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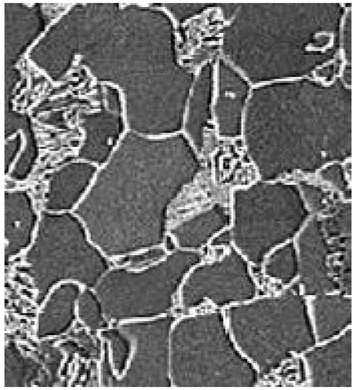
Tubes with nitrate induced SCC in a waste heat recovery boiler



Typical structure of carbon steel: tertiair carbides on the grain boundaries

Nitrate Stress Corrosion Cracking in Waste Heat Recovery Boilers

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Summary

Waste Heat Recovery Boilers (WHRB's) enhance the thermal efficiency of gas turbine power generating plants by capturing the heat from the exhaust gas and utilising it to raise steam for increased electricity production or district heating. Under normal conditions the exhaust gas from the turbine is cooled from around 550°C to 80°C. Care is taken that condensation will not occur in the cooler parts of the boiler.

Nevertheless, during normal operation, dry ammonium nitrate deposits can be formed in the WHRB. These deposits will become wet when the unit is started or shut down, when the temperature falls below the dew point. The deposits may also 'sweat' (i.e. absorb atmospheric moisture and become liquid) during extended plant outage periods. In consequence, Intergranular Corrosion Attack (IGA) and Stress Assisted Intergranular Corrosion Attack (SA-IGA) (in general called stress corrosion cracking) can occur in carbon steel construction materials.

the sensitivity to IGA for a total of 86 steels, of known compositions, was tested. The steels were subjected to aerated ammonium nitrate solutions of 90°C with concentrations ranging between 2 and 35 per cent. After an exposure of 65 hours, cross sections of the steels were studied.

If IGA occurred, the steel was considered sensitive to ammonium nitrate at that (critical) percentage. During the investigations it was observed that alloying elements in several types of steel influenced its resistance to IGA in

6. References

ammonium nitrate. Elements such as molybdenum, manganese and chromium have a positive effect on the resistance to nitrate induced IGA, SA-IGA and stress corrosion cracking, whereas carbon and copper are detrimental. The microstructure of the steel also appeared to be important. In many specimens taken from in-service failures, strings of carbide precipitates were found to be present at grain boundaries. The precipitates were identified to be ternary carbides. It seems, therefore, that the presence of carbides at grain boundaries increases the susceptibility of a steel to intergranular corrosion.

1. Introduction

In a combined cycle power plant, electricity is generated by means of a gas turbine. The exhaust gas from a gas turbine has a temperature of approximately 550°C and still contains a lot of energy. In a waste heat recovery boiler (Heat Recovery Steam generator, HRSG), heat in the exhaust gas is used to produce steam which may be used to drive a steam turbine to produce additional electricity or exported for use in a district heating system.

If only water vapour and carbon dioxide were present in the flue gas condensation would only occur at the water dew point. Even when gases such as nitric oxides (NOx) and hydrochloric acid (HCl) are present, condensation still will occur at temperatures very close to the water dew point. However, the presence of sulphur trioxide (SO3) has a major impact on the dew point of the flue gas. Based on data from literature, (Yen Hsiung Kiang, 1981; Land, 1977, KEMA report, 1990), a computer program was written to calculate the dew points and corrosiveness of various gas compositions. Figures 1 and 2 show the huge difference in dew point between the SO3 gas and the other gases.

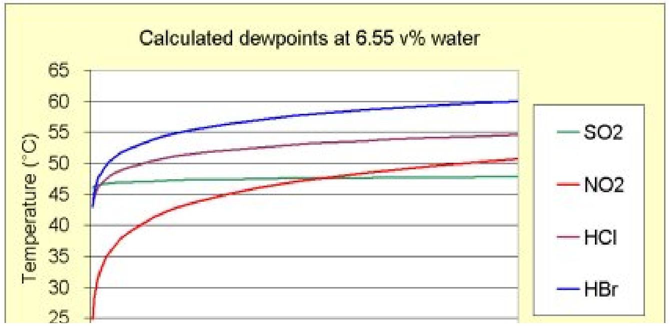

Figure 1 Dewpoint of HCl, HBr, SO2 and NO2 containing gasses with 6.55 % water content.

SO3 is an oxidation product of SO2 which, in turn, is formed when sulphur-bearing compounds are burnt. At temperatures below about

300°C, SO_3 starts to react with water to form concentrated sulphuric acid. Even at low SO_3 concentrations in flue gas, the temperature at which sulphuric acid will begin to condense (often referred to as the sulphuric acid dew point) is well above the water dew point.

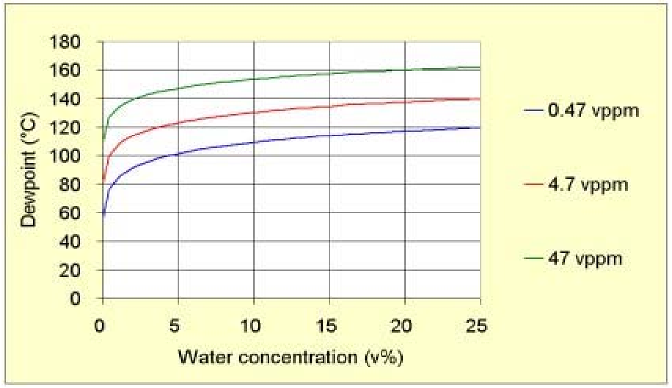

Figure 2 Dewpoints of SO_3 containing gasses with increasing water content.

When the temperature drops below the sulphuric acid dew point the sulphuric acid starts to condense either as small fog droplets or as a film onto the walls. If a fog is formed most of the droplets are carried away with the flue gas and the corrosion rate of exposed, unprotected steel exposed will be low. However, if film type condensation occurs the corrosion rate of unprotected steel can be quite high, due to direct contact with the sulphuric acid film. If calculations are to be made for the corrosion rates for new boiler designs it is strongly advised to assume that film condensation will occur.

In most installations the formation of sulphuric acid is simply prevented by keeping the temperature above the sulphuric acid dew point. However during start-up and shut-down operations the temperature will necessarily fall below the sulphuric acid or water dew points and condensation will occur.

When waste heat recovery boilers were first introduced it was considered that dew point corrosion would be the most important problem to be overcome. In recent years, however, an unforeseen corrosion problem has emerged: that of nitrate stress corrosion cracking (SCC).

2. Field Experience

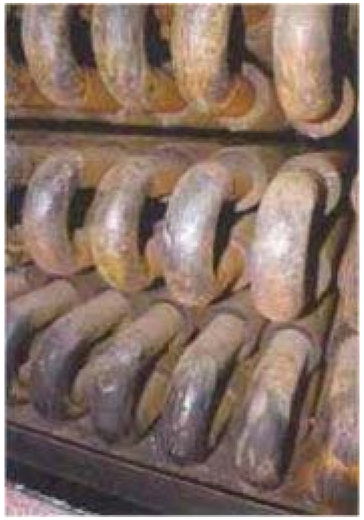

Figure 3

Finned boiler tubes with nitrate induced SA-IGA in the bents. Finned pipes are used to increase the surface area of the heat exchangers.

In the 1990's several failures caused by SCC occurred in the WHRB of combined cycle power plants in the Netherlands (KEMA 2000). The cracks were mostly found in the low temperature heat exchangers. In general, these had been fabricated from steel 35.8, a standard plain carbon steel. Most cracking occurred in bends where mechanical stresses were relatively high. Microscopic analysis of samples revealed that intergranular corrosion had occurred and it was frequently reported that complete grains of material had become detached. See Figures 3 and 4.

Because in a few cases very thick deposits of ammonium nitrate were found near the damaged areas, nitrate SCC was identified as the cause. Initially the affected tubes were replaced with alloy 15Mo3 because it was presumed that this material had a higher resistance to nitrate SCC. This assumption was based on various published papers on the better corrosion resistance of the steel 15Mo3 (Bunning et all 1990, Dahl et all 1987, Drodten et all 1991, Krautschick et all 1988). Heat treatments to reduce stress levels were also tried as a remedy. However the material 15Mo3 later also failed by nitrate SCC.See Table 2.

Because of the uncertainties surrounding the failures, the Netherlands electricity companies jointly funded a research project to investigate the causes of nitrate stress corrosion cracking.

3. Corrosive conditions for nitrate SCC

It was agreed that an import step would be to find the source of ammonium nitrate, as it was not a component of natural gas, the fuel used in combined cycle units in the Netherlands.

Combustion air for a gas turbine is filtered before it is used to burn the fuel and cool turbine components. However, small particles (smaller than 5 µm in diameter) such as aerosols can slip through the filter.

The major components of aerosols in the Netherlands monitored over a ten year period were reported to be: 7 µg/m3 sulfate, 3 µg/m3 nitrate, 3 µg/m3 ammonium and 2 µg/m3 chloride (present as sodiumchloride). These amounts

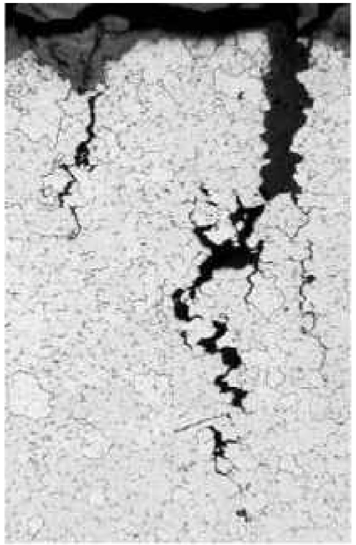

Figure 4

Cross section of tube material reveals SA-IGA.

are low. However, gas turbines use vast quantities of air and just 25 per cent of the oxygen intake is used to burn natural gas. This means that a considerable amount of ammonium nitrate can enter the recovery boiler.

Another source for the nitrate is transition of NOx. NOx has been formed in the gas turbine in a considerable amount. The exact mechanism for the transition of NOx into the nitrate is not known. However, Feitelberg and Correa [2000] identified coal mono-oxide (CO) as one of the most important promoters for the formation of nitrogen di-oxide (NO2) in the combustion turbine exhaust gas. They mentioned a NO and CO concentration in the exhaust gas of 25 ppmv and 50 ppmv respectively. At temperatures between 450°C and 750°C up to 50 per cent of the NO can be oxidised to NO2 within just one second. Since NO2 is a precursor for nitrate, these compounds may very well be formed inside the recovery boiler.

The most likely nitrates to form are ammonium nitrate and sodium nitrate. Because most of the components in a recovery boiler are made of unprotected steel, iron nitrate may form as well. A summary of the physical properties of these nitrates is presented in Table 1.

Table 1: Physical properties of nitrates that may be present in a waste heat recovery boiler.

Material	Formula	Solubility in water at 0 °C (g/l)	Solubility in water at 100 ° C (g/l)	Melting point (° C)	Boiling point (° C)
Ammonium nitrate	NH4NO3	1183	8710	170	210
Iron nitrate*6H2O	Fe(NO3) 3*6H2O	150	—	35	Decomposes at 125
Iron nitrate*9H2O	Fe(NO3) 3*9H2O	Soluble	Soluble	47	Decomposes at 125
Sodium	NaNO3	921 (at	1800	306	Decomposes

nitrate		25°C)			at 380

From Table 1 it can be concluded that iron nitrates would not be sufficiently stable to remain in the boiler. Both sodium and ammonium nitrate are comparatively stable. Ammonium nitrate is remarkable because of its relatively low melting and boiling points.

Because of this, ammonium nitrate will deposit in the cooler parts of the boiler, near the flue gas outlet. Based on the physical data, sodium nitrate should be deposited nearer to the middle of the recovery boiler because of its higher melting point.

To date, only ammonium nitrate deposits have been found in the cooler parts of recovery boilers, close to the chimney stack. Under normal conditions, the flue gas will be cooled to about 80°C. At this temperature, however, ammonium nitrate is solid and is most likely to have been deposited on the tube walls. Because ammonium nitrate can not leave the recovery boiler in a vapour state it will accumulate over time on the heat exchanger surfaces near the stack. As long as the temperature of the flue gas is well above the dew point this will not produce problems despite the fact that ammonium nitrate is slightly hygroscopic. However, if the temperature drops below the dew point, for instance during start-up, shut-down or periods of downtime, only a limited amount of water will be necessary to produce a very concentrated solution of ammonium nitrate on the heat exchangers.

SCC in carbon- and low alloy steels can occur in environments that contain carbonates, phosphates, hydroxides and nitrates (Perdieus et all 1977, Mc Evely 1990). The areas of susceptibility to SCC for several ionic species are identified in a corrosion potential/pH - or Pourbaix - Diagram, see Figure 5.

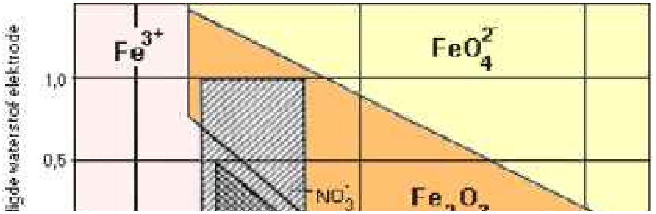

Figure 5

Pourbaix diagram of iron. Shaded areas indicate danger zones where SCC caused by nitrates, phosphates, carbonate/bicarbonate and hydroxide respectively can occur.

Due to small amounts of SO3 that are often present in flue gas, condensed moisture will be acidic. In addition, the relatively high oxygen content in the exhaust from the gas turbine (approx. 15 per cent oxygen) means that, in general, the corrosion potential will be relatively high. Both conditions increase the likelihood of SCC in steels that are exposed to nitrates.

4. Materials testing

Steel that is in contact with a more concentrated ammonium nitrate solution is attacked along the grain boundaries by intergranular corrosion. In locations where high mechanical stresses occur and /or a critical deformation rate is exceeded, IGA will lead to the development of cracks (SA-IGA). This, in turn, is called often in general SCC, which was observed in the WHRB failures.

In this investigation, the influence of the following factors on intergranular corrosion were studied:

- · corrosion potential
- · chemical composition of steel
- · structure of the steel.

4.1 Influence corrosion potential (related to oxygen content).

To investigate the influence of the corrosion potential, a carbon steel was exposed in a 5 per cent ammonium nitrate solution at 50°C at different constant potentials. At a potential of - 400 mV versus a Saturated Hydrogen Electrode (SHE) the corrosion was minimal (Figure 6).

At a potential of +100 mV SHE severe IGA occurred in the steel. Within a period of 16 hours steel was attacked to a depth of 300 µm. (Figures 7 and 8). The observed intergranular corrosion showed a remarkable resemblance to the microstructure found in the failures from recovery boilers.

These results indicate that IGA only occurs above a certain potential. Taking into account the relative high oxygen content in the exhaust of a gas turbine of around 15 per cent it will be difficult to remain below the critical potential.

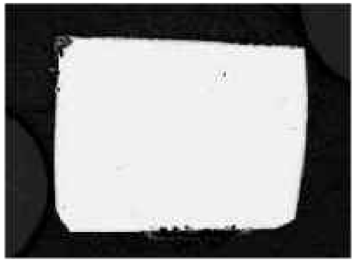

Figure 6.

Sample held at a potential of -400 mV SHE in a 5% NH_4NO_3 solution at 50 °C; just some pitting occurred

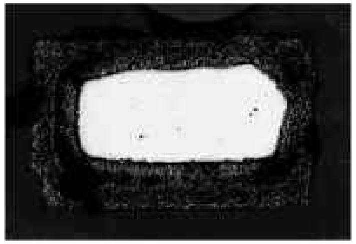

Figure 7.

Sample in the same solution but at +100 mV SHE. Intergranular corrosion consumed a large part of the sample within 16 hours.

4.2 Chemical composition of steel

Much research has been done on SCC; in particularly the corrosion resistances of carbon steel and 15Mo3 were compared . (Bunning et all, 1990; Dahl et all, 1987; Drodten et all, 1991; Krautschick et all, 1988).

In the present investigation steels ranging from carbon steel up to 9 per cent Cr steel were tested, with emphasis on the real chemical composition. For a total of 86 steels, with known compositions for at least 10 elements, the sensitivity to Intergranular Attack (IGA) was tested. The steels were subjected to aerated ammonium nitrate solutions of 90°C with concentrations ranging between 2 and 35 per cent. After an exposure of 65 hours, cross sections of the steels were studied. If IGA occurred for 3 grains deep or more, the steel was considered sensitive to ammonium nitrate at that (critical) percentage.

A correlation between the critical nitrate percentage and the chemical composition was found. For carbon steel, 15Mo3, 13CrMo4.4, 10CrMo9.10, 9 per cent Cr and 12 per cent Cr steels the regression formula was calculated to be:

Critical nitrate per cent = 6Mo + 2Cr + 1Mn + 8 - 12Si - 8Cu - 1C

(R2=0.85)

The correlation between measured and calculated critical nitrate percentages is given in Figure 9. With an R2 of 0,85 the fit of the formula is only moderate.

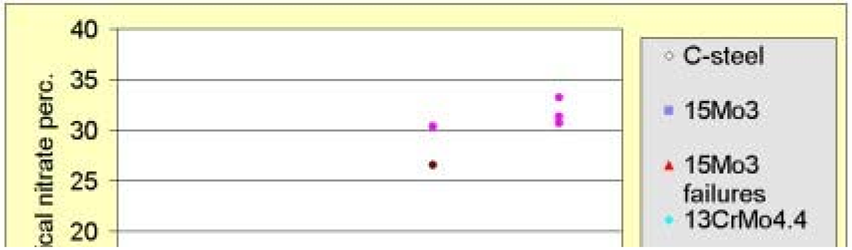

Figure 9. Correlation between measured and calculated critical nitrate concentrations for C-steels, 15Mo3, 13CrMo4.4, 10CrMo9.10, 9% Cr and 12% Cr steels.

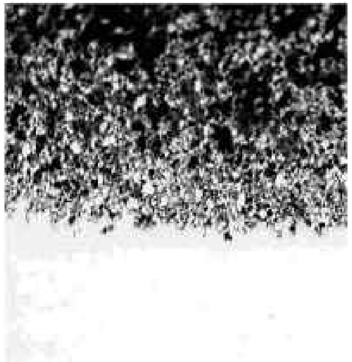

Figure 8.

Detail of the corrosion front in the sample from figure 3b shows the intergranular nature of the attack.

However, if the carbon steels are left out a better fit can be obtained.For the steel 15Mo3, 13CrMo4.4, 10CrMo9.10, 9% Cr and 12% Cr the regression formula becomes:

Critical nitrate per cent = 20Mn + 10Mo + 2Cr + 1Si - 5 - 35C - 7Cu

(R2=0.95)

The correlation between measured and calculated critical nitrate percentages is given in Figure 10 for the last mentioned group of steels.

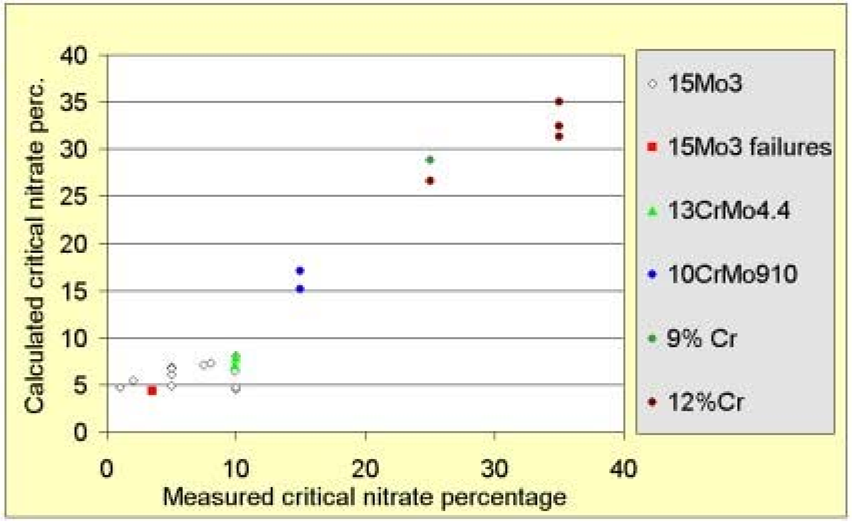

Figure 10. Correlation between measured and calculated critical nitrate concentrations for 15Mo3, 13CrMo4.4, 10CrMo9.10, 9% Cr and 12% Cr steels.

From this work it can be concluded that the elements Mo, Mn and Cr have positive effect on the resistance to nitrate induced IGA, whereas the elements C and Cu are detrimental. If Si has any effect it is uncertain. From this study it can be concluded that the resistance to nitrate induced IGA can be estimated quite reliably, based upon the chemical composition of the steel alone.

As a rule of thumb it can be stated that carbon steels and 15Mo3 have the same resistance to IGA. The steel 13CrMo44 has a slightly higher resistance than carbon steel and 15Mo3. Steel 10CrMo9.10 is obviously better than these steels.

All steels from heat exchanger failures from recovery boilers had a rather low calculated critical nitrate percentage. They all were lower than 6.5 %. These field data are summarised in Table 2 (KEMA, 1995). From these field examples only the steels of cases A 1994 and B 1995 were tested, because the tests were finished in 1997.

Table 2: The calculated critical nitrate value for IGA of the materials from heat exchanger failed due to nitrate induced stress corrosion cracking.

Case	Steel	Analysis						Calculated critical nitrate	
		C	Mo	Mn	Cu	Si	Cr	Form.1	Form. 2
A 1994	St 35.2	0.11	0.02	0.61	0.21	0.31	0.08	3.4	-
B 1995	15Mo3	0.17	0.25	0.67	0.14	0.22	0.08	-	4.4
B 1997	15Mo3	0.15	0.27	0.61	0.18	0.23	0.14	-	3.9
C 1997	St 35.2	0.12	0.02	0.46	0.20	0.22	0.07	4.4	-
D 1997	St 35.2	0.11	0.01	0.48	0.04	0.25	0.06	5.3	-
D 1997	15Mo3	0.12	0.33	0.61	0.32	0.21	0.08	-	4.5
E	St	0.08	0.01	0.49	0.14	0.15	0.07	5.8	-

1997	35.2								

In practice, it is probably that the corrosive nitrate environment will not exceeded a concentration of about 10 per cent for most of the time. Thus, a steel with a composition similar to, or better than, 10CrMo9.10 (a calculated critical nitrate percentage of at least 10 per cent) is advised, because this steel will resist the IGA under practical conditions.

So far no attention had been given to the contribution of the microstructure of the steel. It was expected that an even better correlation would be found if the microstructure were taken into account.

4.3 Microstructural Effects

During the study of samples of material from the failed recovery boilers it was noticed that the steels often had considerable amounts of grain boundary carbide precipitation. Sometimes all grain boundaries were covered with carbides (carbide ribbons). The carbides where identified as ternary cementite. An example of this can be seen in Figure 11.

Ternary cementite is formed in heat treatment during cooling in the temperature range between 723°C and 400°C. At 723°C up to 0.025 per cent carbon will dissolve in ferrite. However during cooling the solubility of carbon will decrease. At these temperatures carbon can diffuse to the grain boundaries where it will precipitate as a thin layer of cementite (Fe3C). Pearlite (a eutectic mixture of ferrite and cementite) is partly dissolved and converted to ternary cementite on the grain boundaries. Cold work will accelerate the formation of ternary cementite even at low temperatures.

The present work on in-service material failures has shown that in addition to the corrosion potential and chemical composition of a steel, ternary carbides are also of great influence at initiating nitrate induced stress corrosion cracking. In the past, the microstructure of a material was hardly considered during design and construction of WHRB's.

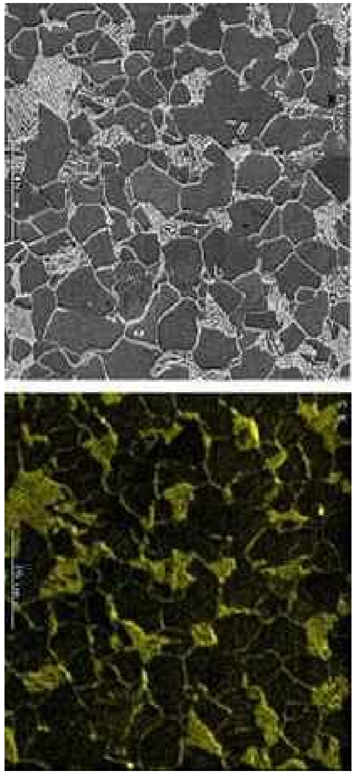

Figure 11

(A) -SEM image of the microstructure of a 15Mo3 steel that showed nitrate induced SCC. (B) - Carbon WDX mapping of the same area shows the distribution of carbon (white is carbon, black is no carbon).The pearlite islands are normal in this material. The large amount of ternary cementite that has deposited on the grain boundaries is not normal, however.

To the best of our knowledge, only one paper has been published in which was mentioned that carbide precipitates on the grain boundaries of carbon steel had a detrimental effect on the resistance to SCC (Langenscheid, 1989). However, results from the present study indicated that microstructure also appears to have a significance influence on field service life. Further studies are planned with carbon and low alloy steels to measure the influence of ternary cementite on the sensitivity to SA-IGA and SCC.

5. Conclusions

- Ammonium nitrate was found in waste heat recovery boilers and is most probably formed by the combination of NOx from the exhaust of the gas turbine with aerosols in the combustion air. Crystals of nitrate tend to deposit in the cooler regions of a WHRB.
- During start-up and shut-down the metal temperatures in the boilers tend to fall below the dew point. Condensing water (with some sulphuric acid) will dissolve the precipitated ammonium nitrate, resulting in the formation of a concentrated nitrate solution on the steel surface.
- Carbon steel and low alloy steel are sensitive to IGA in ammonium nitrate solutions if the nitrate concentration is above a critical composition, and the corrosion potential of the material in the environment is more anodic than a critical potential.
- The critical concentration for nitrate induced IGA can be calculated from the chemical composition. The elements Mn, Mo and Cr have a positive effect on the corrosion resistance while Cu and C have a negative effect.
- Ternary cementite precipitated as a continuous ribbon on the grain boundaries of carbon and low alloy steels will increase the sensitivity to nitrate induced IGA.

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