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Alloy corrosion in a coal gasification system(*)

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Abstract. — The corrosion performance of alloys in coal gasification systems is of increasing industrial interest as more advanced coal-fired power generating systems are developed. It is necessary to consider the performance of candidate materials under likely exposure conditions to ensure that components have adequate lifetimes. Materials performance can influence the economic feasibility of these systems. This paper reports the high temperature corrosion performance of a range of materials exposed in British Coal's air-blown, spouted fluidised bed coal gasification pilot plant. The exposures were carried out in the hot gas path of this plant for periods of up to 660 hours, in three distinct temperature ranges between 330 and 920 °C (i.e. ranges representative of possible evaporator, superheater and ductwork conditions). By characterising the gasifier product gas using carefully selected elements and compounds, activity windows have been defined for sulphur and oxygen for this environment in the required temperature ranges. Standard metallurgical analyses were carried out on exposed alloys to determine their performance in the required temperature ranges. It was found that MA956 performed best in the higher temperature ranges, whilst alloys containing 22-28% chromium performed better in the lower temperature ranges.

1. Introduction.

The development of coal gasification plant, especially for use in combined cycle power generation systems, has led to the need to identify materials to withstand the corrosive product gas found in such systems during periods of operation and downtime [1]. The combination of CO, CO₂, CH₄, H₂, H₂S, H₂O, N₂, NH₃, and HCl found in gasifier product gas can result in complex corrosive degradation, including oxidation, sulphidation and carburisation [2]. Sulphidation in particular can cause rapid attack on metallic materials [2]. As a result, candidate alloys are those which form protective Cr₂O₃ and Al₂O₃ scales for these environments. Of particular interest are alloys for use at temperatures up to ~ 450 °C for evaporators. Materials for use in superheaters (i.e. up to ~ 650 °C) are of interest and materials suitable for use as uncooled ductwork or instrumentation probes (i.e. up to ~ 950 °C) would be desirable in some gasification systems. Component lives of 10-25 years are required, which with a corrosion allowance of 5 mm, for example, would require maximum metal loss rates in the range of 23-57 µm/1000 hours.

There are several types of gasification processes, e.g. fixed bed, fluidised bed or entrained flow [3], which all operate at pressure in power generation systems. The gasifier used in these studies was an atmospheric pressure gasifier pilot plant, based on British Coal's air blown

(*) C British Coal Corporation London 1993.

spouted fluidised bed technology, located at the Coal Research Establishment, Cheltenham, England [4]. This air-blown type of gasifier results in a product gas that is more oxidising than the product gas from other oxygen-blown gasification processes.

Initially a gas characterisation study was carried out which exposed various elements and compounds in the temperature ranges of interest. In subsequent plant runs, ten possible candidate alloys, based on iron, nickel and cobalt, were exposed at similar temperatures. This paper reports the results of this gas characterisation study and the comparative performances of the alloys in relation to their compositions.

2. Experimental.

2.1 PLANT DESCRIPTION AND PROBE LOCATIONS. — The coal gasification pilot plant used in this study was an atmospheric pressure, air-blown, spouted fluidised bed coal gasifier which consumed ~ 12 tons coal/day. The materials samples were exposed on thermocoupled probes near to the inlet, middle and exit from the product gas cooler (Fig. 1). The operating conditions of the gasifier plant during the three runs (A, B and C) in this study are shown in table I. The compositions of the product gas and the range of temperatures observed on the sample probes are given in table II.

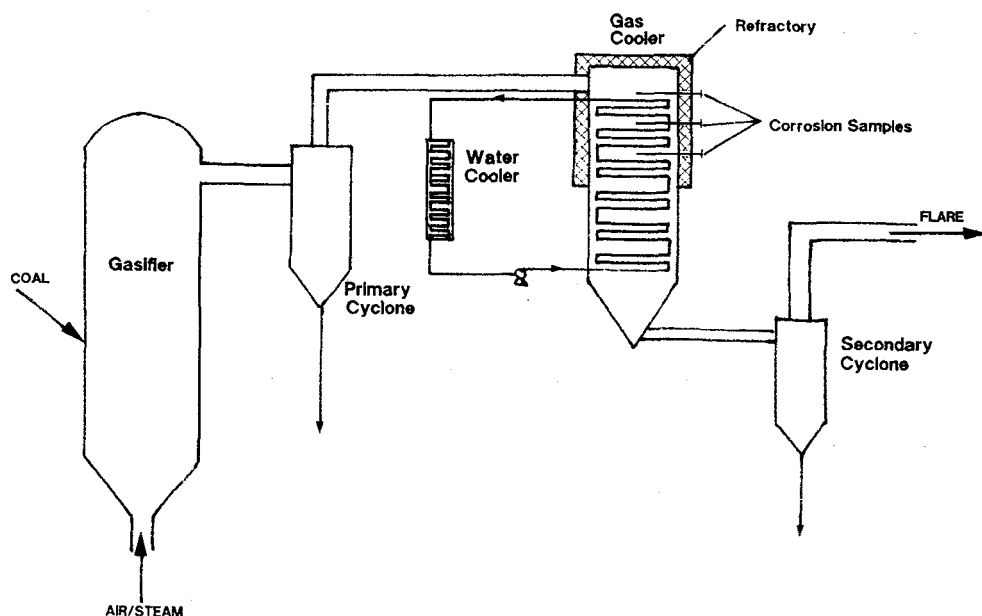


Fig. 1. — Schematic diagram showing the layout of british coal's atmospheric pressure gasifier pilot plant.

Table I. — *Operating conditions of gasifier plant.*

Operating Conditions	Run A	Run B	Run C
Sample Exposure Time		960 h	890 h
Coal Feed Time	550 h	660 h	616 h [*]
Limestone Feed Time		32 h	77h

^{*} 20h in combustion mode - 596h in gasification/reheat mode.

Table II. — *Composition of product gases and temperature ranges at different positions.*

Component	Run A	Run B		Run C	
	Coal Feed	Coal Feed	Coal and Limestone Feed	Coal Feed	Coal and Limestone Feed
CO	N/A	15.4%	15.8%	16.0%	18.1%
CO ₂	N/A	11.2%	11.2%	10.0%	8.8%
H ₂	N/A	13.5%	15.4%	12.0%	13.1%
CH ₄	N/A	0.7%	0.6%	0.7%	0.8%
N ₂	N/A	59.3%	57.0%	60.0%	59.2%
Steam [*]	N/A	12.1%	12.5%	10.0%	10.9%
H ₂ S	N/A	2500ppm	377ppm	1300ppm	330ppm
COS	N/A	114ppm	49ppm	88ppm	65ppm
CS ₂	N/A	22ppm	N/A	17ppm	15ppm
HCl	N/A	300ppm	N/A	112ppm	7ppm
Top Probe Temp.	700-840°C	780-920°C		600-870°C	
Middle Probe Temp.	500-670°C	590-730°C		430-700°C	
Bottom Probe Temp.	350-530°C	450-620°C		330-600°C	

Compositions presented as percentage by volume (dry basis) except for ^{*} percentage by weight.

2.2 EXPOSURE OF ELEMENTS AND COMPOUNDS AND ANALYSIS TECHNIQUES. — In an attempt to characterise the *in-situ* plant atmosphere, an assessment has been made of the phase changes observed on the pure metals and compounds using basic thermodynamic principles. A series of powdered elements and compounds were exposed in alumina boats at the three sample locations during one full operational period of gasification (Run A). The elements exposed were Co, Fe, Mo, Cr and Nb, while the compounds were Fe₂O₃, Cr₂O₃, MnCrO₄, MnO and NbC. X-ray diffraction (XRD) analysis was carried out on the exposed samples.

2.3 EXPOSURE OF ALLOYS AND ANALYSIS TECHNIQUES. — Table III shows the range of ten alloys exposed by clamping onto sample support bars in the three temperature ranges during two subsequent periods of gasification (Runs B and C). The elemental compositions of the alloys are given in table IV.

Table III. — *Exposure locations of alloys.*

Alloy	Exposure Location	
	Run B	Run C
410ss / 347ss / 800H / 310ss	T M B	T M B
Haynes 150 / Haynes 230 / Haynes 160	- M B	- - -
Haynes 556 / Haynes 188	T - B	- - -
MA956	- - -	T M -

Exposure Locations: T=Top M=Middle B=Bottom

Table IV. — *Nominal compositions (wt%) of exposed alloys.*

Alloy	Fe	Ni	Cr	Al	Co	W	Mn	C	Si	Ti	Mo	Other
410ss	Bal	-	12	-	-	-	-	-	-	-	-	-
347ss	Bal	11	18	-	-	-	2	-	1	-	-	-
MA956	Bal	-	20	4.5	-	-	-	-	-	0.5	-	0.5 Y ₂ O ₃
800H	Bal	32	21	0.4	-	-	<1.5	0.08	<1	0.4	-	<0.75Cu
Haynes 556	Bal	20	22	0.3	20	2.5	1.5	0.1	0.4	-	3	0.02 La 0.2 N 1 Co+Ta 0.02 Zr
310ss	Bal	20	25	-	-	-	2	-	1.5	-	-	-
Haynes 188	<3	22	22	-	Bal	15	-	-	0.35	-	-	<0.015 B 0.02 La
Haynes 150	20	-	28	-	Bal	-	0.65	0.08	0.75	-	-	-
Haynes 230	<3	Bal	22	0.3	<5	14	0.5	0.1	0.4	-	2	0.005 La
Haynes 160	4	Bal	28	-	27	-	0.5	0.05	2.75	-	-	-

After exposure, samples were metallographically prepared and examined by both optical microscopy and scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDX).

The alloys were assessed in terms of the thickness of any external scale, depth of any pits and the depth of any internal corrosion found on each sample.

3. Results.

3.1 GAS CHARACTERISATION. — The XRD analyses of the pure metals and compounds exposed in three probe positions are given in table V. Each sample had become covered by a loose carbonaceous deposit during the plant exposure and, in a small number of cases, it was impossible to find the original sample. With these exceptions (and also in the case of occasional samples exhibiting an amorphous phase), valid results were obtained on a useful selection of samples from all three temperature ranges.

Table V. — *XRD analysis of elements and compounds.*

Element or Compound	XRD Identification at particular exposure location		
	Bottom	Middle	Top
Co	Co(15) Co ₉ S ₈ (100)	Co ₉ S ₈ (100) Co ₄ S ₃ (5)	Co ₉ S ₈ (100) CoO(100)
Fe	FeS(100)	Fe ₃ O ₄ (100) FeS(40)	Fe ₃ O ₄ (10) FeS(100) Fe _{1-x} S(100)
Mo	Mo(100) Mo ₃ S ₄ (50)	Amorphous phase	MoO ₂ (100) MoS ₂ (50) Mo ₂ S ₃ (15)
Cr	Cr(100) Cr ₂ O ₃ (10)	Amorphous phase	N/A
Nb	Nb(100) NbO(10)	N/A	N/A
Fe ₂ O ₃	Fe ₃ O ₄ (100)	Fe ₂ O ₃ (50) Fe ₃ O ₄ (50) Fe _{1-x} S(20)	Fe ₂ O ₃ (50)
Cr ₂ O ₃	Cr ₂ O ₃ (100)	Cr ₂ O ₃ (100)	Cr ₂ O ₃ (100)
MnCr ₂ O ₄	Mn _{1.5} Cr _{1.5} O ₄ (100)	N/A	Mn _{1.5} Cr _{1.5} O ₄ (100)
MnO	MnO(10) MnS(20)	Mn ₃ O ₄ (50) MnS(100)	Mn ₃ O ₄ (100) MnS(100)
NbC	NbC(100) Nb ₂ O ₅ (20)	NbO ₂ (25) Nb ₂ O ₅ (100)	Nb ₂ O ₅ (100)

() indicates the relative intensities of the peaks.

From the XRD results presented, it is noteworthy that of the valid results obtained from the Co, Fe and Mo samples (the latter at the higher temperatures only), conversion of these elements to sulphides and, in most cases, oxides had occurred. In the case of the compounds which had been exposed, i.e. Fe₂O₃, Cr₂O₃, MnO and MnCr₂O₄, only the MnO and the Fe₂O₃ (at the middle probe position) were partially converted to the sulphides; the rest showed no discernible change. The NbC was converted to oxides, i.e. a mixture of NbO₂ and Nb₂O₅ at the middle position, Nb₂O₅ at the top position whilst partial conversion to Nb₂O₅ has occurred at the lower position.

These results, which by necessity make a number of assumptions (see discussion), indicate that the reactant activities of the process gas during this period of gasification were as follows:

$$\begin{aligned} 500\text{ }^{\circ}\text{C} &= p_{\text{S}_2} \geq 10^{-13} \text{ bar} \leq 10^{-8} \text{ bar}; \quad p_{\text{O}_2} \geq 10^{-28} \text{ bar}, \\ 650\text{ }^{\circ}\text{C} &= p_{\text{S}_2} \geq 10^{-10} \text{ bar} \leq 10^{-7} \text{ bar}; \quad p_{\text{O}_2} \geq 10^{-20} \text{ bar}, \\ 500\text{ }^{\circ}\text{C} &= p_{\text{S}_2} \geq 10^{-7.5} \text{ bar} \leq 10^{-6} \text{ bar}; \quad p_{\text{O}_2} \geq 10^{-15} \text{ bar}, \end{aligned}$$

Thermodynamic phase stability diagrams for relevant M-S-O systems at temperatures of 800 °C, 650 °C and 500 °C have been selected and the results of the XRD observations have been superimposed on these. An example of that constructed for 650 °C is shown in figure 2.

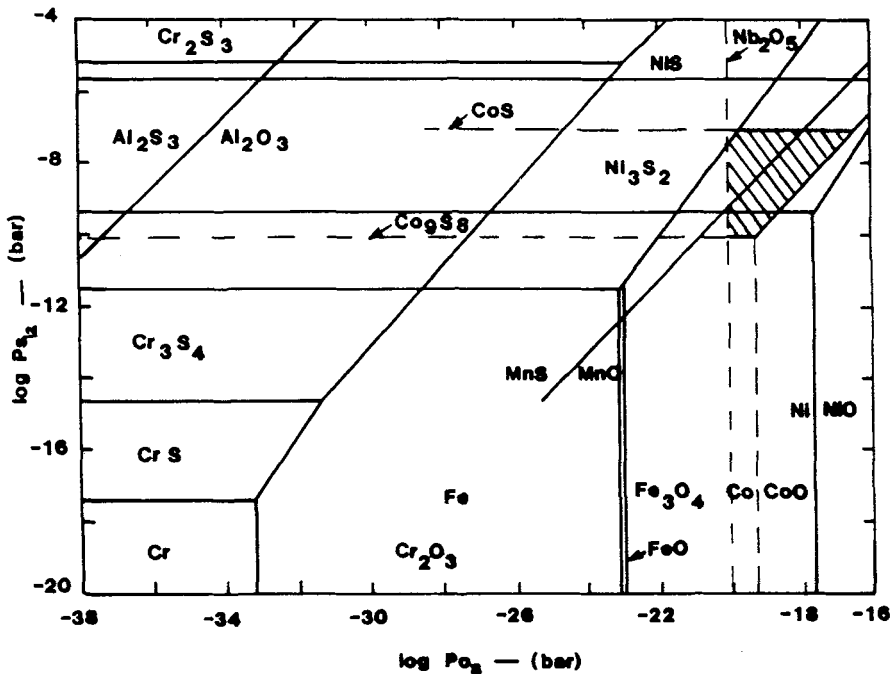


Fig. 2. — Thermodynamic phase stability diagram for selected M-S-O system at 650 °C.

3.2 METTALOGRAPHIC EXAMINATION OF ALLOYS. — The results of the metallographic examination of the alloys (summarised in Tab. VI) were as follows:

a) Fe-based alloys: 41O ss experienced extensive corrosion in the highest temperatures range, producing oxide/sulphide scales of up to 4 mm thick, whilst at the lower temperatures the samples contained pits of up to 50-100 μm . 347 ss produced oxide/sulphide scales of up to 2 mm in the highest exposure temperature range, with pits, some containing iron sulphides, of up to 125-160 μm on the lower temperature probes.

For MA956 exposed at the higher temperature, the vast majority of the sample was covered in $\sim 10\text{ }\mu\text{m}$ oxide scale, though this became a $\sim 130\text{ }\mu\text{m}$ thick oxide/sulphide scale near the

Table VI. — *Results of the metallographic examination of alloys exposed during runs B and C.*

Alloy and Exposure Location	Corrosion Product (μm unless mm stated)		
	Scale thickness Run B/C	Internal attack Run B/C	Pit Depth Run B/C
410ss-T	4mm / 24	0 / 40	0 / 305
410ss-M	12 / 20	0 / 10	25 / 100
410ss-B	80 / 15	0 / 0	0 / 50
347ss-T	2mm / 20	190 / 0	0 / 0
347ss-M	4 / 2	10 / 0	30 / 160
347ss-B	10 / 4	0 / 0	14 / 125
MA956-T	- / 130*	- / 160	- / 20
MA956-M	- / 10	- / 0	- / 20
800H-T	20 / 15	150 / 140	690 / 30
800H-M	15 / 10	75 / 20	40 / 20
800H-B	4 / 2	140 / 0	10 / 25
Haynes 556-T	650 / -	250 / -	400 / -
Haynes 556-B	30 / -	0 / -	6 / -
310ss-T	80 / 120	20 / 0	660 / 6
310ss-M	30 / 70	50 / 40	6 / 50
310ss-B	1 / 20	2 / 2	20 / 30
Haynes 188-T	50 / -	60 / -	800 / -
Haynes 188-B	2 / -	0 / -	6 / -
Haynes 150-M	2 / -	60 / -	40 / -
Haynes 150-B	4 / -	0 / -	0 / -
Haynes 230-M	2 / -	0 / -	0 / -
Haynes 230-B	5 / -	0 / -	18 / -
Haynes 160-M	4 / -	0 / -	0 / -
Haynes 160-B	2 / -	0 / -	0 / -

Exposure Locations: T=Top M=Middle B=Bottom

* Only in small area of sample near corner - otherwise 10 μm oxide scale

corner of the sample, where internal attack of 160 μm was also present. Analysis showed that the scale was a chromium-rich oxide with an aluminium-rich inner layer (Fig. 3). In places there were some sulphides in the scale and occasionally there were internal sulphides. A sample exposed in the middle temperature range contained a protective aluminium-rich scale beneath a ~ 10 μm iron sulphide scale, as well as a little pitting of up to 20 μm depth.

Alloy 800H produced an oxide/sulphide scale of ~ 20 μm at the highest temperature with pitting and internal attack in all ranges. Sulphides were observed within pits on the lower temperature sample.

Haynes 556 experienced severe corrosion in the highest temperature range, with an ox-

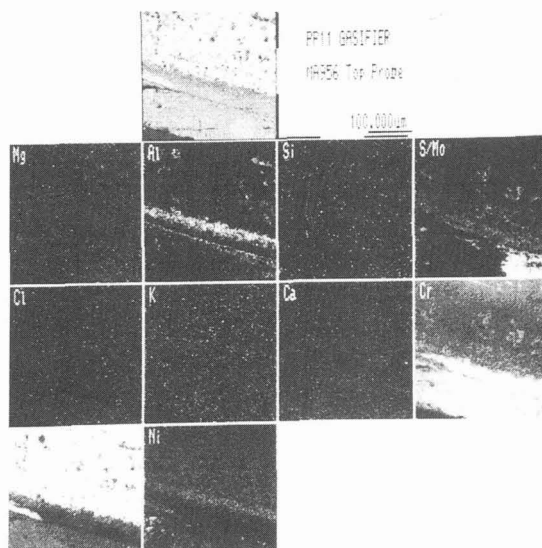


Fig. 3. — SEM/EDX digimap analysis of an MA956 sample exposed at the highest exposure temperature.

ide/sulphide surface scale and internal sulphidation along grain boundaries. In the lowest temperature range, a sulphide containing oxide scale up to $\sim 30 \mu\text{m}$ thick was present on top of a thin chromia-rich scale at the surface.

310 ss produced thick oxide/sulphide scales in the highest temperature ranges in both runs. In the middle temperature range, the 310 ss samples had pits to a depth of $50 \mu\text{m}$ with internal sulphidation beneath a chromium-rich scale. In the lower temperature range, some sulphides were observed within a $\sim 20 \mu\text{m}$ oxide scale, which had an iron and nickel-rich outer layer (Fig. 4); in addition, pits of up to $30 \mu\text{m}$ were also present.

b) Co-based alloys : Haynes 188 produced thick oxide/sulphide scales in the highest temperature range. Haynes 150 contained internal sulphidation to a depth of $60 \mu\text{m}$ beneath a chromium-rich scale in the middle temperature range. Only very thin oxide scales were present on these alloys in the lowest temperature range.

c) Ni-based alloys : Haynes 230 and Haynes 160 exposed in the middle and lowest temperature ranges both formed a thin protective chromium-rich oxide scale, with the only other sign of corrosion being some small pits (of \sim upto $18 \mu\text{m}$) on the lowest temperature Haynes 230.

4. Discussion.

4.1 GAS CHARACTERISATION. — The use of powdered elements and alloys to characterise the activities of species within the coal gasification gases is a simple method, although there are limitations in this simplistic approach, e.g.:

- (a) the temperature ranges quoted for each probe position were of the order of 150°C but it has been necessary to select a single temperature from within each range for assessment;
- (b) basic assumptions concerning gas phase equilibria have had to be made;

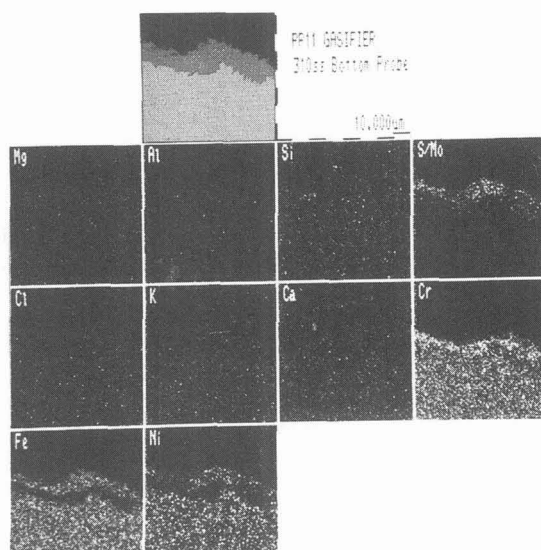


Fig. 4. — SEM/EDX digimap analysis of a 310 ss sample exposed at the lowest exposure temperature.

(c) reaction kinetics will obviously play an important role but this factor has not been considered.

However, this technique has enabled the character of the plant atmosphere, depicted in the form of “activity windows”, to be derived for the reactants S and O at each of the three probe positions.

4.2 ALLOY PERFORMANCE. — The exposure of several alloys based on iron, cobalt or nickel has allowed a comparative assessment of corrosion resistance of these alloys to be made in three different temperature ranges of industrial interest (evaporator, superheater and duct-work).

It should be noted that the relatively low chromium content alloys 410 ss and 347ss (12 and 18% Cr respectively) experienced excessive corrosion in all the temperature ranges tested. The results of this study also suggest that 800H is little more corrosion resistant than 347ss in this type of atmosphere; which is consistent with the observations made in work using a laboratory simulated gasification atmosphere at 700 °C [5].

In the highest temperature range MA956 was found to be the least damaged alloy, with a thin adherent scale covering most of the sample surfaces (excessive corrosion at the corners of samples is common in corrosion testing [5] and it is felt may be ignored). This good performance of MA956 is consistent with previous studies in similar environments [6, 7]. 310 ss was the best of the other alloys tested in this temperature range.

In the middle temperature range, MA956 again performed well, and the performances of 310 ss, as well as the Haynes alloys 150, 160 and 230 were encouraging. Similar performances of Haynes 160 in a laboratory gasification atmosphere at 700 °C has been reported elsewhere [5].

In the lower temperature range all the Haynes alloys and 310 ss performed well, though there were signs of sulphides forming in some of the protective chromia scales and signs of

some pitting.

These results suggest that at least for the 600 hours exposure to the coal gasifier gases used in this study, chromia oxide scales can be protective at temperatures below $\sim 700^{\circ}\text{C}$, with the chromia/alumina scales formed on MA956 being protective to higher temperatures.

Most of the corrosion damage observed on the alloys in this study was caused by high temperature corrosion, though the presence of a small number of pits may indicate some downtime corrosion may be anticipated in a real plant. When selecting alloys for use in a real plant other materials issues will also need to be considered, such as the waterside corrosion performance in heat exchangers, the joining of alloys, the cost of materials etc.

5. Conclusions.

The exposure of ten reference elements and compounds in three temperature ranges in the hot gas path of British Coal's large scale atmospheric fluidised bed coal gasifier has enabled the process atmosphere to be characterised. Analyses of the samples after exposure have enabled "activity windows" for S and O to be derived.

Analysis of a range of alloys exposed to 600-660 hours of coal gasification atmosphere has shown that MA956 formed a protective oxide layer even at 900°C , whilst alloys containing 22-28% chromium formed protective oxide layers at temperatures below 700°C .

410 ss, 347 ss and 800H were unsatisfactory for long term usage in any of the temperature ranges investigated.

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