

The Reaction Between Aluminium Metal and Aqueous Solutions of the Nitrite Ion

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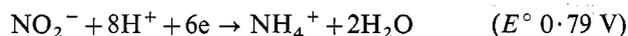
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Abstract

The reaction between aluminium metal and a 0.1 wt % solution of sodium nitrite at room temperature is described. Initially the reaction is slow, but after an induction period the aluminium corrodes catastrophically. The products of the reaction were identified as ammonia, hydrogen and bayerite. A possible mechanism of the reaction is suggested.

Many commercial inhibitor solutions for automobile cooling systems contain sodium nitrite at a concentration of about 0.1 wt %. The nitrite ion is, of course, very effective in preventing the corrosion of iron.¹ However, it is not uncommon for there to be aluminium or aluminium alloy components such as engine heads or water pumps as well as iron components in the cooling system of a car. Since the standard electrode potentials² for the reactions



are separated by more than 2 V, it is clearly possible for aluminium to react with the nitrite ion. We have accordingly investigated the reaction between aluminium and solutions containing 0.1 wt % of sodium nitrite.

The reactivity of a wide variety of aluminium samples was examined. These ranged from turnings drilled from a Koch-Light high-purity block (99.999% pure) to turnings from a casting alloy (93.6% pure), and included samples taken from aluminium components off two commercial vehicles of different make. All reacted in a similar way although the rate of reaction varied between samples. Initially, the rate of reaction was very slow, but after an induction period whose duration depended in part on the sample of metal, and the ratio of the area of aluminium surface to the volume of nitrite solution, the reaction rate accelerated rapidly causing considerable corrosion of the metal.

¹ Munro, L. A., 'Chemistry in Engineering' (Prentice-Hall: New York 1964).

² Pourbaix, M., 'Atlas of Electrochemical Equilibria in Aqueous Solution' (Pergamon Press: London 1966).

For example, in one experiment at room temperature with 20 g of technical grade aluminium turnings (Ajax Chemicals, 98.5% pure) in 2000 cm³ of deionized water, there was little to be seen in the first 50 h of contact. However, the turnings then blackened considerably, and small bubbles of gas began to appear on the metal surface. The smell of ammonia became apparent. The next ten hours were the period of maximum activity. The aluminium corroded catastrophically with rapid evolution of a gas. The gas was identified as hydrogen by demonstrating that it diffused much more rapidly than air through a porous pot and that it popped when ignited. Just prior to, and during, the period of rapid reaction, a white solid was precipitated on the surface of the metal and the containing vessel. X-ray diffraction analysis of the white solid showed it to be bayerite or β -Al(OH)₃. Following the period of rapid reaction, the rate quickly decayed and reaction had essentially ceased after 100 h although unchanged metal still remained.

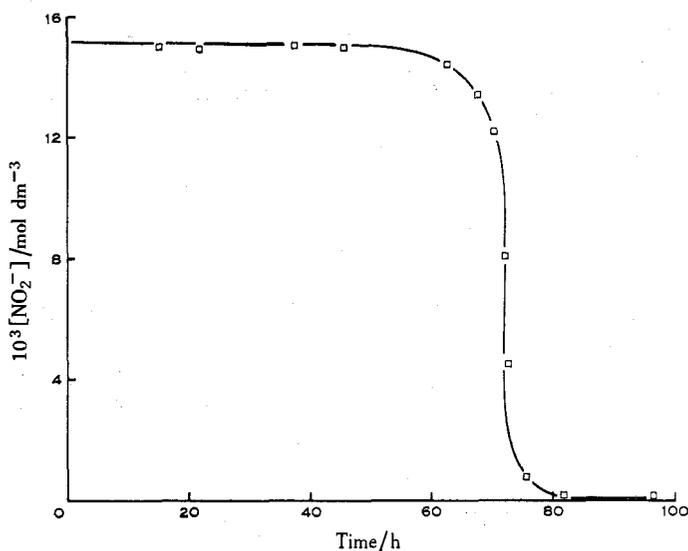


Fig. 1. Loss of nitrite ion from a 0.1 wt % solution in contact with aluminium turnings.

The same reaction was followed quantitatively by analysing the solution at regular intervals for nitrite content. The results are shown in Fig. 1. It can be seen that the long induction period is followed by a rapid reaction in which the nitrite ion is lost from solution. The presence of ammonia in the solution was confirmed by a colorimetric method based on the formation of a blue phenolamine. It was also noted that the pH had risen from an initial value of 7 to 11.

The reaction appears to go in three overlapping stages. In the first, nitrite ion is reduced to ammonia; this causes some disruption in the air-formed protective oxide film. In the second, the exposed aluminium metal reacts directly with water. A crude estimate of the amount of hydrogen given off shows that it is greatly in excess of the amount of nitrite in solution. This implies that much of the corrosion is due to the aluminium-water reaction. Finally, aluminium hydroxide, formed as one of the products of corrosion, blankets the metal surface, and causes the reaction to cease.

The lengthy induction period and the slow rate of reaction during this time may well be the reason for the statements in the literature that aluminium is inert with

respect to nitrite solutions³ or that nitrite is a useful inhibitor for aluminium.⁴ However, from our experiments it is clear that nitrite should not be used by itself as an inhibitor in automobile cooling systems with aluminium components, since a relatively sudden failure of an aluminium component could result.

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³ 'Metals Handbook' Vol. 1 (Am. Soc. Metals: Washington 1961).

⁴ Salem, T. M., Horvath, J., and Sidky, P. S., *Corros. Sci.*, 1978, **18**, 363.