SOME SERVICE FAILURES ARISING FROM VARIOUS TYPES OF CORROSION

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SYNOPSIS.

Five examples of service failures, in heat-and corrosion-resisting alloys, involving various forms of corrosion, are briefly described, and recommendations made to avoid their recurrence are indicated.

Introduction.

The Research Laboratory of the Development and Research Department of The Mond Nickel Company Limited, has been concerned in developing new heat and corrosion-resistant alloys to meet the demands of designers of gas-turbine chemical plant and electrical equipment. Premature service failures in these materials are not common, and when they do occur they can usually be traced to misuse or maltreatment of the material during fabrication or application, or to some form of accidental contamination or damage. Important lessons have nevertheless been learned from post-mortem examinations of service failures, and the following five examples have been selected as of interest not only to works' metallurgists but also to designers, to whom these special materials offer new possibilities, and to fabricators, to whom they present certain problems.

1. Welded Stainless-Steel Tank.

The first case concerned 100 gal. welded stainless-steel tanks, used for storing flavouring essences. These tanks developed serious leaks after a relatively short time in service, owing to the special form of corrosive attack known as "weld decay." This effect occurs in unstabilised stainless steels, and is avoided by the use of steels containing titanium or niobium. The leaks occurred near welds around the bottom outlet sumps of the tanks. Examination of one tank revealed a large crack in the bottom plate, running alongside the weld joining this plate to the conical sump. Microscopical examination showed the crack to be intercrystalline and associated with grain-boundary corrosion. The crack and corrosion were in a zone where the grains were outlined by precipitated carbides. Sections cut through the weld between the bottom plate and one of the side plates also revealed a similar band of grain-boundary carbides in the bottom plate, about 1 mm. away from the weld head. Here, however, only slight intergranular corrosion had occurred. The zones of carbides did not appear on the other side of the weld in the side plate. Analysis of the component sheets showed that the side sheets and the parts of the sump were made from 18% chromium, 8% nickel austenitic stainless steel containing 3% molybdenum. The bottom plate, however, was a straight 18% chromium 8% nickel steel and did not contain molybdenum or any other carbide-stabilising elements.

The localised corrosion in the zone of grain-boundary carbide is typical "Weld decay" and had obviously occurred due to the inadvertent use of unstabilised stainless steel. This effect was not, however, sufficient to account for the early failure of the tank, as shown by the relatively slight corrosion in the affected zone along the weld in the side of the tank. It seems likely that the corrosion near the sump had been greatly accelerated by stresses which could have been residual, resulting from the welding, or vibratory, transmitted to the sump along connecting piping.

2. Stainless-Steel Bubble Caps.

Stress-corrosion can occur in stainless steel in the absence of such conditions as the carbide precipitation in the first example. As interesting case recently investigated was the failure, by severe cracking, of stainless-steel bubble caps after only a few months' service in distillation
columns at an oil refinery. The caps were deep-drawn from stainless-steel sheet; slots had then been punched out of the rim, which was afterwards flared out. The failures occurred in caps on the top tray only of the columns, where they were exposed to reflux containing small proportions of ammonium hydroxide and ammonium chloride, at a temperature of about 110°C.

Stress-corrosion was suspected, and microscopical examinations of one of the failed caps showed branched cracks, both inter-and transcrystalline, which are typical of this form of failure in stainless steel (Figures 1 and 2). As shown in Figure 1, severe cracking had occurred around the slots and this also extended to the radius between the wall and the flat top of the cap.

In order to find out what changes in material or processing procedure were necessary to overcome this trouble, the bubble cap manufacturers asked The Mond Nickel Company to carry out laboratory stress corrosion tests on unused caps made from three different grades of austenitic stainless steel, the analyses of which are given in Table 1. The caps from each grade of steel were produced by three different fabrication procedures, namely:
- Series 1—Pressed, serrated, annealed, and flared.
- Series 2—Pressed, serrated, flared, finally annealed.
- Series 3—Pressed, serrated, flared.

In each case the annealing treatment was 15 minutes at 1085°C, followed by air cooling. Series 3 corresponded to the normal procedure used for the caps which had failed in service. It should be stated that the usual annealings were, of course, carried out during the deep drawing operation for all three series.

The stress-corrosion tests were carried out by totally immersing the caps, supported on rubber insulators, in a tank of boiling 42% magnesium chloride solution (boiling point 154°C) as described by Scheil.*

In this solution branched cracks typical of stress-corrosion failure gradually developed in all but the specimens which had received the final annealing treatment. The extent of the cracking, the time until the first appearance of cracks, and the resonance on testing for "ring" at the end of the exposure, are summarised in Table 2. The cracks appeared mainly on the curved region between the wall and the flat top, as seen in Figure 3. Since they were not obviated by the annealing applied before flaring, it would appear that this intermediate annealing treatment was inadequate.

Steel B showed less susceptibility to cracking than the other two grades. Since it contained molybdenum, it was expected to be better than Steel A., which did not contain the element. Its superiority to Steel C, however, was difficult to explain, although it was possibly due to different processing techniques applied to the original sheet which might have produced differences in grain size and differing amounts of ferrite in the structure.

The manufacturer of the bubble caps was recommended to use steel of type B, and to apply the final annealing treatment to the finished caps. Since final annealing became standard practice, by design or coincidence no further failures have occurred.

An interesting feature of this investigation was the close similarity between the cracks produced in the laboratory test and those which occurred during service. Not only did they occur in the same positions on the caps, but their appearance under the microscope was very similar.


Tubes made of a nickel-chromium base heat-resisting alloy failed after only 85 hours' service in a heat-exchanger at a temperature at which the alloy should have behaved quite satisfactorily. The fracture was intercrystalline and had occurred with no detectable elongation. This feature ruled out failure by creep or simple overstressing and suggested that the prime cause of the failure was fatigue.

Patches of brown-coloured deposit were found irregularly distributed inside the tube and spectrographic analysis of portions of the brown material gave very strong indications of the

Figure 1
STAINLESS-STEEL BUBBLE CAP
Piece of failed cap, showing stress-corrosion crack

Figure 2
STAINLESS-STEEL BUBBLE CAP
Stress-corrosion crack (x 100)
presence of lead, tin and bismuth. It was known that a fusible-alloy filler had been used in bending the tubes to their final form, and it was concluded that the brown deposits were the oxidised remains of residual particles of the alloy left in the tubes. Traces of the same elements were detected on the surfaces of the fracture. Microscopical examination showed that, beneath several of the deposits, alloying with the tube material had occurred.

It was concluded that the failure of this tube was due to fatigue under the corrosive influence of traces of lead, tin and bismuth.

A failed air-heater tube in the same alloy examined subsequently revealed a very similar type of fracture. In this case fatigue failure had been accelerated by the notch effect of defects in the bore, arising during manufacture of the tube, but traces of bismuth and lead were again found, and probably contributed to the failure. In this instance no fusible alloy had been used and contamination probably arose from residual traces of drawing compounds left in the tube.

4. Electric furnace heating element.

A nickel-chromium alloy heating element failed after only 100 hours’ service at 1000°C in a furnace used for gasification of coal.

The surface of the failed element was found to be covered with patches of corrosion in the form of “Wart-like” scale excrescences. The microstructure beneath these corroded areas contained light-and dark-grey constituents. The dark-grey constituent had penetrated along the grain boundaries below the main corroded layer.

Similar corrosion of this type had been seen before on nickel-chromium alloys which had been exposed to sulphur-bearing gases at high temperatures. A sodium azide iodine spot test on the polished microspecimen confirmed the presence of sulphides in this instance also.

Investigation showed that although the heating element was enclosed in a silica muffle, it was possible for gases from the coal to come into contact with it, and it was concluded that the sulphur in these gases was the cause of the failure. The remedy in this case was obvious.


A number of nickel-chromium alloy tubes were separated by asbestos from other tubes during their final heat-treatment. When they were taken from the furnace it was noticed that very heavy scaling had taken place where the tubes had been in contact with the asbestos. The heavily attacked sides of two tubes are shown in Figure 4. This material normally has but a thin uniform oxide skin after heat-treatment. Micro-examination of transverse sections through the tubes showed that, beneath the layer of scale, a layer of the metal contained corrosion products resembling those formed by sulphur attack. At the most heavily scaled part of the tubes the wall thickness had been reduced by about 8%, and penetration of the corrosion, mainly along the grain boundaries, extended to a depth of equal to a further 8% of the original wall thickness.

The presence of sulphides was confirmed by chemical spot tests on the micro-section and also by chemical analysis of a sample of scale removed from one of the tubes, which had a sulphur content of over 1%. It was concluded that sulphur present in the asbestos had caused the corrosion. The amount of sulphur present must have been considerable, since parts of the tube wall which had not been in direct contact with the asbestos showed some signs of sulphur attack.

It is hoped that these few examples have served to indicate the wide variety of factors which can cause failure of nickel-chromium and nickel-chromium-iron alloys. Contamination by traces of foreign matter, surface damage through mishandling, undetected residual stresses, and unforeseen corrosive influences can all lead to serious and expensive failure, and it is only by controlling such factors in manipulation and use of these newer alloys that full advantage of their special properties is to be obtained.

ACKNOWLEDGEMENT.

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Figure 3
STAINLESS-STEEL BUBBLE CAP
Top view, showing cracks produced during laboratory stress-corrosion test.

Figure 4
CORRODED NICKEL-CHROMIUM ALLOY TUBES
TABLE 1.
ANALYSIS OF BUBBLE CAP MATERIALS SUBJECTED TO STRESS CORROSION TESTS.

<table>
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<th>Chemical composition per cent</th>
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<tr>
<td>Carbon</td>
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<tr>
<td>Steel A.</td>
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<td>Steel B.</td>
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<tr>
<td>Steel C.</td>
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TABLE 2.
RESULTS OF STRESS-CORROSION CRACKING TEST OF STAINLESS STEEL BUBBLE CAPS.

The times stated are the hours of exposure to boiling 42% magnesium chloride solution (B.P. 154°C) before cracking was first observed. All specimens were previously tested in magnesium chloride solution boiling at 143°C for a period of 440 hours without fracture.

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<tr>
<td>Steel A</td>
<td>Branched cracks, in places completely penetrating the metal. Affected area (about 2&quot; × 3&quot;) located on flat and severely curved region, not at serrations. (236 hours).</td>
<td>Apparently unaffected.</td>
<td>Severe branched cracks penetrating the metal over a length of more than 2&quot;. No cracks at serrations. Poor resonance. (27 hours).</td>
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<tr>
<td>Steel B</td>
<td>Nearly unaffected except for some fine superficial hair cracks at a late stage in the test causing slight loss of resonance. (265 hours)</td>
<td>Apparently unaffected.</td>
<td>One large branched crack 2½&quot; long over flat and curved regions. Poor resonance. (96 hours).</td>
</tr>
<tr>
<td>Steel C</td>
<td>Very numerous branched cracks around central hole and over flat and curved regions. Very poor resonance. (48 hours.)</td>
<td>Apparently unaffected.</td>
<td>Numerous severe cracks in flat and curved regions and in sides. Very poor resonance. (27 hours).</td>
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