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Metallic Components in Coal–Gasification

Fuel Gas Paths

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Abstract

Gasification systems offer the potential to generate electricity from coal much more efficiently and with substantially less environmental impact (i.e. lower CO₂, SO_x, NO_x and particulate emissions) than conventional pulverised fuel combustion systems. There is a wide variety of gasification processes and fuel gas path options that continue to be investigated. However, the hot fuel gas path environments produced by all these gasification systems have the potential to be extremely aggressive for materials during plant operation and downtime periods.

This paper reports on a series of tests carried out to investigate the performance of candidate materials for two types of component in hot fuel gas path environments i.e. the fuel gas cooler and metallic filter elements. One series of laboratory tests was carried out for up to 3000 hours at temperatures in the range 450–550°C in which materials were exposed to gases that simulate both oxygen and air-blown gasification systems. The materials in these tests were exposed both bare and with a coverage of the appropriate deposit for the type of gasification system. A second series of test was carried out to investigate the downtime corrosion behaviour of candidate heat-exchanger materials in which materials covered with a deposit were exposed to humid atmospheres. A third series of tests was carried out

combining the first two test methods; i.e. materials were exposed alternately to high temperature fuel gas environments and downtime conditions. The performance of the materials in all these tests was assessed using standard optical and SEM/EDX techniques, as well as dimensional metrology. The combined results from these assessment methods allowed the materials to be ranked in terms of their performance in each of the types of test. The relative importance of these different test methods in the selection of materials for different fuel gas path components is discussed.

Keywords: materials issues, gasifier, heat exchanger, filter, downtime corrosion, deposits.

Introduction

A number of coal gasification systems have been developed [ref01], based on different types of gasification process, e.g. entrained flow, fixed bed, oxygen blown fluidised bed. Variations on these processes may use either oxygen or air as their oxidant in the gasifier vessel and can be controlled to give varying degrees of conversion of the coal to fuel gas, from complete (>99% conversion) to partial (e.g. 75% conversion). Once generated, the fuel gases need to be cooled and cleaned before use, e.g. being burnt in gas turbines. All gasification technologies require a heat exchanger (often called either a syngas cooler or fuel gas cooler) between the gasifier and the gas cleaning system. The function of this heat exchanger varies depending on the type of gasifier, gas cleaning requirements (e.g. hot dry cleaning or wet scrubbing) and steam cycle needs. However, gasifier hot gas path environments are potentially very aggressive for materials both during plant operation and off-line periods. This has the effect of imposing a temperature window for the safe operation of these heat exchangers (with current materials restricting their use to modest steam conditions and preventing their use as superheaters with commercially viable lives). Thus, in different gasification systems evaporators are used to produce saturated steam at 10 MPa/320 °C with metal temperatures of 320–400 °C depending on the syngas temperature [ref02]. However, there is a drive towards raising evaporator steam conditions to 18 MPa/350 °C, with corresponding metal temperatures

of 380–450 °C. Under these steam conditions, the use of highly alloyed materials will be required to give economically viable heat exchanger lives in gasifier hot gas paths [#ref03]. However, some gasification cycles would be more efficient (and economically viable) if at least some superheating could be carried out by a heat exchanger in this location in the hot gas path: this would involve steam at temperatures of 500–550 °C with corresponding metal temperatures of 550–600 °C [#ref02]. Both water tube and smoke tube heat exchanger designs are reported in the literature for gasifier heat exchangers. These radically diverse types of designs will have dissimilar characteristics in terms of deposit formation, due to the different gas flows around or through them. Significant differences in the hot gas path environment exist between the various gasification systems which utilise different fuels, but unfortunately these simply have the effect of changing the balance between different potential degradation modes arising. It is possible to carry out the gas cleaning by water scrubbing the cooled fuel gases, but this leads to lower cycle efficiencies and requires the provision of a scrubbing and waste-water treatment facility, which generates liquid waste for later disposal. The first generation gasification systems have been built to use water scrubbing for gas cleaning. Hot dry gas cleaning, using barrier filters to remove particulates and catalysts/sorbents to remove gaseous species (e.g. sulphur, chlorine, ammonia), offer higher cycle efficiencies as well as lower capital and operating/disposal costs. However, hot dry gas cleaning is still at the developmental stage and so only parts of the processes are included in the latest demonstration plants.

There are many significant differences between the various gasification systems [#ref01], both in terms of the operation of the actual gasification process and the requirements for different downstream components with different ranges of operating conditions. These give rise to economic and efficiency differences between the systems that are beyond the scope of this paper. However, from the perspective of materials performance and optimum materials selection, the component operating conditions and the environments produced in each of the systems are critically important.

Table 1 lists published bulk gas compositions produced by some of these gasification systems.

Table 1 Gasifier Gas Compositions

Gas Species	Units	Oxygen Blown			Air Blown
		Entrained Slagging		Fluidised Bed	Fluidised Bed
		Dry Feed	Slurry Feed		
CO	%	62–64	35–45	30–40	15–20
CO ₂		2–4	10–15	10–15	5–8
H ₂		27–30	27–30	24–28	10–15
H ₂ O		0–3	15–25	11–20	5–12
N ₂		1–5	0–2	0–2	40–50
CH ₄		n/a	n/a	3.5	2–4
H ₂ S *	vpm	2000–12000	2000–12000	2000–12000	300–5000
NH ₃		200–500	2000–5000	200–500	500–1500
HCl *		50–1000	50–1000	50–1000	50–500

* Dependent on coal sulphur and chlorine content

Further differences arise from the minor and trace gas species which are very important in determining materials performance, both through direct reaction and indirectly through deposit formation and subsequent reaction. The levels of these minor and trace gas species in these gasification systems are rarely reported in the published literature.

The majority of the coal gasification processes which have reached the pilot and demonstration plant scale are based on pressurised oxygen blown entrained flow slagging gasifiers [4] but a number of air blown pressurised fluidised bed gasification (PFBG) processes have been developed. The use of partial gasification systems results in

hybrid cycles, in which unburnt carbon from the gasifier is burnt in a combustor to raise steam for the steam cycle [#ref05–#ref07].

The overall aim of this study was to assess the potential corrosive effects of deposits formed on heat exchangers and metallic filter elements in ABGC and IGCC systems. The effects of deposits on High Temperature Gaseous Corrosion (HTGC), Downtime Corrosion (DTC) and synergistic interactions were assessed. This work helps to identify the operating conditions and materials that could produce rapid material failures due to interactions with the deposits formed during gasification plant operation.

Degradation Modes

The performance of materials in various simulated and real coal–gasification atmospheres has been investigated by research groups in the US, Japan and Europe for more than 25 years [#ref02–#ref03, #ref08–#ref25]. The initial generic studies investigated the performance of materials in a range of highly reducing atmospheres with varying levels of sulphidation at high temperatures. Later studies have tended to concentrate on higher alloyed materials and/or lower exposure temperatures. Following plant experience, more recent studies have been targeted at increasingly realistic exposure simulations to match the degradation morphologies observed in practice [18].

Several potential degradation processes have been established during the studies carried out in these types of environment [#ref02–#ref03, #ref08–#ref25], including:

- elevated temperature gas phase induced corrosion: this includes oxidation, sulphidation, carburisation/metal dusting and chlorination;
- corrosion induced by surface deposits either as particles from the gasifier or by species condensing onto those particles or directly onto the component surfaces;
- dewpoint corrosion: induced by high temperature deposits absorbing moisture or gaseous species (such as HCl or H₂S)

reacting with condensing water during part-load operation (to form HCl and polythionic acids) or deposits forming on cooler gas path surfaces;

- downtime corrosion: induced by high temperature deposits becoming damp during plant shut-down, gaseous species (e.g. HCl, H₂S, etc.) reacting with condensed water during plant shut-down (e.g. forming HCl and polythionic acids) or hygroscopic deposits being exposed to damp air during plant shut-downs (e.g. during the course of maintenance operations);
- interaction of any of the above degradation modes with mechanical factors, e.g. creep or fatigue, to produce synergistic degradation, e.g. creep-corrosion or corrosion-fatigue;
- spallation of corrosion products: of critical importance on the clean side of the filter unit from where spalled scale may enter the gas turbine and cause erosion damage.

In any gasification system, different combinations of degradation mode will be found on components along the hot gas path due to variations in operating temperature and local plant environment (deposition, local gas composition, i.e. the extent of gas clean-up, gas temperature at that point in the system, component temperature, etc.).

Most studies of materials in gasifier hot gas paths (mainly heat exchangers materials) have targeted elevated temperature gas phase induced corrosion with increasing levels of realism allowing the successful development of predictive models for sulphidation / oxidation [e.g. #ref15, #ref24–#ref25]. However, pilot plant tests have shown that deposit covered components can suffer rapid failure due to both dewpoint and downtime corrosion. Thus, it is important to avoid (or at least minimise) damage by these degradation modes.

Experimental

Materials

Table 2 gives the composition of the heat exchanger alloys and metallic filter alloys used and also lists the alloys corresponding Pitting

Resistance Equivalent Number (PREN (including tungsten)) as given by:

$$\text{PREN} = \% \text{Cr} + 3.3(\% \text{Mo} + 0.5\% \text{W}) + 16\% \text{N}$$

It has been established that the pitting behaviour of stainless steels can be broadly related to composition using empirical relationships such as PREN [26]. Crevice corrosion is influenced by many factors and therefore PREN is generally not so useful for prediction of this type of behaviour. In the HTGC tests the AISI 316L and Hastelloy X were in the form of Sintered Metal Powder (SMP).

Table 2. Compositions of Alloys (¹Only tested in HTGC tests, ²not tested in HTGC tests)

Alloy	Nominal Composition (wt %)					PREN
	Cr	Ni	Fe	Mo	Others	
Fecralloy ¹	18		Bal		4.6Al 0.3Si 0.25Y	18.0
Alloy 800H	21	32	Bal		0.75Mn	21.0
AISI 316L	16.8	11.2	Bal	2.3	1.5Mn	24.0
AISI 310	25	20	Bal		1.5Mn 1.5Si	25.0
IN690 ¹	29	Bal	9		0.5Si 0.5Cu 0.5Mn	29.0
Haynes HR160	28	Bal	3.5	1.0	30Co 2.7Si 1W 0.5Mn	29.7
Haynes 556 ²	21.6	19.9	Bal	2.8	18Co 2.4W 0.2N	38.0
Sanicro 28 ²	27	31	Bal	3.5	2Mn	38.6
IN 625 ²	21.5	Bal	2.5	9.0	0.5Mn	51.2
Hastelloy X ¹	22	Bal	18	9	1.5Co 1Si 1Mn 0.6W	52.7
C276 ¹	15.5	Bal	5.5	16	3.8W 2.5Co 1Mn 0.35V 0.08Si	74.6

High Temperature Gaseous Corrosion

HTGC tests using controlled atmosphere furnaces were carried out using the parameters detailed in Table 3. Specimens were exposed to either the 'high H₂S' (= IGCC) or 'low H₂S' 1 (= ABGC) simulated gases, the gas compositions of which are given in Table 4. The components of the test gas were supplied from two gas cylinders and mixed at the entrance of the furnace. The moisture was added to the hydrogen sulphide / carbon monoxide gas stream by bubbling the gas through a heated flask containing deionised water.

Table 3. Test Parameters (*High = IGCC and Low = ABGC)

Test	Time (hrs)	Temp (°C)	Gas H ₂ S Level*
1	3000	450	High
2	1000	550	High
3		550	Low 1

Table 4. Gas Compositions

Gas	Gas Compositions (vol.%)							
	CO	CO ₂	H ₂	H ₂ S	H ₂ O	HCl	CH ₄	N ₂
'High H ₂ S'	Bal	4.0	31.0	1.00	3.0	0.04	–	–
'Low H ₂ S' 1	18.0	8.4	14.7	0.02	10.4	0.06	2.5	Bal
'Low H ₂ S' 2	6.9	3.2	5.6	0.01	4.0	0.12	–	Bal

Simulated deposits were applied to samples with a recoat interval of 1000 hours. Either the 'High H₂S' 1 or 'Low H₂S' 1 deposits (Table 5) were used (i.e. to match the test gas). Samples were also tested without an applied simulated deposit. These deposits were produced by mixing the dry deposit components together with propan-2-ol to produce a slurry. This slurry was applied to one side of the test

specimens and the solvent evaporated before testing. After testing, maximum oxide thickness measurements were made on polished cross-sections of samples using optical microscopy.

Table 5. Deposit Compositions

Deposit	Deposit Compositions (wt.%)						
	Flyash	Char	NaCl	KCl	FeCl ₂	PbS	ZnS
'High H ₂ S' 1	90	–	3.74	–	6.26	–	–
'Low H ₂ S' 1	–	90	3.74	–	6.26	–	–
'High H ₂ S' 2	90	–	2	1	2	4	1
'Low H ₂ S' 2	–	90	2	1	2	4	1

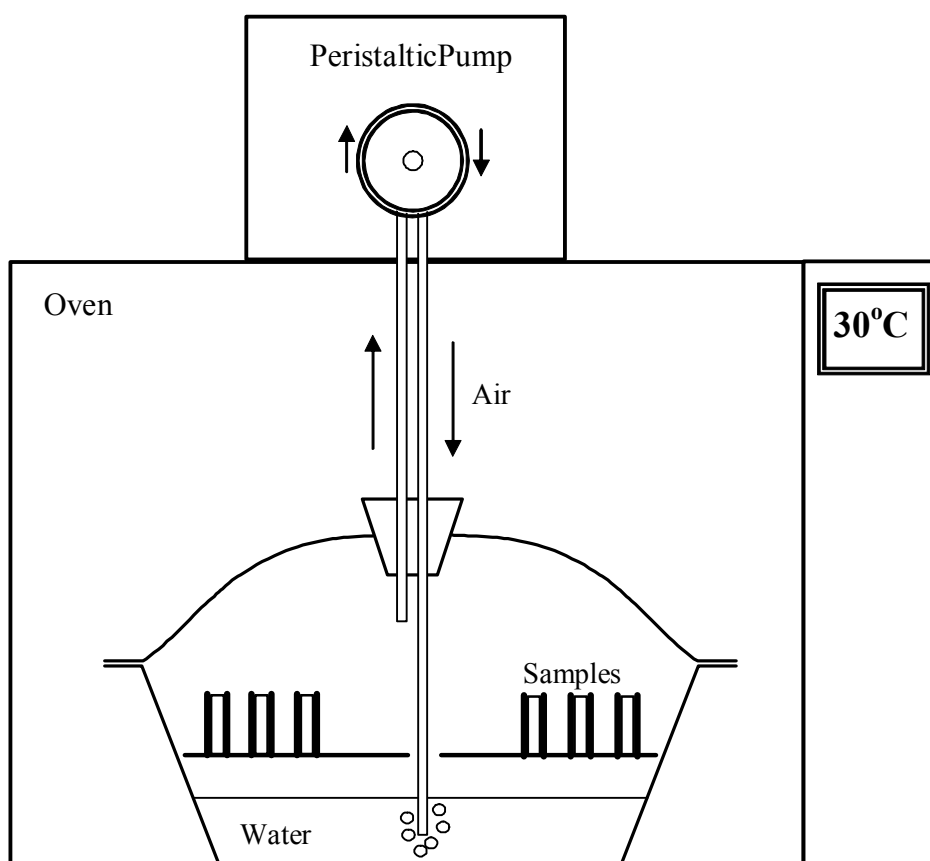


Figure 1. Diagram of DTC Testing Setup.

Downtime Corrosion

DTC testing was carried out using a modified EPRI downtime corrosion test using the setup shown in Figure 1. Specimens were coated with the 'Low H₂S' 1 deposit (Table 5) and were exposed to water saturated air at 30 °C for 25 hour cycles. After exposure the deposit was removed and the specimens cleaned and examined before the next cycle. Longer cycles were also used to investigate whether the more resistant materials had an initiation period greater than 25 hours. Damage was assessed by visual inspection and depth of attack measured microscopically [ref27].

Synergistic Damage

Samples were exposed to cycles of HTGC testing followed by DTC testing for four cycles. The furnace exposure was for 500 hours at 400°C in the 'Low H₂S' 2 gas mixture (Table 4). DTC exposure was for 100 hours at 70°C. Deposits with composition 'Low H₂S' 2 (Table 5) were applied prior to the furnace exposure.

Results & Discussion

High Temperature Gaseous Corrosion

The results of the HTGC testing are shown in Figures 2 to 4. The maximum oxide thickness was used as the measure of damage in the HTGC tests as the sulphide layer was incorporated with the deposit. Figure 2 gives the maximum oxide thickness for the 3000 hour test at 450°C in the simulated IGCC gas. During this test the Hastelloy X specimen (SMP) was removed after 2000 hours with a maximum oxide thickness corresponding to 100% of the metal particle size. After 3000 hours the AISI 316L (SMP) also had a maximum oxide thickness corresponding to the metal particle size.

Figure 3 gives the maximum oxide thickness for the 1000 hour test at 550°C test in the simulated IGCC gas. As above, the Hastelloy X specimen has a maximum oxide thickness corresponding to 100% of the metal particle size. Comparison of Figures 2 and 3 indicate the effect that the test temperature increase from 450 to 550 °C had (even though the test times differ). Overall the damage to the materials is

comparable between these tests indicating similar oxide thicknesses after 1000 hours at the higher temperature compared with those measured after 3000 hours at 450 °C.

Figure 4 gives the maximum oxide thickness for the 1000 hour test at 550°C test in the simulated ABGC gas. Comparing Figures 3 and 4 clearly shows that the IGCC gas is far more aggressive than the ABGC gas towards the majority of the materials. However, the damage on the Fecralloy and AISI 310 samples was comparable for both gas compositions even when a deposit was present.

In Figures 2–4 the effect of the applied deposits compared to the case without deposit is mixed. The deposits either cause an increase in the oxide thickness or for some alloys appears to be protective. For some alloys the effect of the deposit is severe.

The data generated by this part of the work can be used for material selection and/or setting plant operating conditions. The failure criteria used for the lifetime calculations will depend on the material form and location in the system. For example, wastage of a heat exchanger or oxide/sulphide blocking of filter media pores, use different life–assessment criteria.

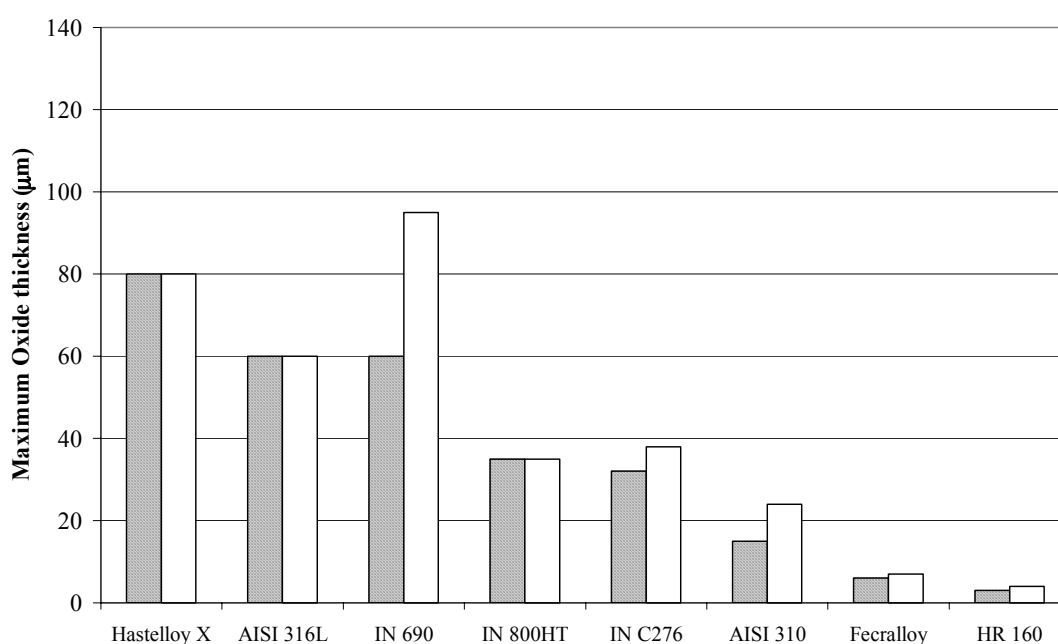


Figure 2. High H₂S gas at 450 °C 3000 hours (Hastelloy X only 2000 hours) (Shaded is without deposits and unshaded with deposits)

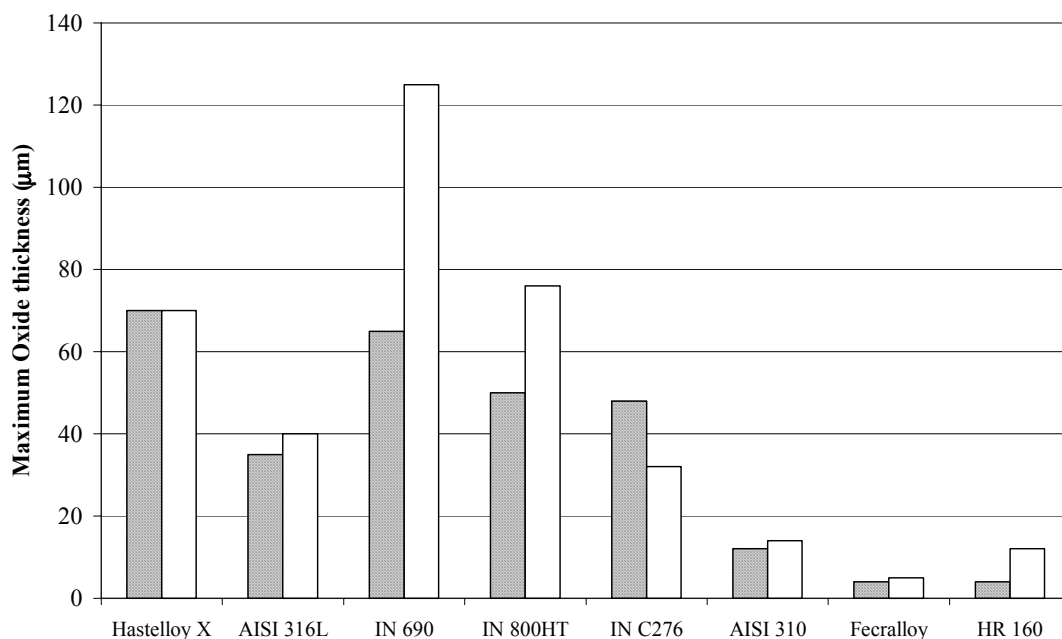


Figure 3. High H₂S at 550°C 1000 hours (Shaded is without deposit and unshaded with deposits)

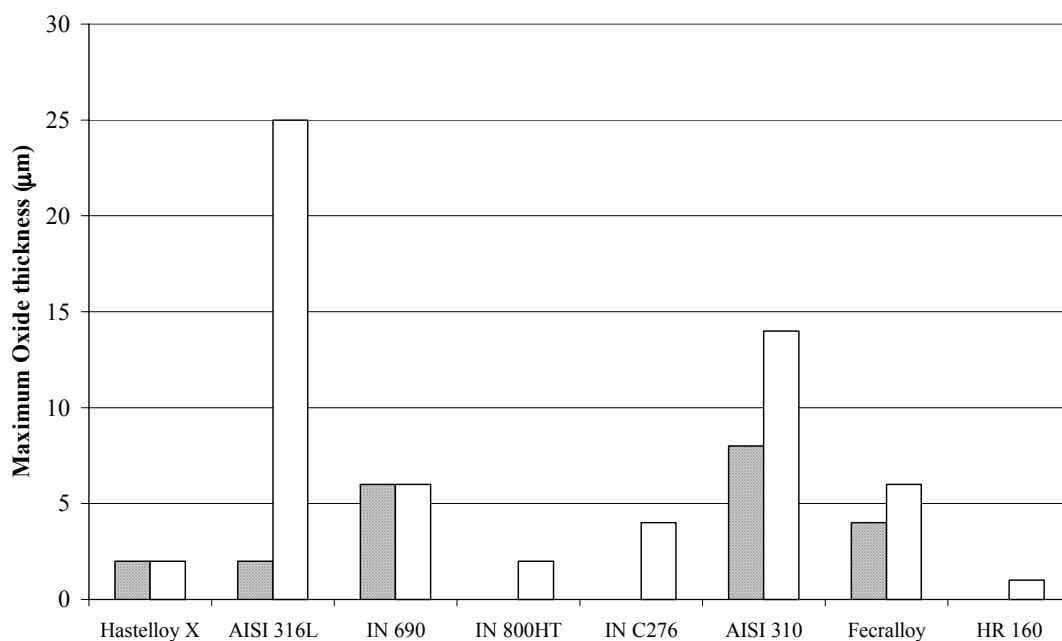


Figure 4. Low H₂S at 550°C 1000 hours (Shaded is without deposit and unshaded with deposit) (no bar indicates <1 µm)

Downtime Corrosion

The severity of attack on the materials tested varied significantly with Alloy 800H and AISI 316L being the most severely attacked, as shown

in Figure 5. In general the attack was a mixture of pitting and crevice corrosion but Alloy 800H also showed intergranular attack. The other materials showed little or no attack and no effect of increasing the test cycle time from 25 to 75 hours was evident. AISI 310 had many more pits than Haynes 160 (only one pit) and Sanicro 28. Alloy 800H was very severely attacked over almost all of the exposed surface; a feature of this damage was that over areas of intense attack a thin hard black layer had formed. The attack on the AISI 316L changed from an under-deposit/crevice type observed for periods of up to 50 hours to predominately pitting after longer exposures. The ranking of the overall resistance of the materials to the DTC test matches the PREN ranking well (Table 2).

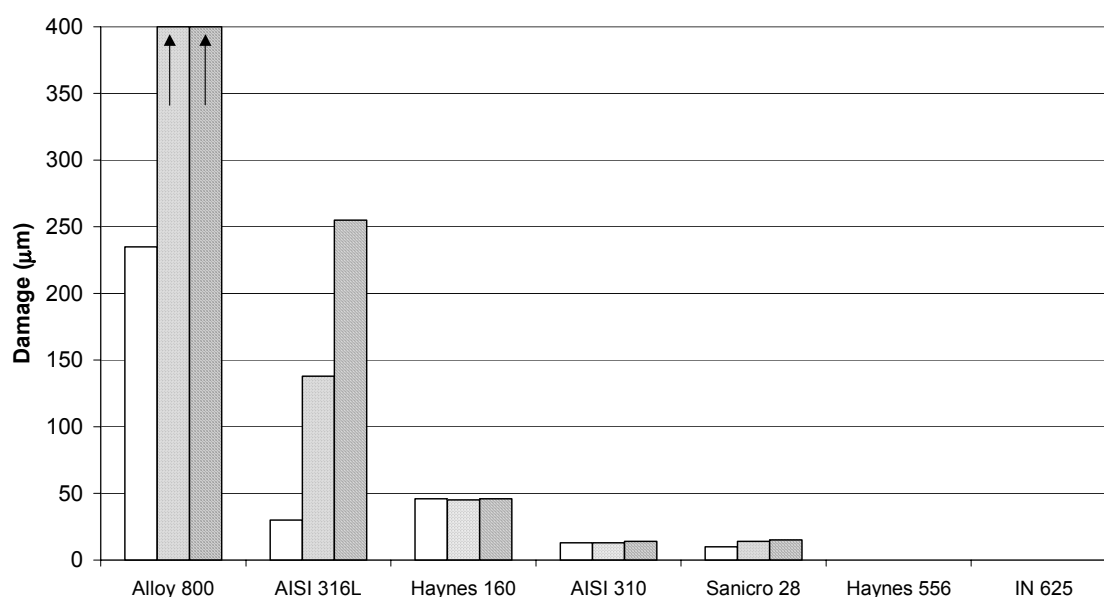


Figure 5. Measured Damage on Samples During DTC Testing (Bars 1–3 for each material are 50, 75 and 100 hours respectively)

The DTC test is more applicable to heat exchanger material testing than metallic filters. Heat exchangers have a uniform surface constructed from one or two materials that is well represented by the DTC test. Metallic filters can have many materials in various forms e.g. fibre, mesh, plate etc. in their construction. This more complex system could lead to galvanic interactions between materials, surface area effects and a more complex crevice/under-deposit system.

Synergistic Damage

The data obtained in the synergistic tests are given in Figure 6. A number of the alloys have been severely damaged. This HTGC/DTC synergy is only one of the many combinations of synergistic conditions that could be expected. The complex exposure environments within gasification systems, combined with the mechanical duties of the various components, make it highly likely that other synergistic influences may play an additional role. There are many possible combinations of exposure variable that could lead to enhanced materials degradation. For example, the metallic filters would be exposed to thermal cycling due to pulse cleaning and start-up/shut-down cycles possibly leading to corrosion fatigue. Only limited studies have been carried out on such synergistic damage modes [18]. This is a topic that requires much more thorough study for gasifier hot gas path components.

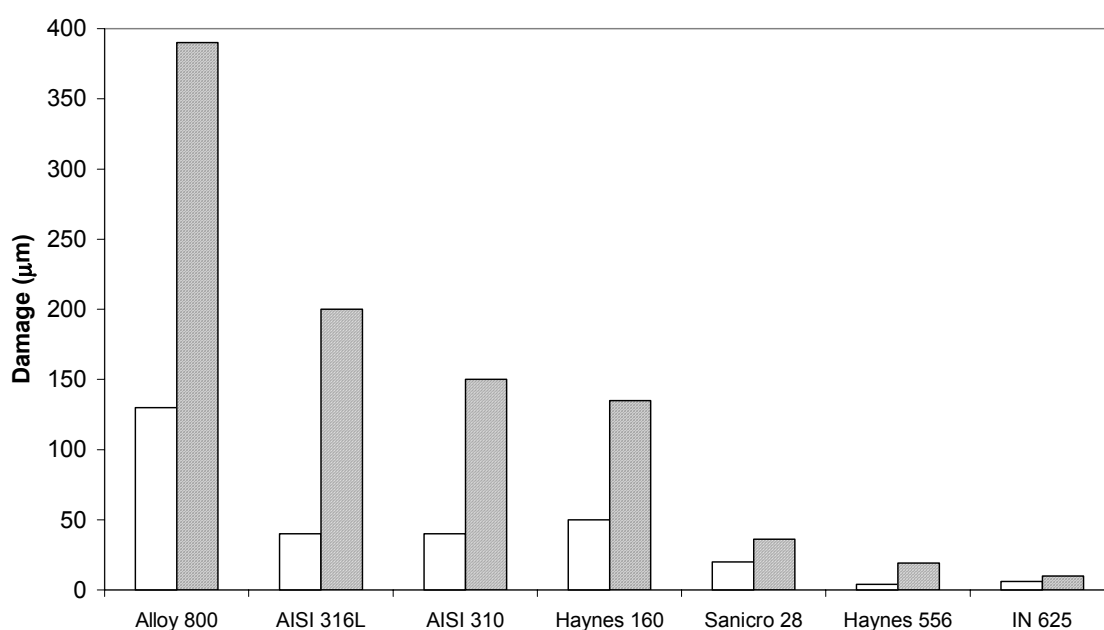


Figure 6. Damage Measured on Samples in Synergistic Tests – Four cycles of 500 hours at 400°C / 100 hours at 70°C (unshaded bar is typical and shaded bar is maximum)

Conclusions

Several series of HTGC, DTC and combined HTGC/DTC tests have been carried out for conditions representing IGCC and ABGC gas coolers and metallic filters. Specific conclusions from these tests are:

- In the HTGC tests in the IGCC gas changing the temperature from 450 to 550°C caused a significant increase in the corrosion experienced by all alloys tested.
- For a number of alloys, HTGC tests with deposits was more damaging than tests without deposits.
- The data indicates longer lives for components in ABGC systems than IGCC systems.
- In the DTC tests, a good agreement was found for pitting corrosion with the ranking predicted by PREN_W.
- In HTGC testing (400°C) incorporating a DTCA period, many of the alloys showed significant damage.
- Alloys selected for gasification plant usage need to have a combination of both high temperature and downtime corrosion resistance.
- Synergistic testing in gasification environments requires more extensive study to elucidate particularly damaging conditions being encountered during plant operation.

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