INTERCRYSTALLINE CRACKING OF MILD STEEL IN SALT SOLUTIONS.

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A number of investigators have examined instances of intercrystalline cracking of mild steel either occurring during service[1] or experimentally induced by the action of sodium hydroxide solutions.[2]

Many of the cases of failure in service appear to have been induced by the action of caustic alkali on the steel. In order that fracture should be produced it is clearly necessary that the material should be under stress of some kind, either applied or internal. A considerable amount of internal stress often exists in mild steel boiler plates and similar materials which have been subjected during manufacture to processes such as punching and riveting. Stromeyer showed that cracking was produced in steel stressed in tension under the action of sodium hydroxide but that the same steel in compression remained uncracked.

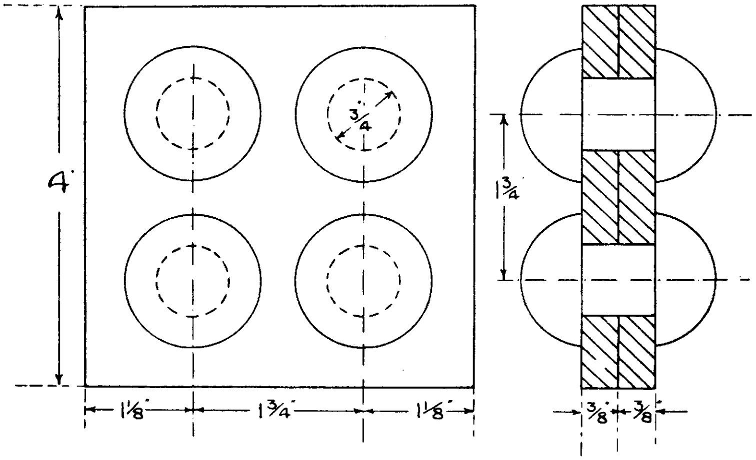

FIG. 1.

The present paper describes the action of other agents in producing cracking of steel in a state of stress.

Cracking Induced in Riveted Plates.—In the first instance a number of mild steel riveted plates were prepared. The dimensions of the plates

[1] Andrew, *Transactions of Faraday Society*, 1913-14, Vol. IX, pp. 316-317.
Wolff, *Journal, Iron and Steel Institute*, Vol. II, 1917, p. 137.
Merica, *Chemical and Metallurgical Engineering*, May 1917, p. 496.
Desch, *Journal, Iron and Steel Institute*, Vol. II, 1917, p. 172. Discussion on Wolff's paper.
Rosenhain, *Journal, Iron and Steel Institute*, Vol. II, 1920, p. 23.

[2] Stromeyer, *Journal, Iron and Steel Institute*, Vol. II, 1917, p. 159. Discussion on Wolff's paper.

are indicated in Fig. 1. A number of plates with ½-inch rivet holes were also prepared. Some of the plates had punched rivet holes, while in others the holes had been drilled. The riveting was effected by a hydraulic riveter under a pressure of 40 tons for the ¾-inch rivets and 20 tons for the ½-inch rivets. The rivets were heated only to the minimum temperature necessary for the work, in order that comparatively high

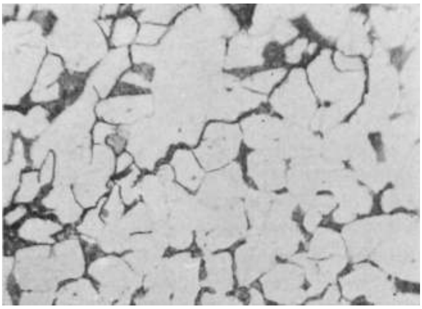

FIG. 2 (× 250).—Intercrystalline cracks produced by the action of calcium nitrate solution.
(Reduced by one-quarter.)

stresses might be induced. The plates were examined and were free from cracks. The rivets had indented the plates which were distinctly warped by the pressure applied in riveting. This distortion was accompanied by considerable strain hardening, the Brinell hardness numbers on a section between two rivet holes varying from 110 to 150.

The plates were placed in a solution consisting of 4 parts of calcium

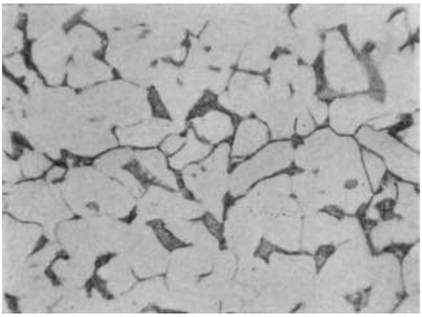

FIG. 3 (× 250).—Intercrystalline cracks produced by the action of calcium nitrate solution.
(Reduced by one-quarter.)

nitrate to 1 part of water at a temperature of about 145° C. and were examined at intervals. No corrosion or cracks could be detected on the outside surface of the plates after 23 days, but in 28 days two of the plates with ¾-inch punched rivet holes and one of the plates ¾- withinch drilled rivet holes showed a large number of distinct cracks. The other plates, including 4 with ½-inch rivets, showed no cracks after 74 days; a number of these were then cut up, but no cracks were found on the inner surfaces.

Plates produced in the same way, but normalised after riveting, showed no signs of cracks after 74 days in the calcium nitrate solution.

The cracks produced as described above were examined and in every case were found to be intercrystalline (Figs. 2 and 3). The microstructure of the plates was normal.

Chemical analysis of the steel of the plates gave the following results:—

Carbon	·18	per cent.
Silicon	·062	"
Manganese	·63	"
Sulphur	·036	"
Phosphorus	·060	"

A further number of plates with ¾-inch punched rivet holes were made under less drastic conditions. These plates showed practically no distortion. Higher temperatures had been employed, a considerable amount of scale remaining on the plates and rivets. There was no evidence of strain hardening; the Brinell hardness only varied from 130 to 141. No cracks were found in any of these plates after being immersed for 100 days in the calcium nitrate solution at about 145° C.

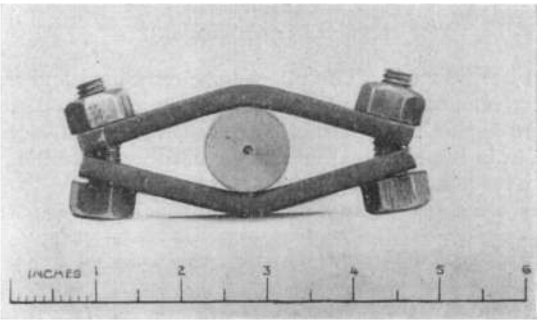

FIG. 4.

Chemical analysis of the steel of these plates gave the following results:—

Carbon	·19	per cent.
Silicon	·014	"
Manganese	·65	"
Sulphur	·052	"
Phosphorus	·062	"

The notched bar impact figure of both the above steels was good and no alteration in impact figure could be detected after treatment in calcium nitrate solution.

Cracking Induced by Various Solutions.—The amount of stress in specimens of the form described was too uncertain for carrying out comparative tests and another form (shown in Fig. 4) was subsequently used. This consisted of two plates of mild steel, ¼-inch thick, 1-inch wide, and 4-inches long, bent and screwed together over a hard steel cylinder of 1-inch diameter. The results of maintaining these specimens in a number of solutions, heated nearly to boiling, and in other media are shown in Table I.

Chemical analysis of the steel of the plates gave the following results :—

Carbon	·08	per cent.
Silicon	·011	"
Manganese	·55	"
Sulphur	·098	"
Phosphorus	·074	"

TABLE I.

Solution.	Concentration. Salt : Water.	Temperature.	Remarks.
Calcium nitrate	4 : 1	148° C.	Cracked in 4½ days.
Potassium hydroxide . . .	2 : 5	126° C.	" " 3 "
Ammonium nitrate	5 : 1	124° C.	" " 3 "
Sodium nitrate	3 : 1	127° C.	" " 2½ "
	2 : 1	120° C.	" " 2½ "
	1 : 2	109° C.	" " 3 "
	1 : 4	104° C.	" " 2½ "
	1 : 5	100° C.	" " 4 "
	1 : 8	100° C.	" " 5½ "
Sodium carbonate	3 : 1	127° C.	Not cracked after 98 days.
Sodium nitrate to which was added 5 per cent. of sodium carbonate	3 : 1	127° C.	Cracked in 7 days.
Sodium nitrate to which was added 10 per cent. of sodium carbonate	3 : 1	127° C.	" " 9½ "
Sodium nitrate to which was added 10 per cent. of sodium carbonate.	1 : 4	105° C.	" " 20 "
Ammonium sulphate . . .	1 : 1	117° C.	Not cracked after 34 days. (badly corroded).
Calcium chloride	3 : 1	150° C.	Not cracked after 105 days.
Fused mixture of sodium and potassium nitrates	Equal parts of salts	250° C	" " " 29 "
Air (steam oven)	—	100° C.	" " " 105 "

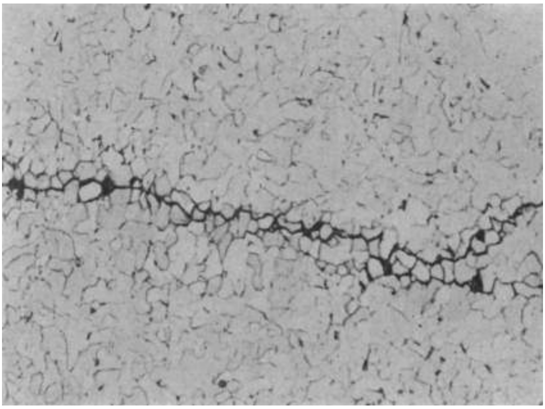

FIG. 5 (× 100).—Intercrystalline cracks produced by the action of potassium hydroxide solution.

(Reduced by one-quarter.)

In all cases where cracking of the steel occurred the cracks were intercrystalline in character (Figs. 5 and 6). In the potassium hydroxide solution and the more dilute solutions of sodium nitrate, a network of fine intercrystalline cracks was produced. In the case of the more concentrated solutions some intercrystalline cracks were first formed but ultimate failure generally occurred by fracture through the crystals.

The Effect of Varying Initial Stress.—A number of specimens of bent plate identical with the above were annealed for 1 hour at 200, 300, 400, 600, and 900° C. respectively after assembling and previous to placing in calcium nitrate and potassium hydroxide solutions. The plate annealed at 200° C. cracked in the calcium nitrate solution in 7 days. The specimen which had been immersed in the fused sodium and potassium nitrate mixture at 250° C. for 29 days (Table I) cracked in the calcium nitrate solution in 8½ days. The plate annealed at 300° C. cracked after 11 days in the calcium nitrate solution. None of the plates annealed at higher temperatures had cracked after 50 days.

Two specimens similar to one another but bent through a smaller angle than the standard form cracked in 8 and 6 days in calcium nitrate and

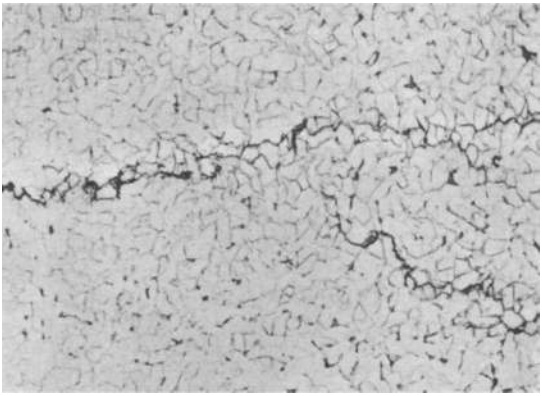

FIG. 6 (× 100).—Intercrystalline cracks produced by the action of sodium nitrate solution.
(Reduced by one-quarter.)

potassium hydroxide solutions respectively. Other specimens similar in form but varying in length of plate were placed in the calcium nitrate solution with the results indicated.

Length of Plate.	*Remarks.*
4 inches	Cracked in 4½ days.
4½ "	" " 7 "
5 "	" " 7½ "
5½ "	" " 7 "
6 "	" " 7 "

The influence of varying initial stress on the time in which cracking occurred is also illustrated by results obtained with cold rolled steel strip mounted and bent as shown in Fig. 7. Immersed in the calcium nitrate solution at about 148° C. the outer strip cracked in 5 days, the second in 6½ days, while the third and fourth were not cracked after 50 days.

Behaviour of Heat Treated Steel.—Specimens bent to the standard form shown in Fig. 4 were also obtained from previously heat treated steel as follows:—

Treatment before Bending.	*Solution.*	*Remarks.*
Mild Steel—		
Annealed 900° C. for 1 hour. . .	Calcium nitrate .	Cracked in 2½ days.
	Potassium hydroxide	,, ,, 2½ ,,
Annealed 1150° C. for 1 hour. . .	Calcium nitrate .	,, ,, 2 ,,
Heated to 930° C. and quenched in water.	Calcium nitrate .	,, ,, 2½ ,,
	Potassium hydroxide	,, ,, 2 ,,
·34 *per cent. Carbon Steel—*		
Annealed 900° C. for 1 hour. . .	Calcium nitrate	Not cracked after 42 days.
Oil hardened from 900° C., tempered at 680° C.	Calcium nitrate	,, ,, ,, 84 days.

The Action of Potassium Hydroxide.—The action of the potassium hydroxide solution was very different from that of the salt solutions which produced cracking. In a fresh solution, stressed steel cracked in a few days but after the solution had been in use for some time the steel became coated with a black deposit of oxide and cracking was inhibited. This is not solely due to the alteration of surface of the steel since the solution now fails to crack fresh similar specimens which are introduced and which themselves become coated much more quickly than the original specimens. A deposit consisting of magnetic oxide and some carbon-

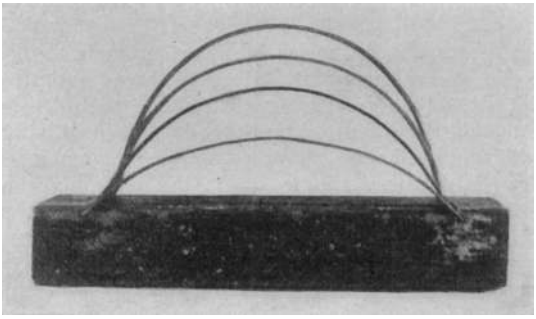

FIG. 7.

aceous matter accumulated at the bottom of the vessel. The inhibiting effect of the presence of oxide lends support to the view that cracking is brought about through the agency of hydrogen.[1]

Action of Steel on Nitric Acid and Nitrate Solutions.—According to Berzelius the action of iron on cold dilute nitric acid results in the formation of ammonia and yields a mixture of ferrous and ammonium nitrates, but the reaction varies with concentration and temperature.[2]

With solution concentration less than 24 per cent. nitric acid, two-thirds of the iron which goes into solution reacts to produce ammonia and nitrogen.[3]

Acworth [4] found that by the action of steel on a saturated solution of ammonium nitrate containing 4 per cent. of free nitric acid a gas was evolved consisting mainly of nitrogen, and a reddish brown basic nitrate of iron was simultaneously formed. No measurable evolution of gas occurs

[1] Andrew, *Transactions of the Faraday Society*, 1913-14, Vol. IX., pp. 316-317.

[2] See also Acworth and Armstrong, *Journal, Chemical Society, Abstracts*, 1877, Vol. 32, p. 79.

[3] Whiteley, *Iron and Steel Institute Carnegie Scholarship Memoirs*, 1918, Vol. IX, p. 10.

[4] Acworth, *Journal, Chemical Society Abstracts*, 1875, Vol. 28, p. 840.

when pure nitrate solutions are treated with iron, but the more electro-negative metal zinc acts slowly on ammonium nitrate solutions giving a mixture of nitrous oxide and nitrogen.

It seems probable that iron is not without a similar action, since small amounts of basic nitrate of iron were found after prolonged action of nitrate solutions. This was most noticeable in the case of ammonium nitrate which had a marked corrosive action on the steel.

Instances of Failure in Practice.—Cases have occurred of cracking of steel

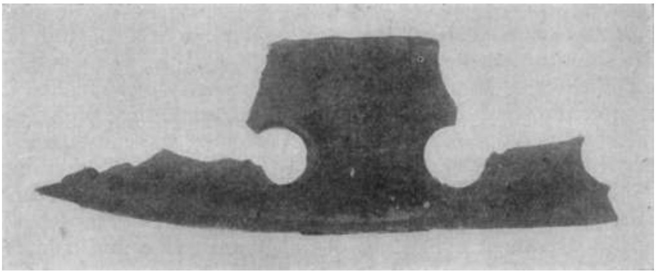

FIG. 8.

plates of vats and evaporating pans used in the manufacture of ammonium nitrate. The cracking occurred chiefly at rivet holes and also at positions where bent plates had been used in construction (see for example Figs. 8 and 9). Rivet heads also fractured on the side in contact with the solution. Some samples of fractured plate examined showed evidence of severe strain hardening (Brinell hardness 130 to 200); the rivet holes had probably been punched and no steps were taken to eliminate internal stresses. Similar cracking was observed in plates which had been in contact with

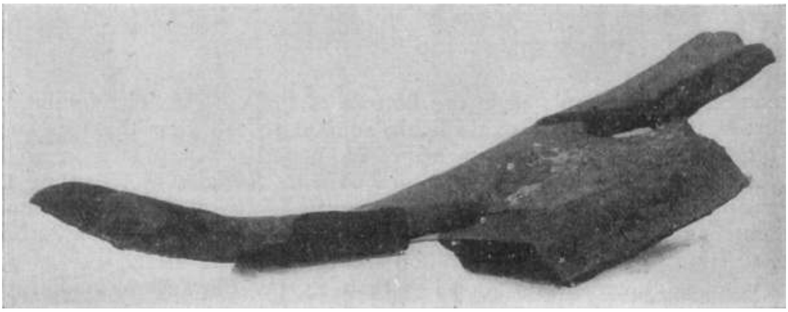

FIG. 9.

sodium, potassium or calcium nitrate solutions. The time taken for the cracks to appear varied from 24 hours to 1 month.

Summary and Conclusions.—One of the determining factors in the production of cracks is the presence of internal or applied tensile stress, and fracture occurs only when these stresses are above a certain value. In the experiment with bent strips (Fig. 7) the outer strips failed, while the stresses in the inner strips were presumably insufficient to produce cracking. Similarly the riveted plates which cracked were those in which there is reason to believe the internal stress was highest. This point is further illustrated in the case of the annealed plates; the stresses are partially relieved at 200° C., 250° C. and 300° C., but the plates still cracked though after a longer time. At higher temperatures the stresses though they may not be entirely removed, have fallen below the minimum value required to produce cracking. There is no evidence to show that internally stressed steel (in the unhardened condition) is liable to crack spontaneously at ordinary temperatures. Moreover, a condition of slightly elevated temperature alone has not been found to be responsible for producing cracks in such material. Stressed specimens which remained uncracked for 4 weeks in a fused salt bath at 250° C., 15 weeks in calcium chloride solution at 150° C., 14 weeks in sodium carbonate solution at 127° C., or 14 weeks in air at 100° C., all cracked within a few days when heated in calcium nitrate solution at 148° C.

This property of inducing rapid cracking in stressed mild steel has been observed in the case of solutions of sodium, potassium, calcium, and ammonium nitrates. A similar action of solutions of caustic alkalis is already well known. In all cases the cracks produced by the solutions are intercrystalline; under similar circumstances a medium carbon steel both in the annealed and in the sorbitic condition did not crack.

Both Andrew and Merica attributed the formation of intercrystalline cracks in mild steel after treatment in caustic soda solutions to weakening of the grain boundaries by the absorption of hydrogen by the intercrystalline amorphous material. Further support for the view that cracking in potassium hydroxide takes place through the agency of hydrogen is given in a previous section. It seems clear that solutions of nitrates also yield a product having a selective action on the intercrystalline material whereby intercrystalline cohesion is reduced.

It is suggested that in this case the active agent is nitrogen (or an oxide of nitrogen).

The addition to sodium nitrate solutions of sodium carbonate, which would reduce the dissociation of nitrate in solution and might thus tend to check the reaction, was found to retard the rate of cracking.

In the absence of applied or internal tensile stress penetration cannot be appreciable, since the action appears to be without detriment to the properties of the steel, in the absence of accompanying stress.

In conclusion the author wishes to thank Mr. R. H. Greaves, M.Sc., for many suggestions and much valuable advice given during the course of this work.