ABSTRACT
The atmospheric corrosion of zinc, magnesium and MgAl alloys in humid air has been investigated in the laboratory. The corrosion effects of CO₂, soluble salts, SO₂ and temperature have been addressed. Four weeks exposures were performed under well-controlled conditions, monitoring corrosion rates and studying the formation of corrosion products. The corroded samples were investigated by X-ray diffraction, optical-, electron- and atomic force microscopy and ion chromatography. The main purpose is to help understand the corrosion processes.
NaCl is corrosive towards all investigated materials. In the absence of CO₂, the NaCl induced corrosion is characterised by severe pitting, with well-separated anodic and cathodic areas. The anodic environment is acidic due to hydrolysis of MCl(aq). In contrast, the cathodic environment has a high pH, due to NaOH(aq). On zinc, the high pH forms a thick semi-conducting ZnO film at the cathodes. On MgAl alloys the passivating alumina-containing film tends to dissolve in the alkaline environment. This depletes the film in aluminium and corrosion can proceed. However, increased aluminium content increases the ability to withstand NaCl induced corrosion. Generally, the corrosion rate of zinc and magnesium alloys increases with temperature in the absence of CO₂.
Carbon dioxide is shown to depress the NaCl-induced corrosion of zinc and magnesium alloys. This is explained by the protolysis of carbonic acid in the surface electrolyte, neutralizing high pH values at the cathodes and resulting in the formation of a hydroxy-carbonate film that interferes with the electrochemical reactions. On zinc, the increased rate of formation of the carbonate film with temperature compensated for the faster electrochemical reactions, resulting in a temperature independent corrosion rate in the presence of CO₂. On magnesium, the effect of CO₂ is also evident in the absence of salt. In this case, CO₂ inhibits a type of pitting corrosion induced by noble inclusions in the metal matrix by forming a carbonate film.
Comparing Na⁺, Mg²⁺, Zn²⁺ and NH₄⁺ salts, it was shown that sodium salts are by far the most corrosive towards zinc. This is due to the inability of sodium to form insoluble precipitates. Therefore sodium can balance the charge of the hydroxide in the surface electrolyte, supporting high pH. In contrast, the divalent cations form precipitates in the cathodic areas that block the cathodic sites. The corrosion of zinc is shown to be directly correlated to the amount of sodium ion in the surface electrolyte and does not depend on whether the anion is chloride or sulphate.
In contrast, it was shown that the corrosivity of NaNO₃ on zinc was only a third of that of NaCl and Na₂SO₄. This is explained by the oxidising action of nitrate, and of its product nitrite. The anodic dissolution is inhibited by the pH increase caused by the oxidation of the nitrogenous species. Further, the presence of NaNO₃ slightly inhibits the atmospheric corrosion of zinc induced by NaCl or Na₂SO₄.
The deposition of SO₂ on magnesium and its alloys is very fast and only limited by transport in the gas phase. Exposure to SO₂ results in corrosion, with magnesium sulphite being the dominant corrosion product. However, the rate of the NaCl-induced corrosion is decreased by low concentrations of SO₂.
Keywords: Atmospheric corrosion, zinc, magnesium, CO₂, temperature, salt deposits, NaCl, SO₂