPs is the most intense, with a highest intensity ratio CZn/CAl of 0.62 being detected. Meanwhile, the depletion of Zn in PFZ is most evident as the lowest intensity ratio (CZn/CAl = 0.02) observed. The CZn/CAl detected within grains is 0.03–0.04, much lower than that in GBPs, but notably higher than that in PFZs. A similar behavior of enrichment and depletion is observed for Mg and Cu, but the intensities vary one from each other.



Figure 8. The location of the EDS line-scan, as indicated in red line in (a), and (b) the obtained concentration profile of solute.

C. Exfoliation

Exfoliation is a special form of intergranular corrosion that proceeds laterally from the sites of initiation along planes parallel to the surface, generally at grain boundaries, forming corrosion products that force metal away from the body of the material, giving rise to a layered appearance. Exfoliation corrosion occurs predominantly in Alalloys that have marked directional structures.

Exfoliation is characteristic for the 2XXX (Al-Cu), 5XXX (Al-Mg), and 7XXX (Al-Zn-Mg) series alloys

which have grain boundary precipitation or depleted grain boundary regions. For 7178 Al alloy, EDS line profiling was performed across grain boundaries at locations that include precipitates and locations away from precipitates to analyze the PFZ. The concentration profiles in the form of concentration ratios for various elements relative to Al are shown in figure 9. Al– Zn–Mg–Cu–Cr precipitates are shown.



Figure 9. TEM micrographs of grain-boundary in AA7178 showing Nano EDS line profiling across the GB precipitate.

D. Stress Corrosion Cracking

Stress corrosion cracking (SCC) is the growth of crack formation in a corrosive environment. It can lead to unexpected sudden failure of normally ductile metal alloys subjected to a tensile stress, especially at elevated temperature. SCC requires three simultaneous conditions, first a susceptible alloy, second a humid or water environment, and third a tensile stress which will open the crack and enable crack propagation. SCC can occur in two modes, intergranular stress corrosion cracking (IGSCC) which is the more common form, or transgranular SCC (TGSCC). In IGSCC, the crack follows the grain boundaries. In transgranular stress corrosion cracking (TGSCC), the cracks cut through the grains and are oblivious to the grain boundaries.

Crack growth: The subcritical nature of propagation may be attributed to the chemical energy released as the crack propagates. That is,

elastic energy released + chemical energy =
surface energy + deformation energy

The crack initiates at K_{Iscc} and thereafter propagates at a rate governed by the slowest process, which most of the time is the rate at which corrosive ions can diffuse to the crack tip. As the crack advances so *K* rises (because crack length appears in the calculation of stress intensity). Finally, it reaches K_{Ic} , whereupon fast fracture ensues and the component fails. One of the practical difficulties with SCC is its unexpected nature.

Figure 10 shows the regions of different crack propagation under stress corrosion cracking. In region I, crack propagation is dominated by chemical attack of strained bonds in the crack. In region II, propagation is controlled by diffusion of chemical into the crack. In region III, the stress intensity reaches its critical value and propagates independent of its environment.





The poor resistance to stress corrosion cracking is exhibited by Al alloys such as 2XXX, 7XXX and 8XXX Al alloys. In Al alloys, SCC is characteristically intergranular and requires an anodic phase at the grain boundaries for crack propagation to occur. A cleavage-like fracture surface with the presence of striations is prevailed in 2650 T6 Al alloy as shown in figure 11.



Figure 11. Fracture surfaces produced during fatigue crack growth in the 2650 T6 alloy.



Figure 11. SEM micrograph of fracture surface within elongated grain structure of AA6005A-T6 CGR sample exposed to a solution of 3.5% NaCl at pH = 1.5. Micrograph was taken near the tip of the stress corrosion crack at the midplane of the sample. Evidence of both brittle intergranular fracture and ductile fracture were observed in regions of SCC.

Fractures surfaces of AA6005A-T6 CT specimens showed evidence of both brittle intergranular fracture and ductile fracture in regions of SCC (figure 11). The mix of ductile and brittle fracture along the fracture surface suggests that SCC is occurring along small "channels" in the material, and the remainder of the material between these channels is failing by overload. The mix of brittle and ductile fracture along the fracture surface suggests that SCC growth is discontinuous along the crack front. In this case, SCC would occur only along discrete corrosion paths (regions of intergranular fracture), and regions between the intergranular SCC are fractured in a ductile manner when the fracture criterion is satisfied for the remaining ligament.

E. Corrosion Fatigue

Corrosion fatigue can occur when an aluminum structure is repeatedly stressed at low stress levels in a corrosive environment. A fatigue crack can initiate and propagate under the influence of the crack-opening stress and the environment. Similar striations may sometimes be found on corrosion fatigued samples, but often the subsequent crevice corrosion in the narrow fatigue crack dissolves them.

Fatigue strengths of aluminum alloys are lower in such corrosive environments as seawater and other salt solutions than in air, especially when evaluated by low-stress long-duration tests. Like SCC of aluminum alloys, corrosion fatigue requires the presence of water. In contrast to SCC, however, corrosion fatigue is not appreciably affected by test direction, because the fracture that results from this type of attack is predominantly transgranular.

IV. Atmospheric Corrosion

Atmospheric corrosion is defined as the corrosion or degradation of material exposed to the air and its pollutants rather than immersed in a liquid. This has been identified as one of the oldest forms of corrosion and has been reported to account for more failures in terms of cost and tonnage than any other single environment. Many authors classify atmospheric corrosion under categories of dry, damp, and wet, thus emphasizing the different mechanisms of attack under increasing humidity or moisture.

Corrosivity of the atmosphere to metals varies greatly from one geographic location to another, depending on such weather factors as wind direction, precipitation and temperature changes, amount and type of urban and industrial pollutants, and proximity to natural bodies of water. Service life may also be affected by the design of the structure if weather conditions cause repeated moisture condensation in unsealed crevices or in channels with no provision for drainage.

V. Uniform Corrosion

General corrosion, or uniform corrosion, occurs in the solutions where pH is either very high or very low, or at high potentials in electrolytes with high chloride concentrations. In acidic (low pH) or alkaline (high pH) solutions, the aluminum oxide is unstable and thus non-protective.

VI. Galvanic Corrosion

Economically, galvanic corrosion creates the largest number of corrosion problems for aluminum alloys. Galvanic corrosion, also known as dissimilar metal corrosion, occurs when aluminum is electrically connected to a more noble metal, and both are in contact with the same electrolyte.

VII. Crevice Corrosion

Crevice corrosion requires the presence of a crevice, a salt water environment, oxygen (Fig. 1). The crevice can result from the overlap of two parts, or gap between a bolt and a structure. When aluminum is wetted with the saltwater and water enters the crevice, little happens initially. Over time, inside the crevice oxygen is consumed due to the dissolution and precipitation of aluminum.

H₂O + NaCl



Figure 1: Crevice corrosion can occur in a saltwater environment if the crevice becomes deaerated, and the oxygen reduction reaction occurs outside of the crevice mouth. Under these conditions, the crevice becomes more acidic, and corrosion occurs at an increasing rate.

VIII. Deposition Corrosion

In designing aluminum and aluminum alloys for satisfactory corrosion resistance, it is important to keep in mind that ions of several metals have reduction potentials that are more cathodic than the solution potential of aluminum and therefore can be reduced to metallic form by aluminum. For each chemical equivalent of so-called heavymetal ions reduced, a chemical equivalent of aluminum is oxidized. Reduction of only a small amount of these ions can lead to severe localized corrosion of aluminum, because the metal reduced from them plates onto the aluminum and sets up galvanic cells.

The more important heavy metals are copper, lead, mercury, nickel, and tin. The effects of these metals on aluminum are of greatest concern in acidic solutions; in alkaline solutions, they have much lower solubilities and therefore much less severe effects.

IX. Erosion-Corrosion

Erosion-corrosion of aluminum occurs in high velocity water and is similar to jet-impingement corrosion. Erosion-corrosion of aluminum is very slow in pure water, but is accelerated at pH > 9, especially with high carbonate and high silica content of the water.

Aluminum is very stable is neutral water; however it will corrode in either acidic or alkaline waters. To prevent erosion-corrosion, one may change the water chemistry or reduce the velocity of the water, or both. For the water chemistry, the pH must be below 9, and the carbonate and the silica levels must be reduced.

X. Filiform Corrosion

Filiform corrosion (also known as wormtrack corrosion) is a cosmetic problem for painted aluminum. Pinholes or defects in the paint from scratches or stone bruises can be the initiation site where corrosion begins with salt water pitting. Filiform corrosion requires chlorides for initiation and both high humidity and chlorides for the propagation of the track.

The propagation depends on where and how the alloy is used. The filament must be initiated by chlorides, and then it proceeds by a mechanism similar to crevice corrosion. The head is acidic, high in chlorides, and deaerated and is the anodic site. Oxygen and water vapor diffuse through the filiform tail, and drive the cathodic reaction. Filiform corrosion can be prevented by sealing defects with paint or wax, and keeping the relative humidity low.

XI. Microbiological Induced Corrosion

Microbiological Induced Corrosion (MIC) applies to a corrosive situation which is caused or aggravated by the biological organisms. A classic case of MIC is the growth of fungus at the water/fuel interface in aluminum aircraft fuel tanks. The fungus consumes the high octane fuel, and excretes an acid which attacks and pits the aluminum fuel tank and causes leaking. The solution for this problem is to control the fuel quality and prevent water from entering or

IV. CONCLUSION

Metal matrix composites have entered in industry with extreme interest from the automobile and sectors due to their aerospace superior mechanical properties and applications. Many researchers have been worked for the machining of metal matrix composites. In this paper a brief overview is provided related research, focusing on turning mechanisms. The PCD cutting tool has been found better for turning of MMCs than PCBN, SCD and carbide based cutting tool materials. The coated cutting tool performs better as compared to the uncoated cutting tools but leads in high wears after rupture of coating. The performances of multi-layer coated tool were found near to PCD turning tool. Surface Roughness increase with the process variables except the speed, speed made adverse effect on surface roughness. MRR increases with the process parameters except the concentration of reinforced particles due the presence of hard particles. Even though, ceramic for the conventional alloys the deformation behavior and the friction law governing chip-tool interface friction during machining has not yet been well defined. In addition, the effect of reinforcement particles on the deformation mechanisms during machining of MMCs is also not fully understood. There is still research required to clarify these interactions before we can go deep into the new possible concepts and further developments regarding MMCs and machining.

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