



Microcalorimetric Methods for Corrosion Rate Measurement

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Field of application:

Corrosion Studies

Instrument:

BoMic 2277 4 Channel Isothermal
Microcalorimeter System

1. BACKGROUND

The development of microcalorimetric techniques at AB Bofors started in 1980, primarily for stability testing of propellants and high explosives and for compability testing of various explosive/material combinations. In 1984 a special microcalorimetric gas flow technique was developed, which made it possible to carry out experiments under welldefined atmospheric conditions. This technique immediately opened new application fields for microcalorimetry, e.g. characterization of moisture-sensitive explosives, corrosion processes and material ageing.

We use the term compability to describe how well two materials function together. We may, for instance investigate how an adhesive or a plastic component affects the properties of an explosive. Using the microcalorimeter we can measure the heat generated by the components individually and in combination and thereby determine to what extent they have reacted with one another. If the components have reacted they are generally unsuitable for use in a product design - they are then classified as incompatible designwise.

Compatibility investigations have been carried out for many years, but to detect slow reactions between components it was always necessary to raise temperature considerably. The advantage of microcalorimetry is its sensitivity. It makes it possible to work at rather low temperatures and still measure reactions and physical processes that may occur.

If one part in a thousand of a particular substance reacts in one week we can normally detect it directly in the microcalorimeter. Previously, we were obliged to work at elevated temperatures (100 °C), but microcalorimetry's sensitivity enables us to work at 50-70 °C.

Explosive substances and metals are used together in designs. This has led us to investigate how metal powders, primarily Mg, react in various environments. A special flow cell has been designed to study reactions in continuous gas streams of various composition. Air with an arbitrary humidity is normally used, but we can study reactions with gases of virtually any composition.

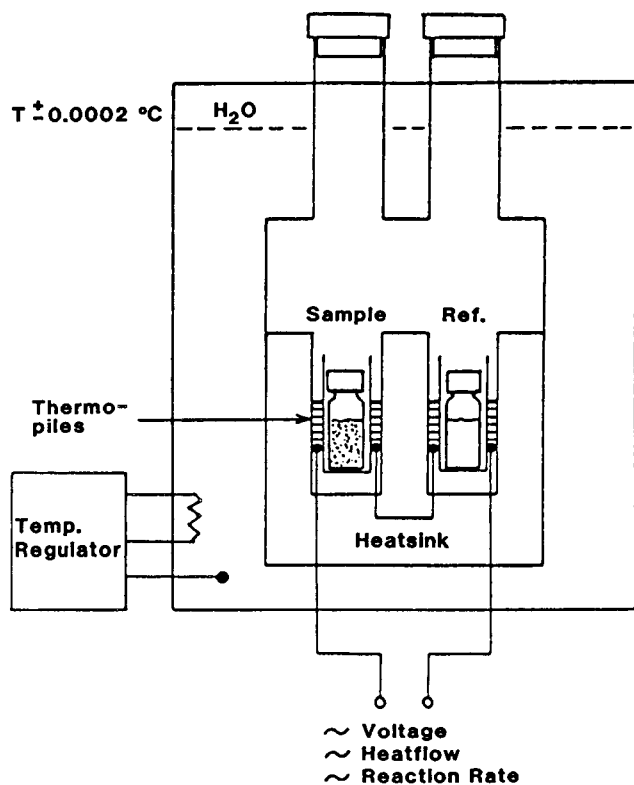
This study of Mg powder aroused a general interest in corrosion studies. The results indicated that the microcalorimetric technique could be used to study the corrosion characteristics of all the metals frequently used in product designs. Metals such as steel and aluminium have been investigated in the form of rods, foils and sheets.

Table showing corrosion studies already investigated.

Metal	Mg	Al	Ordinary Fe	Stainless Fe
Air at various %RH	•	•	•	
Distilled water	•	•	•	
Seawater	•	•	•	
65% Nitric acid				•

2. EQUIPMENT

The equipment used for these investigations was a BoMic 2277 4 channel isothermal microcalorimeter. Experiments were conducted within the range 10-90 °C. A detailed description of the equipment can be found in Reference 1.



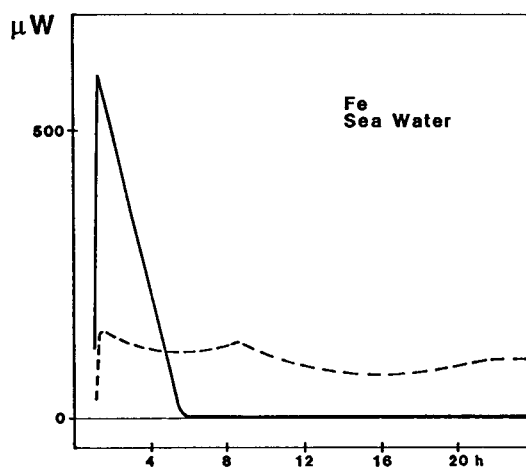
The instrument is based on a large water thermostat, maintained at a temperature, which is constant to within 0.0002°C. The system is equipped with 4 independent calorimetric units of the twin type (sample and reference). The difference in heat flows from the sample and reference vessels is measured using a large number of thermopiles. The heat flow to (endothermic) and from (exothermic) can be monitored continuously.

The accuracy of measurement is better than 1 μW (microwatt).

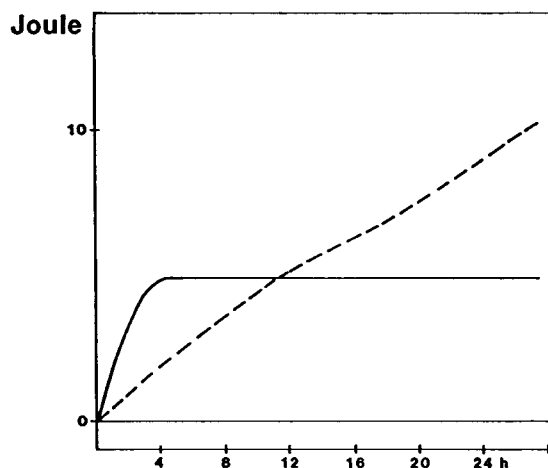
The microcalorimeter can continuously measure the heat flow and thereby the changes in energy content in the form of reaction heat, absorption heat, condensation heat etc.

Samples are weighed out in test cells and brought to the desired temperature before being introduced into the calorimeter. It takes a few hours before sample has stabilized in the calorimeter. The static sample vessels are normally expendable 3 ml glass ampoules. The gas flow ampoule is a 5.5 ml steel vessel manufactured from stainless steel.

The instrument is connected to a PC computer for data recording and for display and plotting. We obtain graphs with heat flow in μW plotted vs time.



These graphs can be converted to energy graphs in which released or absorbed energy is plotted vs time.



3. DETECTABLE CORROSION RATES

What quantities of heat are involved in metal corrosion?

In the case of transition of metallic iron to its oxides the enthalpies concerned are of the order of 400 kJ/mol.

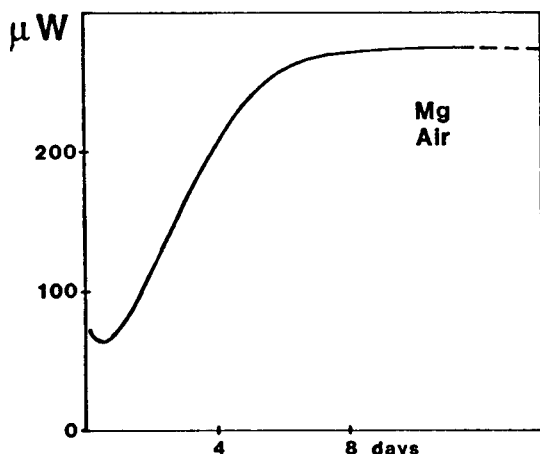
In corrosion tables we find a limit of 0.1 mm/year. With a slower corrosion rate a metal is generally considered corrosion-resistant (Reference 3). If we recalculate this corrosion rate into the units used in microcalorimetry, μW (microwatts) we find that a corrosion rate of 0.1 mm/year corresponds to a constant heat flow of approx. 20 μW per cm^2 of the samples's surface area.

The calorimeter is sensitive to heat flows of less than 1 μW and will allow us to use samples in the range 3 to 5 g. Samples in this size range give surface areas of several cm^2 . This enables us to measure the corrosion rates on materials which are normally considered to be fairly corrosion resistant.

4. TEST RESULTS

4.1 Magnesium powder. Flow cell. Air at constant humidity.

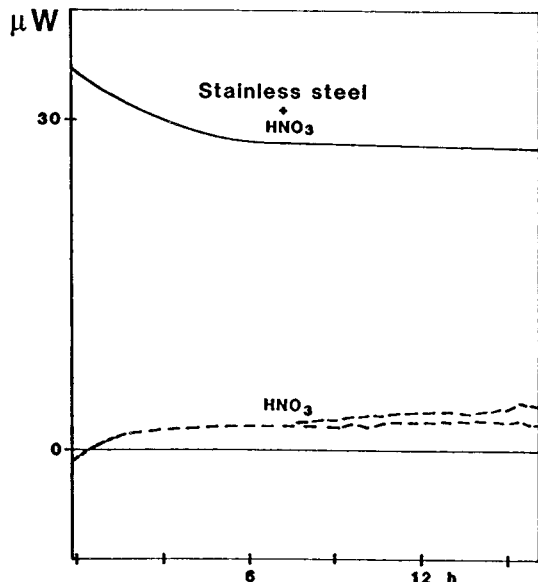
The graph shows the heat flow of a Mg powder (surface area 500 cm^2) at 70°C and 48 %RH. The measurement is carried out in the flow cell previously mentioned (Reference 2).



The results indicate that the Mg oxides/hydroxides generated increase the corrosion rate in humid air.

4.2 Stainless steel in 65% Nitric acid. Sealed ampoules.

Stainless steel rods, with a surface area of 24 cm^2 , were placed in a glass ampoule. The vessel was then filled with 65% nitric acid and sealed. Microcalorimetric measurements were then made at 50°C . Heat flows of $30 \mu\text{W}$ were observed over the first 12 hours. This experiment demonstrates the slow corrosion rate of this material in the presence of 65% nitric acid.

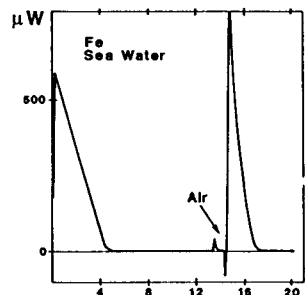


4.3 Steel welding rods in sea water. Sealed ampoules.

Samples of mild steel rods, cut from a simple welding electrode, were tested in sealed glass ampoules. Each sample had a surface area of 8 cm^2 .

The steel rods were placed in glass ampoules which were partly filled with sea water, leaving an air space, and then sealed. Samples were measured at 50°C . Initially a powerful reaction was observed. The reaction rate fell to zero after four hours.

If the sample ampoule was removed, ventilated, resealed and measured again, a second exothermic response was observed. This too returned to zero after a short period.



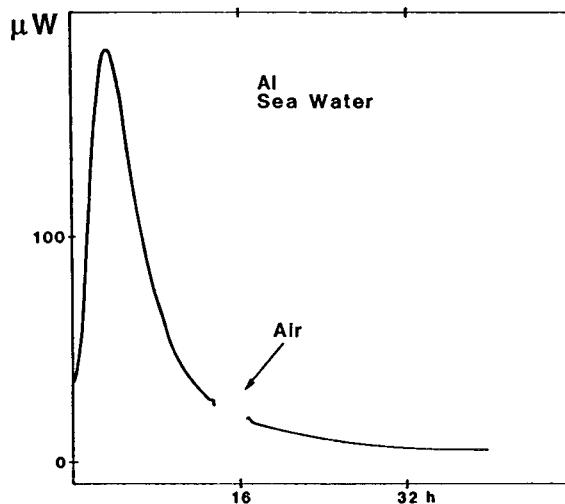
Our interpretation of the results is that the steel is oxidized by the oxygen in the air in the presence of humid air and that the air has been consumed after 4 hours.

The same sample in dry air or fully submerged in the water shows a much lower rate of corrosion.

4.4 Aluminium rods in sea water. Sealed ampoules.

Aluminium rods with a surface area of 3.5 cm^2 were placed in glass ampoules which were partly filled with sea water, leaving an air space, and then sealed. The experimental curve of heat flow measured against time is shown below. When the ampoule was removed, ventilated, resealed and measured again, the heat production was observed to continue at the same rate.

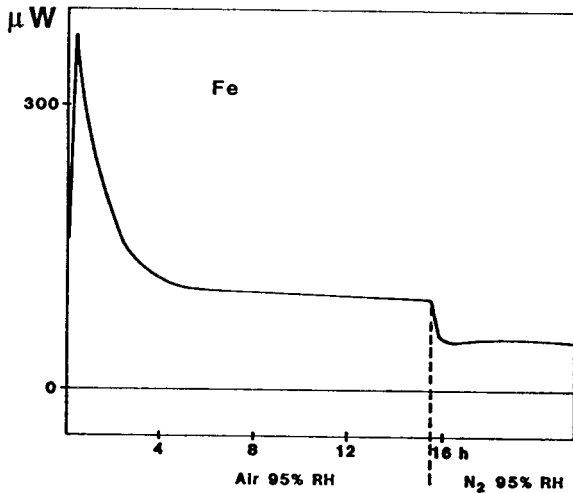
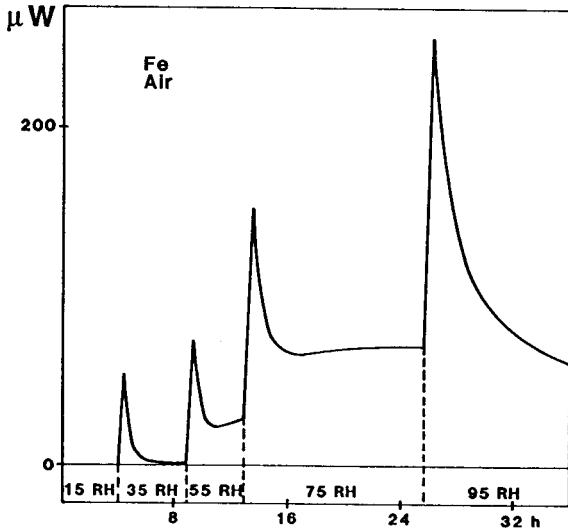
These results appear to show that Al generates an oxide in humid air which protects it from further corrosion. Oxygen was not the limiting factor in this test.



4.5 Mild steel rods at various humidities. Gas flow cell.

Mild steel welding rods, with a surface area of 13 cm^2 , were tested in a gas flow cell. A constant stream of air was flowed through the cell at a rate of 30 ml/hr. The relative humidity (RH) of the air flow was increased, in series of steps, over the range 15% to 95% RH.

During blank experiments, a pulse of heat was observed at each change in RH. This heat was caused by the absorption of moisture on the inner surface of the gas flow cell. After a short period this heat production always fell away and the calorimetric signal returned to a steady zero.



When a reacting sample was present in the gas flow cell, a similar pulse of heat to that in the blank experiments was observed. However, the calorimetric signal did not return to zero but took up a new steady state, indicating the degree of reaction between the sample and the gas flow at that level of RH.

By changing the gas flow from air to nitrogen, when using the same RH values, a reduced level of heat production was observed.

5. DISCUSSION

These simple experiments demonstrate the potential of microcalorimetry as a direct method for the study of the corrosion of metals in a wide range of controlled environmental conditions. Light alloys are being progressively more extensively used in our product designs. Their ageing properties are now being routinely investigated by this method.

A further area of application of the technique presently under consideration is the study of the effect of surface treatments to these materials to protect them from corrosion.

6. REFERENCES

1. J. Suurkuusk, I Wadsö, *Chemical Scripta* (Sweden). 20 (1982) p 155.
2. LG Svensson, Per E Lagerkvist, Nils G Gellerstedt, *Proc. of the ADPA Symp on Compatibilities of Plastics and Other Materials with Explosives, Propellants and Pyrotechnics.* (1985) p 19.
3. *Corrosion tables for stainless steels and titanium.* Jernkontoret, Stockholm 1979.
4. LG Svensson, *Proc. of Pyroteknikdagen.* (1986) p 159.