Corrosion Behaviour of Steels Used in Boiler Plants

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Boiler corrosion is due to many enviornments such as steam, flue gases, etc; The neutral aqueous medium can cause severe pitting type of corrosion in boiler steels compared to acid and alkaline media. This paper deals with (i) the corrosion behaviour of C-Mn and Cr-Mo steels used in boiler plants in NH_4NO_3 solution at three different temperatures and (ii) stress corrosion behaviour of two different Cr-Mo steels exposed to three varied concentrations of caustic solution at room temperature for a period of 30 days by using C-ring method as the test procedure. Acceleration of stress corrosion was also attempted. The observations indicate that the corrosion rate of C-Mn steel is higher and Cr-Me steels are not prone to stress corrosion cracking under test conditions.

It is well known that corrosion in boilers is caused by various boiler atmospheres such as steam, flue gases, hydrogen and other gases like CO_2 , CO, Cl_2 SO_2 and dissolved organic and inorganic salts and high temperature. Hence a designer has to consider the above parameters during the selection of materials for boiler applications.

The available steels available for the boiler design can be classified as (i) Carbon steel, (ii) alloy steel, (iii) stainless steel and (iv) heat-resistant steels. Alloy steels used for boiler application generally contain one or more of the following elements : Molybdenum, Chromium and Silicon. Molybdenum is principally used to give higher strength, chromium is added to suppress graphitisation and to give improved oxidation resistance. Silicon is to improve resistance to high temperature oxidation further.

This paper describes an experimental work carried out to evaluate and compare general corrosion behaviour of C-Mn and Cr-Mo steels in 5% NH_4NO_3 solution at three different Cr-MO steels in caustic solution.

EXPERIMENTAL

I. GENERAL CORROSION:

Materials

Steels of the following grades,

(a) C-Mn steel (SA 515) and

(b) Cr-Mo steel (T 22, super heater tube, 2.25 Cr-1Mo)

were tested in a solution of 5% NH_4NO_3 (by weight) (Analar grade) in thermostats at room temperature (27°C), 60°C and 90°C. The chemical compositions and mechanical properties of these steels are provided in Tables 1 and 2 respectively.

TABLE 1

CHEMICAL COMPOSITION

Steel grade	%C	%Si	%Mn	%Cr	%Mo	%P	%S
SA 515 Gr. 70	0.35	0.15 to 0.35	0.9	-	-	0.035	0.04
T 11	0.15	0.50	0.3 to 0.6	1.0 to 1.5	0.44 to 0.65	0.03	0.03
T 22	0.15	0.5 to 1.0	0.3 to 0.6	1.9 to 2.6	0.87 to 1.13	0.03	0.03

TABLE 2

MECHANICAL PROPERTIES

Steel grade	Tensile strength (Kg/mm²)	Yield strength (Kg/mm²)	% Elengation
SA 515 Gr. 70	49 to 60	26.71	21
T11	42	21	30
T22	42	21	30

PECIMEN PREPARATION AND TESTING PROCEDURE

he steels obtained were in the form of plates ith more than 25 mm in thickness. These were cut o give coupons of one square inch surface area nd thickness of less than 1/8 inch.

he specimens were polished with the help of olishing papers of various grades and on the olishing wheel. They were then degreased with cetone. Before immersion into solution the pecimens were weighed and the dimensions of the oupons were recorded.

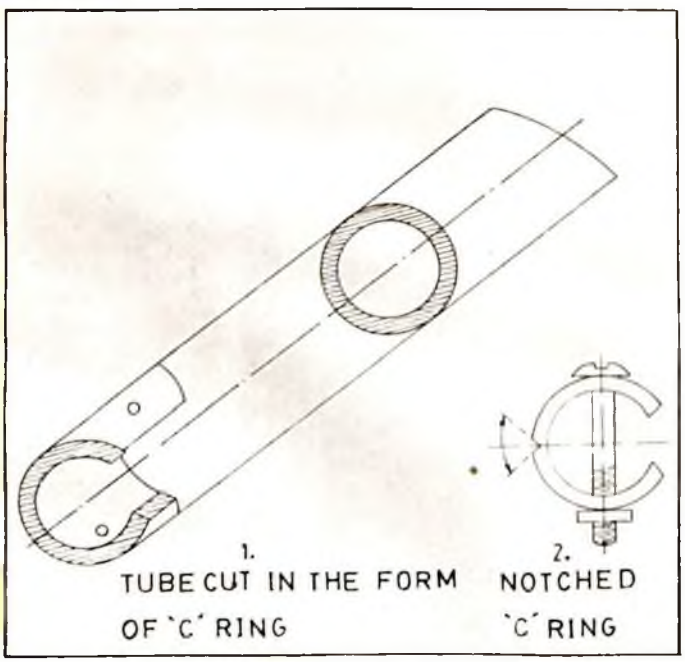
pecimens were suspended by steel wires, the wires eing insulated using araldite to avoid galvanic ffects at the junctions. A reflux condenser was sed for testing at higher temperatures to avoide he loss of solution and to keep the oncentration of the solution constant.

pecimens were removed at intervals, washed with ater and dried in an oven at 120°C for 30 minutes o remove moisture and weighed to find out the oss in weight.

I STRESS CORROSSION

pecimen Preparation and testing

he steels available were in the form of tubes T 11 and 22 grades) with an outer diameter of 45 m and 5 mm thickness. C-ring method was used as he test procedure. Tests were carried out in 15% y weight, 30% by weight and 45% by weight NaOH olutions.



ig. 1 Tube Cut in the form of "C" Ring
ig. 2 Notched "C" Ring

The thickness of the tubes were reduced by machining and the surface polished in the usual way. The tubes were then cut as shown in the Fig. 1.

The C-ring method, which is generally used is a constant strain specimen with tensile stress produced on the exterior of the ring, by tightening a bolt centered on the diameter of the ring (Figure 2). The amount of compression required on the C-ring to produce elastic straining only and the degree of elastic strains can be predicted theoretically. Therefore C-rings can be stressed by calculating the deflection required(1,2) $L = f D^2/4Et Z$ to develop a desired stress:

where L = change in outer diameter giving the desired stress f = desired stress (kg/mm^2) D = mean internal diameter E = modulus of elasticity (kg/mm^2) t=thickness of the ring in mm. Z= correction factor for cooled beam. The C-ring specimens were stressed as in the above method to stress levels of 90% and near yield strength. The higher stress levels were chosen in order to accelerate the test and thereby to cause cracking within a short duration fo exposure.

The two specimen C-rings T 11 and T 22 individually exposed to 15%, 30% and 45% by weight

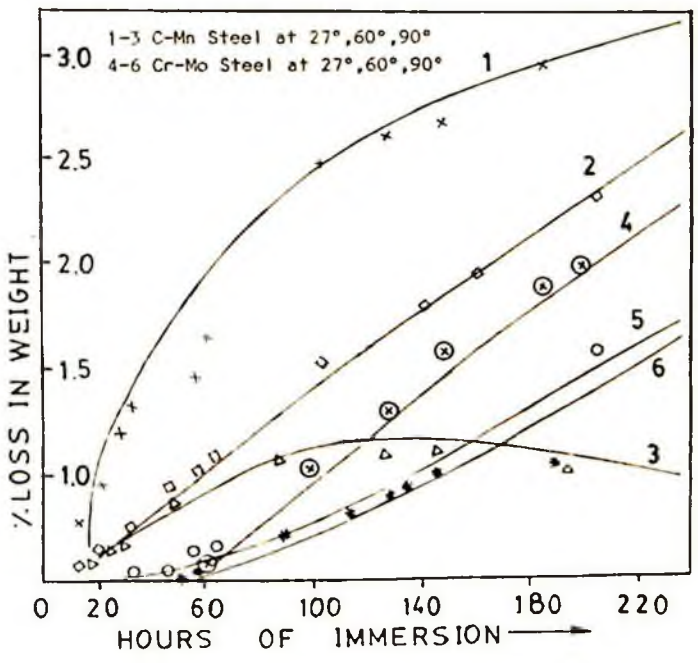


Fig. 3 General Corrosion of C.-Mn and Cr-Mo Steels at Three Different Temperatures In 5% NH_4NO_3 Solution

of caustic solution for a period of 30 days at room temperature, were cleaned and examined.

RESULTS

GENERAL CORROSION

All these tests were performed for a total of 300 hours of immersion. The percentage loss in weight vs time and corrosion rate in mpy vs time for each of the tests conducted for both the steels are given in Figures 3 & 4 . Only general corrosion has been observed on C-Mn steels at 60°C and 90°C; (Photographs 1 and 2) but very little on Cr-Mo steels. However, when the surfaces were cleaned, large number of pits were seen on the surfaces of Cr-Mo steels exposed at room temperature and 60°C (Photographs 3 and 4).

STRESS CORROSION

C-rings exposed to caustic solution was not cracked . Overall size was the same before and after the experiment indicating that there was no general corrosion. However, a dull thin film was seen on the specimens.

ACCELERATION TESTS USING IMPRESSED CURRENTS

Specimens with external impressed current of the order 6 to 8 mA/cm^2 were exposed to 35% by weight of NaOH solution for a period of seven days. The external current increased only the general corrosion and the solution got contaminated with red oxide particles. However, no cracks were observed for a period of seven days of exposure. The corroded surface is shown in the photograph 5.

ACCELERATION TESTS USING NOTCHED SPECIMEN

Notched C-ring specimens as shown in photograph 6 were also exposed in a solution of 35% NaOH solution. No cracking was observed and the surface was relatively free from any sign of general corrosion.



1. The corroded surface of C-Mn steel to 5% NH_4NO_3 solution at 60°C.

2. The occurrence of general corrosion of C-Mn steel exposed to 5% NH_4NO_3 solution at 90°C.

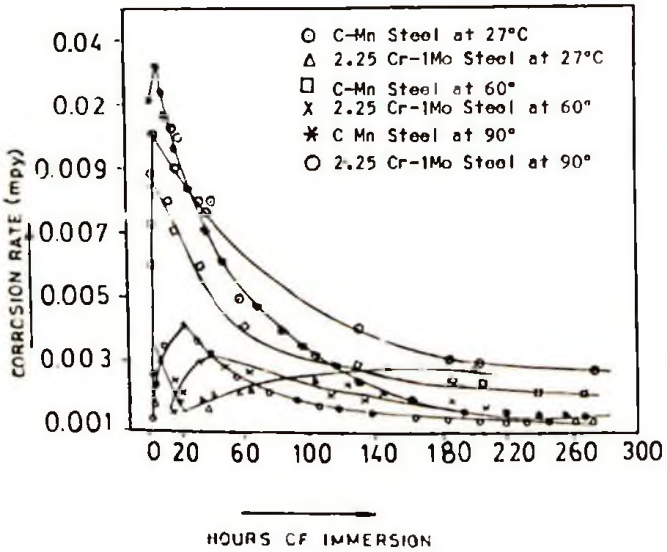


Fig. 4 Corrosion of C-Mn and Cr-Mo Steels in 5% NH_4NO_3 Solution at Different Temperatures



3. The formation of pits on 2.25 Cr-1 Mo steel in 5% NH_4NO_3 solution at 27°C (room temperature)

4. Pitting formation on 2.25 Cr-1 Mo steel in 5% NH_4NO_3 solution at 60°C

DISCUSSIONS

SELECTION OF NH_4NO_3 SOLUTION AS THE MEDIUM

NH_4NO_3 is an acid salt(3,4) viz: that salt which will hydrolyse to form acid solution, cause corrosion with combined hydrogen evolution and oxygen depolarisation at a rate paralleling that of the corresponding acid at the same pH value. Moreover increased corrosivity can be expected from NH_4NO_3 due to the ability of NH_4^+ to complex iron ions, thereby reducing activity of Fe^{2+} and increasing tendency of Fe to corrode. Ammonium nitrate in higher concentrations is more corrosive than the chlorides or sulfates, in part because of the depolarising ability of NO_3^- .

SELECTION OF NaOH SOLUTION AS THE MEDIUM

Cracking in boilers is due to waters which are naturally alkaline or which become alkaline on conversion either by the addition of sodium carbonate or by contact with sodium zeolite. The sodium carbonate in boiler waters decomposes to give free sodium hydroxide(5)

Caustic embrittlement, where the cracking is primarily intercrystalline(6) has been known in boilers and process vessels at highly stressed areas such as rivets, rivet seams, welded areas or rolled-in tube ends(7,8,9). It is the iron oxide (Fe_3O_4) particles that are usually present in the cracks(10). These cracks can develop along the line of rivet holes at tube ends, or at random along any seam. They are always associated with relatively high caustic concentrations in contact with stressed steel. Straub showed that caustic can become concentrated in the capillary spaces of seam and tube ends. It is this condition, combined with high stresses in the metal, that leads to caustic embrittlement. Caustic attacks iron with the liberation of hydrogen(11), and the atomic hydrogen may lead to intercrystalline cracking(12,13,14).



5. The corroded surface with formation of pits on 2.25 Cr 1Mo steel in 35% NaOH solution under impressed current condition.
6. The notched C-ring specimen free from any sign of general corrosion when exposed to 35% NaOH solution.

In the experiments conducted, the pH of 5% NH_4NO_3 solution used was between 6 and 7 (i.e.) almost netural range. Iron has relatively a poor resistance(15) in the neutral range of aerated aqueous solutions. If undisturbed for years, a solid solution may be formed as a corrosion product which is not highly protective and effective to arrest further corrosion.

In the neutral range(16,17) (pH 4 to 10), the corrosion rate is independent of pH and depends only on how rapidly oxygen diffuses to the metal surface. The major diffusion barrier of hydrous ferrous oxide is continuously renewed by the corrosion process.

With the presence of moderate amounts of dissolved oxygen(18,19)corrosion rates are increased because diffusing oxygen prevents cathodic polarisation. Variations in the dissolved oxygen content leads to variations in the physical characteristics of the precipitated ferric hydroxide films. An increase in oxygen supply almost leads to greater corrosion rates.

The attack on iron and steel by acid and alkaline solutions is normally uniform whereas pitting is usual in neutral solutions. This is because the protection afforded by rust is ordinarily irregular. Breaks in the rust layers lead to greater rates of oxygen diffusion at some points than at others. This results in oxygen concentration cells(20).

GENERAL CORROSION

It is seen from the figures 3 & 4 that at all the three testing temperatures, the corrosion rate of C-Mn steel is greater than the Cr-Mo steels. However, full depth of pitting has not been taken into account in the weight -loss method adopted. It is observed that C-Mn steels are more prone to general corrosion as revealed from photographs 1 and 2, than Cr-Mo steels. This is due to alloying the steel with Cr in the latter case. However, pits are noticed only on Cr-Mo steels as noticed from photographs 3 and 4.

STRESS CORROSION

Higher concentrations of NaOH solutions have been used in stress corrosion studies. No cracking was observed. Above pH = 10, corrosion rate correspondingly decreases because steel becomes increasingly passive in presence of alkalies and dissolved oxygen(21). Apparently at higher partial

pressures, more oxygen reaches the metal surface than can be reduced by the corrosion reaction; the excess therefore is available to form the passive film (22). On the basis of the oxide film theory of passivity,the excess oxygen supposedly oxidises the ferrous oxide film to one having greater protective value as a diffusion barrier. According to adsorption theory, the excess oxygen is available to chemisorb on the iron surface forming an adsorbed passive film. This explanation seems to justify the low corrosion on Cr-Mo steels at room temperature due to passivity.

The non-formation of a crack even under impressed currents may be attributed to the composition of steel and it may be regarded that the effects of stress, impressed current and the notch have been completely outweighed by the 2.2.5% Cr in the steels studied under test conditions.

However, variations in stress levels, temperature, concentrations and incrase in the test duration may lead to a better understanding and help to predict the life of the alloys.

CONCLUSIONS

The following conclusions can be drawn from the above experimental results :

(i) The corrosion rate of C-Mn steel is higher than that of Cr-Mo steels.

(ii) The corrosion rates for both the steels increase with increase of temperature.

(iii) The Cr-Mo steels were found to be resistant to SCC under test conditions.

(iv) The impressed current produced only pits.

(v) With the notched C-ring test, no cracks were observed indicating that the material is not prone to SCC.

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