SOME ASPECTS OF SERVICE FAILURES AT ELEVATED TEMPERATURES.

By

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ABSTRACT

Service performance of metals and alloys at elevated temperatures is generally governed by creep and rupture strength required and corrosion conditions likely to be met with. The influence of factors like intergranular oxidation, decarburisation, carburisation, spheroidisation, graphitisation, carbide precipitation and the formation of sigma phase on failure at high temperatures have been outlined. Some recorded service failures are discussed and preventive measures indicated in some cases.

INTRODUCTION:

Efficient performance of gas and jet turbines, components for gasoline and diesel engines used in power plants, equipment for oil-refinery and chemical industries, depends on the availability of alloys capable of withstanding stresses and resisting corrosion at high operating temperatures. Heat-resisting materials are also employed in furnace parts, carburising boxes, roasters where high resistance to creep is not required. Hatfield** and Sykes† have covered the technical developments in high temperature alloys up to 1947. Systematic creep testing under simulated service conditions of the materials used is always done. High temperature properties of such materials have been reported in the technical literature extensively. Failures at high temperatures have been generally noticed to be (i) trans-crystalline and (ii) intergranular which are characterised by differences in ductility. The type of fracture depends on the temperature and the rate of deformation. The precipitation of relatively brittle constituents along cleavage planes causes inter-granular rupture with little or no deformation. Such constituents may be carbides, nitrides etc. Intergranular oxidation aggravates the susceptibility. Some alloys are susceptible to intergranular rupture at high operating temperatures and failures follow by a process of inter-crystalline separation of grain boundaries. Deformation prior to such fracture is limited and no apparent indication of the impending failure is generally noticed. For service at elevated temperatures, freedom from failure is ensured through liberal margins of safety in design based on long-time exhaustive creep tests. The material should however, be capable of withstanding sustained application of stipulated loads and occasional over-load stressing without susceptibility to inter-crystalline embrittlement. Strength of metals and alloys at ordinary and high temperature depends on the microstructure. High temperature generally lowers the strength.

The influence of environment on high temperature service is important. In combustion chambers, severe corrosive conditions prevail and in tubes carrying organic fuels or oils, carburisation is likely to occur.

This short review is restricted to a study of microstructural changes due to oxidation, decarburisation, spheroidisation, graphitisation, carbide precipitation and sigma phase formation at high operating temperatures in relation to service failures.

Oxidation:

Oxidation as is well-known, is a diffusion process. Oxidation of alloys is rather complex.

** Figures pertain to the references appended to this paper.
due to selective oxidation of one or more alloy constituents and due to the fact that an element
which forms a protective layer with a metal may not do so with another. Presence of alloying
elements changes oxidation rates. Scharader\textsuperscript{4} has surveyed the effects of various elements on
scaling and decarburisation of steels. Resistance to oxidation depends on the formation of a pro-
tective layer. For high temperature service, high chromium steels are suitable in view of their
resistance to oxidation due to formation of a thin adherent film of chromium oxide. Chromium
is the chief constituent in most heat-resisting steels used in the temperature range of 550-600°C.
The resistance to oxidation is progressively increased by increasing the chromium content as shown
in Fig. 1 and Fig 2 shows the relative resistance to oxidation of some steels.\textsuperscript{4} The resistance to
scaling is increased by additions of silicon and aluminium by changing the nature of the scale
layer. It has been observed\textsuperscript{1} that in the presence of over 3\% Mo, 16\% Cr, 25\% Ni steel at tem-
perature above 800°C in air suffers severe attack due to the catalytic oxidation by the thermal
dissociation of MoO\textsubscript{3} into MoO\textsubscript{2} and nascent oxygen. Diffusion of oxygen initially takes place
through the grain boundaries\textsuperscript{6}. Certain elements like nickel, cobalt and molybdenum
increase solubility of oxygen in iron and promote its diffusion along grain boundaries. Fig. 3.
shows the oxide at the surface of austenitic stainless steel which has penetrated into the grain
boundary during dehydrogenation service at 620-730°C, for one year. Fig. 4. illustrates
intergranular oxidation at the surface of carbon steel superheater tube. It has been stated
that oxidation\textsuperscript{7} from atmospheric oxygen controls the incidence of intercrystalline failures at
high temperatures.

The presence of vanadium and sodium in fuel oils has introduced serious complications due
to the relatively low melting point of V\textsubscript{2}O\textsubscript{3}, for example, of about 660-690°C, which produces
extremely corrosive liquid oxidation products. No heat resistant alloy is immune to the attack
in presence of small amounts of 0.01\% V in fuel oil.\textsuperscript{8}

\textbf{Carburisation and Decarburisation:}

During processing of organic fuels, gas cracking an\& carburising, carburising conditions
prevail. An increase in chromium and silicon decreases carburisation tendency. Carburisation
causes formation of chromium carbide and thereby reduces resistance to scaling due to impover-
ishment of the matrix in chromium. Fig. 5 depicts carburisation in 27\% Cr steel, in which a thick
carbide envelop has formed at the grain boundaries near the cracks. Fig. 6 shows the microstruc-
ture of a 0.07\% C, 20\% Ni, 25\% Cr steel furnace burner shell which failed under service due to
marked carburisation. A part of it shows the carburised case and below it is the precipitation of
sigma phase. Failure of 18 Cr—8 Ni stabilised stainless steel\textsuperscript{9} used in air craft exhaust systems
was attributed to carburisation by exhaust gases and the precipitation of carbides particularly
at the grain boundaries which lowered the resistance to scaling or corrosion.

Due to partial oxidation, decarburisation results. Surface decarburisation lowers fatigue
resistance. Fig 7 shows decarburisation in low carbon 3\% Cr—0.5\% Mo steel tube after four
months service as a radiant roof in an oil heating furnace at 400\° C.

\textbf{Spheroidisation:}

Oil cracking still tubes are subjected to a temperature of about 650\° C. At this tempera-
ture region, original ferrite and lamellar pearlite structure gradually undergoes spheroidisation
through coalescence of carbide, finally decomposing into ferrite and graphite\textsuperscript{10}. This structure
resembles that of malleable iron.\textsuperscript{11} Spheroidisation lowers the creep resistance. The rate of
spheroidisation in molybdenum steels is decreased by chromium. Aluminium used in deoxi-
dation of steel accelerates spheroidisation.\textsuperscript{10,11}

\textbf{Graphitisation:}

Bursting of a steam pipe at Springdale, a power station\textsuperscript{12} in U.S.A. in 1943 took place due
to graphitisation and indicated that it could occur in a low-carbon molybdenum steels deoxidised
with aluminium at service temperature of 450\° C. Graphitisation\textsuperscript{12-16} is known to occur in
mild steel at temperatures of 450\° C and above. It depends mainly on the steel making process,
Fig. 1—Effect of Chromium Content of Oxidation Resistance of Steel.
(From Corrosion Handbook, Wiley, 1948)
<table>
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<tr>
<th>Zone</th>
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<tr>
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<td>C-0.5Mo</td>
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<td>A3</td>
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<tr>
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<tr>
<td>B1</td>
<td>2Cr-0.5Mo</td>
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**Figure 2** AMOUNT OF OXIDATION (SCALING) IN 250 HOURS (AFTER MILLER, BENZ & DAY^3).
Fig. 3. The Oxide at the Surface of Austenitic Stainless Steel. Penetrating into Grain Boundaries during Dehydrogenation Service at 620/730 deg. C. for one year. (After Rutherford2).

Fig. 4. Intergranular Oxidation of Carbon steel Superheater Tube, (After Rutherford2).
FIG. 5. Carburisation in 27% Chromium Steel at the Grain Boundaries near the Cracks. (After Rutherford).32

Fig. 7. Decarburisation in 3% Chromium 0.5% Molybdenum Steel tube. After 4 months Service at 490°C. (After Rutherford).
presence of alloying elements, heat-treatment, mechanical working and service conditions. Additions of molybdenum$^{17}$ chromium$^{16-18}$ and vanadium suppress tendency towards graphitisation whilst additions of more than $\frac{1}{4}$ lb. of aluminium ton of steel generally promote it$^{17,21}$. Exposure for 10,000 hours at 482-650°C, graphitised killed carbon steels, but in presence of 0.5%, Cr with 0.5% Mo no graphitisation occurred regardless of deoxidation practice$^{18}$. Aluminium treatment facilitates spheroidisation of carbide causing abnormal structures that are more susceptible to graphitisation. Plastic deformation at high temperatures contributes to localised graphitisation$^{21,22}$ which leads to failure in service. It has been noticed that microstructure of failed mild steel tubes in oil cracking stills have completely been graphitised$^{23}$. Fig. 8 shows graphitisation in service of a carbon steel tube which was heated to somewhat below the eutectoid temperature for a period of about three years.

For the prevention of service failures due to graphitisation, the stability of carbide is essential. Low-alloy Ni-Cr-Mo steel is practically immune to graphitisation.

**Carbide Precipitation.**

Austenitic stainless steels are susceptible to intergranular attack at high temperatures. At temperatures of 600-700°C, carbon from the supersaturated solution is precipitated out as chromium carbide which depends on a number of factors like temperature, time, previous mechanical treatment and composition. On prolonged heating small amount of ferrite may also separate. According to generally accepted theory, precipitation of carbide in chromium depletes the surrounding matrix of its chromium and thus lowers its resistance to corrosion besides causing intercrystalline embrittlement. It may be mentioned here that internal strain due to the precipitation of the carbide and of alpha ferrite and correlative electrolytic effects have been put forward to account for the intergranular corrosion. Irrespective of the theory, it has been noticed that the precipitation of carbides lowers the resistance to intergranular corrosion. Failures of tubes in oil refinery service has shown the character of the rupture as intercrystalline without appreciable deformation. Clark and Freeman$^{24}$ concluded that actual failures or pronounced deterioration of 18 Cr—8 Ni cracking still tubes in service for 35,000 to 100,000 hr. at 650-675°C was due to structural changes at the grain boundaries which were dependent on time, temperature and stress. Fig 9 shows intergranular cracking in 18 Cr—8 Ni still tubes which developed during service life of 40,055 hr. at 650-675°C and caused failure. They also noticed carburisation of some of these tubes. Austenitic stainless steels stabilised with strong carbide formers, such as titanium, columbium, tungsten, vanadium and niobium are less susceptible to such inter-granular weakness. It has observed$^{25}$ that aircraft exhaust collector rings of unstabilised stainless steel were more susceptible to intergranular attack during service than the stabilised variety. A few examples of service failures due to carbide precipitation have been discussed by Cotton and Franklin in a paper presented in this symposium.

**Formation of Sigma Phase.**

The formation of sigma phase has recently been discovered and extensively studied in iron-chromium alloys$^{26,27}$. It is a hard, non-magnetic brittle phase. Carbide precipitation precedes as well as accompanies the formation of sigma phase. It may form austenite of suitable composition in the temperature range of about 550-750°C. The formation of sigma phase in austenitic nickel-chrome steels is promoted by high chromium, high silicon, high nitrogen, low carbon, and additions of cobalt, titanium and zirconium$^{28}$. It has been recognized that sigma phase exercises adverse effects on ductility and toughness. Fig. 10 shows sigma phase in 18-8 steel containing molybdenum after exposure at 1500°F for 3,000 hours. Fig 11 depicts brittle zone due to the formation of sigma phase at grain boundaries in 24% Cr—13% Ni steel tube in Radiant Type furnace after operation at 870°C for 3 years. Fig 12 shows the microstructure of the same tube which had failed in service due to intergranular oxidation, there was however, no evidence of simga formation. Perry$^{29}$ mentioned that brittle failure in service of 0.074% C, 24.04% Cr, 21.24% Ni and 0.078% N stainless steel after one year's operation in continuous preheater the temperature range of 700-815°C was associated with marked sigma formation at the grain boundaries.
Fig. 8—Graphitization in Service of Steel Tube (C=0.15%, Mn=0.45%) in Petroleum Cracking Still, for Approximately Three years at somewhat below Eutectoid Temperature, x-100. (After Kinzel and Moore)
Fig. 9—Intergranular Cracking in 18-8 Stainless Steel Tubes Developed During Service at 650-675 deg. C. x-100.
(After Clark and Freeman).
Fig. 11—Brittle Zone due to Formation of Sigma-phase at Grain Boundaries in 24% Cr-13 Ni Tube in Radiant Tube Type Furnace After Operation at 1600 deg. F. for 5 years. x-1000. (After Schei²)

Fig. 12—Failure of a Tube. (Fig. 16) due to Intergranular Oxidation. No sigma phase was present. x-500. (After Schei²)
Miscellaneous Factors:

It has been mentioned that steam is a powerful hydrogenizer of steel when contacting metal at elevated temperatures leading to intergranular brittleness. In the manufacture of ammonia, the presence of chromium in stainless steels, greatly retards the absorption of hydrogen by the steel. Studies of intergranular failures of ferritic steels used as boiler tubes, super-heater tubes, cracking still tubes etc. indicated that such failures rarely occur except in the presence of hydrogen gas.

In low-carbon steels in service for a considerable period at steam temperatures 'ageing' may take place and needles may be precipitated, especially in steels containing high nitrogen. Due to the precipitation of needles during service, the material is embrittled which leads to failure. Fig.13 shows nitrides needles in a failed rivets of flue seams of a Lancashire boiler after 12 years service.

Conclusions:

Service at elevated temperatures may change the microstructure of the material, Metallographic changes such as intergranular oxidation, spheroidisation, graphitisation, decarburisation, carburisation, carbide precipitation, sigma phase formation often play an important role in determining the service life of alloys used at high temperatures.

Acknowledgements:

The authors' grateful thanks are due to the authors of the cited references for reproduction of diagrams and photomicrographs.

References:

Fig. 13—Failure of a Mild Steel Rivet due to Precipitation of Nitride Needles during Service. x—850. (After Tech. Report of British Engine Boiler & Elec. Ins. for 1938—Published in 1948).


Discussion:

Mr. R.A.P. Misra:

The authors referred to the fact that chromium was successful in preventing attack from steam or hydrogen at high temperatures. In one case Ni-Cr-Mo Steel gears carburised in damp carburising compound, were found to be badly pitted. About 1.4% Cr did not prevent the Steel from being attacked by steam at 800 deg.C.

The authors replied that it was well known that when mild steel was heated in an atmosphere of hydrogen, decarburisation took place. But the more deleterious effect was due to the embrittlement caused by possible absorption of hydrogen. The authors had mentioned about the resistance of Ni-Cr stainless steels to hydrogen absorption during the synthesis of ammonia which was due to the formation of layer of chromium nitride preventing diffusion of hydrogen. Besides, it had been reported that diffusion of hydrogen in an iron-chromium alloy was relatively sluggish. Inglis and Andrews* had shown that chromium was beneficial in giving increased resistance to attack by hydrogen and low carbon 3% Cr steel was superior to Ni-Cr-Mo steel as regards its susceptibility to hydrogen attack was concerned. The pitting during the pack-carburisation may be due to other reasons associated with carburising conditions. 1.4% Cr was rather too low to prevent the attack by steam at that elevated temperatures, in any case.

* N.P. Inglis and W. Andrew. ‘The effect on various Steels of Hydrogen at high Pressures and Temperatures’. (Journal of Iron and Steel Institute, 128, 1933, 385).