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Coke deposition on and removal from metals and heat-resistant alloys under steam-cracking conditions

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The kinetics of coke formation and its removal from nickel, copper and alloys have been studied and the results correlated with the morphology of the deposits. Coke deposition from hydrogen–propylene–steam was fast on nickel and slower on copper and the alloys. The deposition on nickel was filamentary in appearance, resulting from a heterogeneously catalysed process, whereas the deposit on the alloys and on non-catalytic copper was essentially uniform. On the alloys, protection appeared to result from the production of scales, containing predominantly Cr_3C_2 and Cr_2O_3, on the surface. At the same time, carburization of the alloy was reduced, apparently as a result of the formation of a silicon-enriched layer at the base of the scale. Steam was found to have little effect on coke formation. However, in the absence of gas-phase hydrocarbons, coke gasification by steam was rapid for nickel but several orders of magnitude slower for the alloys. The main effect of steam is to aid in the formation of scales that are protective against coking and carburization, by promoting oxide formation.

1. Introduction

The pyrolysis of hydrocarbons in the presence of steam (steam cracking) is the preferred industrial process for the production of light olefins [1]. The reaction is free-radical in nature and is unselective, a range of hydrocarbons and coke being produced as by-products. The coke is particularly undesired, since it accumulates on the reactor tube surface to decrease heat transfer and, eventually, to block the reactor [1, 2]. At the same time carbon dissolves in the reactor wall, carburizing the alloy [1–4] and leading ultimately to tube failure.

The importance of the problem is reflected in the attention that has been focused on coke formation, coke removal and on carburization, not least in the selection of alloys suitable for the construction of reactor tubes. The tubes require high-temperature strength coupled with carburization resistance, and this dictates the choice of cast austenitic heat-resistant steels containing rather high silicon levels. Typical modern materials contain ca. 25% Cr and 35% Ni and are niobium-stabilized.

Previous studies in this laboratory have focused on coke formation and removal from metals [2], on the reaction of alloys with oxidizing gases [5], on the carburization of alloys [3] and on the kinetics of coking of different alloys [4]. The present studies are concerned with coke deposition on, and removal from, alloys in the presence of hydrogen–hydrocarbon–steam mixtures.

It is useful to review briefly the mechanism of coke deposition on pure metals [2, 6]. On nickel, hydrocarbons adsorb and dissociate into fragments. These fragments may be gasified, may encapsulate the surface or may dissolve in and diffuse through the metal. Precipitation at a grain boundary results in growth of a carbon fibre with a nickel particle at the tip: this growth continues until the nickel particle is encapsulated with carbon.

The kinetics of coke deposition are in agreement with this mechanism. At low temperatures, catalytic carbon predominates and the apparent activation energy is positive. Mainly filamentous carbon is produced. At higher temperatures, the steady-state coking rate on nickel decreases with increasing temperature, the apparent negative activation energy being attributed to adsorption effects [7, 8]. Filamentous carbon predominates among the products. At higher temperatures still, coke is produced in the gas phase and deposits on and encapsulates the nickel surface. As a result, a positive apparent activation energy is observed and the nature of the coke deposit changes [2, 6]. Depending on the feedstock, the change from positive to negative activation energy may occur between 270 and 900° C and the change from negative activation energy to gas-phase coking from 550° C to above 1000° C [6].

Coke formation on materials such as copper is very different, owing to the absence of catalytic effects [9]. As a result, the kinetics and morphology of the coke are dictated by coking in the gas phase and uncatalysed rearrangements on the surface.

Coke removal depends on the nature of the coke. Filamentous carbon removal is catalytic, the metal particles promoting carbon gasification [2, 6]. Gas-phase coke removal is much slower, since any potential

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TABLE I Compositions of Fe–Ni–Cr alloys used in coking studies

Alloy	Alloying element (wt %)								
	Fe	Ni	Cr	C	Nb	W	Si	Mn	Other
36XT	13.8	44.8	35.5	0.35	1.34	1.70	1.6	0.9	–
36XS	34.1	34.1	25.9	0.43	1.11	1.52	1.6	1.2	–
2535Nb	34.6	35.2	25.0	0.45	1.57	–	2.2	1.0	–
800H	44.1	32	21	–	–	–	1	1.5	0.4 Ti
HK40	50.7	21.6	24.5	0.4	–	–	1.3	0.6	0.8 Mo

catalysts are encapsulated [2, 10]. It is not unusual to observe slow gasification of encapsulating carbon to the point where metal particles are exposed. At this time, gasification accelerates to an extent related to the available metal surface area and the catalytic activity of the metal. Nickel is a good catalyst for gasification; copper is non-catalytic [6, 9].

Materials used in steam-cracking reactor tubes are austenitic Fe–Cr–Ni alloys, usually in cast form. These alloys are known [4, 10] to form an external scale of mixed carbide and oxide, rich in chromium and non-catalytic to coking. Depletion of chromium from the underlying alloy leaves a surface region rich in iron and nickel. The relative importance of the non-catalytic scale and the catalytic alloy surface immediately beneath it in determining overall coking and decoking behaviour is explored in this paper.

2. Experimental procedure

The deposition and removal of coke was monitored continuously using an electronic microbalance (C.I. Electronics Mk IIB). A sample of metal or alloy (approximately 1.5 cm^2 area) was suspended from one arm of the microbalance in such a way that the sample hung in a flow reactor maintained at constant temperature ($\pm 2^\circ$ C). High-purity gases were passed to the reactor via needle valves and calibrated flow meters. Various mixtures of propylene, hydrogen, argon and steam were employed. Steam was generated by bubbling most of the gas through boiling water and removing the excess by passage through a condenser maintained at constant temperature ($\pm 0.1^\circ$ C); a total steam pressure of 0.50 ± 0.02 atm was generated for most experiments. No analysis of gaseous or liquid products was undertaken.

Experiments were carried out with copper, with nickel (both 99.95% pure) and with various alloys, the composition and designation of which are summarized in Table I. Specimens were prepared as described previously [9]. Fresh and used samples were examined using X-ray difraction (XRD), scanning electron microscopy (SEM), energy-dispersive analysis of X-rays (EDAX), stereomicroscopy and optical metallography.

A sample was cut to size, polished, cleaned and suspended from the microbalance [8]. The reactor was assembled and evacuated. Hydrogen was then passed through the reactor (30 min) and the preheated furnace raised to surround the reactor. When the system had reached a steady state the gaseous reactants were admitted to the reactor. On occasions, it was necessary to monitor both coke deposition and coke removal. Coke-depositing gases were flushed from the reactor using hydrogen, and the reactor temperature changed before coke gasification reagents were admitted; the oxidizing gases employed were H_2O/H_2. At the end of any run, the sample was cooled to room temperature under flowing hydrogen.

A total gas flow rate of 630 ml min^{-1} at room temperature and 1 atm pressure was maintained for all experiments. This corresponded to an inlet residence time in the reactor of ca. 7 sec.

3. Results

3.1. Coke formation

Coke was deposited from a mixture of hydrogen, propylene and steam, maintained at a molar ratio of 3 : 1 : 4 and a total flow rate of 630 ml min^{-1}. On occasions, the steam was replaced by argon, the same total flow rate being maintained. Constant steady-state deposition rates were observed after a period of steadily decreasing rate which lasted from several minutes up to an hour.

Coke formation on nickel and copper was found to proceed as expected from the literature [2, 6, 9], the rate of coking first decreasing and then increasing as temperature increased in the case of nickel, and increasing steadily with temperature for copper. A pseudo-Arrhenius plot is shown in Fig. 1. The

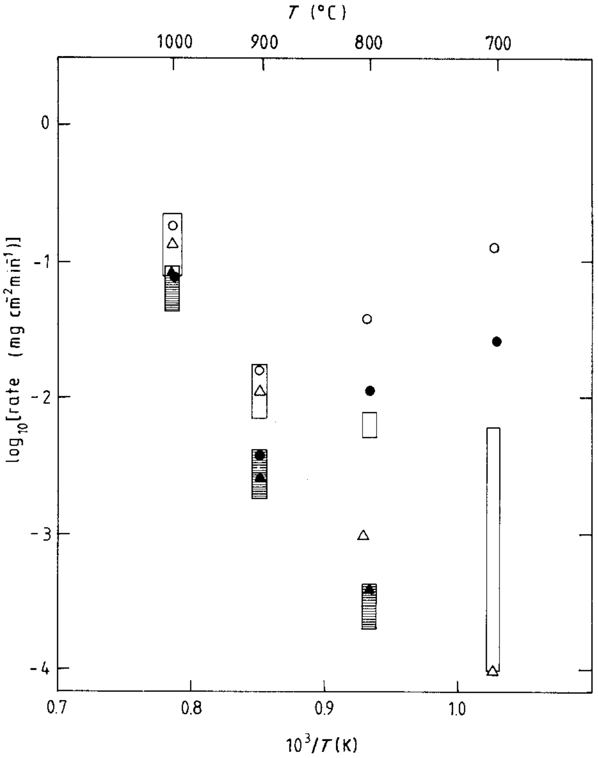


Figure 1 Arrhenius plot of steady-state linear coking rates: (●) nickel, (○) nickel in $H_2–C_3H_6$ [2, 6, 8], (▲) copper, (△) copper in $H_2–C_3H_6$ [8], ▤ alloy, □ alloy in $H_2–C_3H_6$ [8].

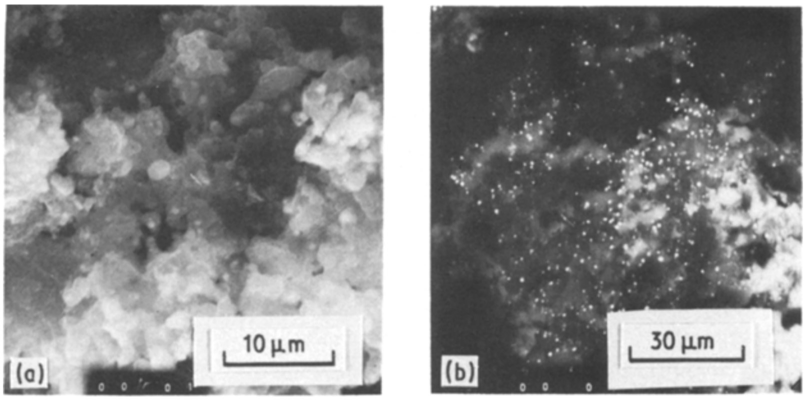


Figure 2 Filamentous coke formed on nickel coked at 800° C for 240 min: (a) SEM image, (b) backscattered electron image.

apparent activation energies observed were nickel (700 to 900° C), $-140 \pm 20\,\mathrm{kJ\,mol^{-1}}$; nickel (900 to 1000° C), $290 \pm 40\,\mathrm{kJ\,mol^{-1}}$; and copper (700 to 1000° C), $260 \pm 30\,\mathrm{kJ\,mol^{-1}}$.

Coke formation was measured on nickel at 800° C using argon in place of steam. No difference could be observed from results obtained in the presence of steam.

The bulk of the carbon deposited on nickel at 800° C was found to be filamentous, with metal particles at the tip of the growing fibre: typical SEM photographs are shown in Fig. 2. In contrast, coke formed at 900° C consisted of mixtures of filamentous coke and a dense layer of encapsulating coke as shown in Fig. 3.

Coke formed on copper at both temperatures showed no evidence of filament formation, the deposits being smooth and encapsulating in both cases (Figs 4 and 5). As would be expected, the morphology of the coke formed on copper was consistent with the formation of gaseous encapsulating coke.

Coke formation from the propylene–hydrogen–steam mixture was then studied using the alloys described in Table I as substrates. Coking rates are shown as a function of temperature in Fig. 1. No significant coke formation was observed at 700° C, the rates at higher temperatures increasing with increasing temperature. The apparent activation energy for all alloys was $270 \pm 30\,\mathrm{kJ\,mol^{-1}}$. Observed rates are summarized in Table II.

Typical morphologies of coke formed on different alloys at 800° C are shown in Fig. 6. The deposits were predominantly thin layers although a small amount of filamentous coke was produced. Longer coking times led to the production of thicker coke layers which buckled and detached from the alloy surface (Fig. 6).

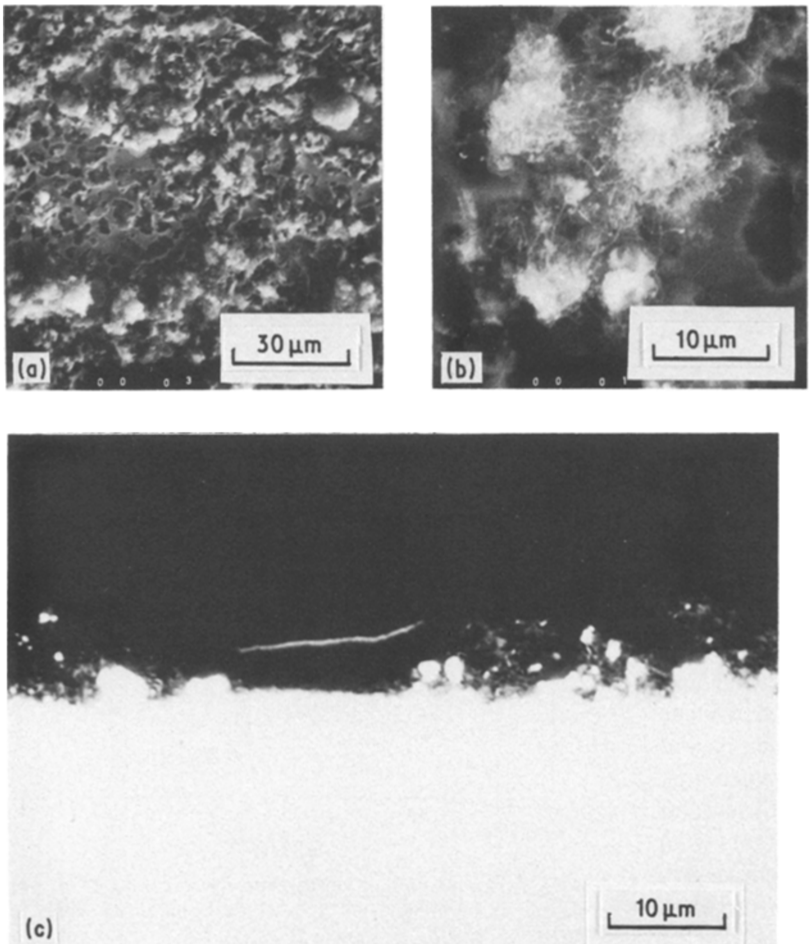


Figure 3 Coke formed on nickel after 3 h at 900° C: (a, b) SEM and (c) cross-section.

TABLE II Steady-state deposition rates on materials coked in 3 : 1 : 4 H_2–C_3H_6–H_2O atmospheres (mg cm^{-2} min^{-1}).

Material	Temperature (° C)			
	700	800	900	1000
Copper	–	4.3×10^{-4}	2.6×10^{-3}	6.9×10^{-2}
Nickel	2.6×10^{-2}	1.2×10^{-2}	3.6×10^{-3}	8.0×10^{-2}
			4.3×10^{-3}	7.1×10^{-2}
36XT	–	2.4×10^{-4}	1.9×10^{-3}	3.6×10^{-2}
			3.8×10^{-3}	7.1×10^{-2}
36XS	–	4.5×10^{-4}	1.8×10^{-3}	8.7×10^{-2}
		1.8×10^{-4}		
2535Nb	–	2.8×10^{-4}	2.0×10^{-3}	8.9×10^{-2}
800H.	–	2.5×10^{-4}	1.9×10^{-3}	7.5×10^{-2}
			2.1×10^{-3}	
HK40	–	2.2×10^{-4}	2.0×10^{-3}	2.9×10^{-2}
			2.5×10^{-3}	6.0×10^{-2}

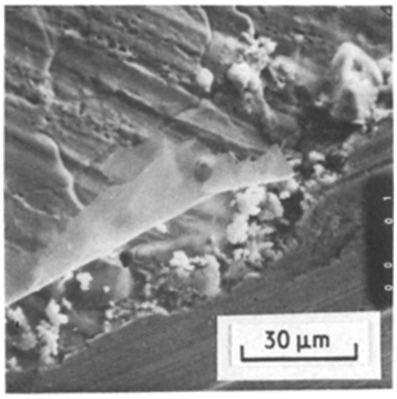


Figure 4 SEM micrograph of thin coke layer formed on copper reacted for 300 min at 800° C.

At 900° C, the deposits on alloys had the macroscopic appearance of dense layers (Fig. 7) but when viewed at higher magnification, considerable surface irregularities became apparent (Fig. 8). EDAX analysis indicated the presence of particles apparently containing pure nickel at the tips of filaments formed on Alloy 36XT and of particles rich in chromium near the ends of filaments formed on 800H. Metal particles were identified in deposits formed on other alloys, but their analysis was inconclusive.

Examination of cross-sections of deposits produced on 36XT, 800H and HK40 (Fig. 9) revealed that coke was deposited as filaments or agglomerates rather than as layers parallel to the alloy surface.

Coke deposits on all alloys at 1000° C had the same appearance, as shown in Fig. 10. Back-scattered electron micrographs of cross-sections revealed nickel particles in the deposit formed on nickel and the formation of layered deposits as seen in Figs 10, 11 and 12. The sphere-like morphology seen in Fig. 11 appears to originate at irregularities below the surface of the deposit.

The composition of crystalline deposits formed on different materials were then examined using X-ray diffraction. The results, summarized in Table III, show that coke deposited on nickel at all temperatures consisted essentially of graphite having an (0 0 2) lattice spacing of 0.335 nm, and crystallite size of ca. 30 nm. Graphite was produced on other materials in detectable amounts only by coking at 1000° C. Deposits formed on copper and the alloys at lower temperatures exhibited a very broad diffraction peak centering around a *d* spacing of 0.340 nm: this would indicate that the coke contained very small crystallites (approximately 2 nm in size), possibly involving graphite. Austenite (γ), Cr_2O_3, Cr_3C_2 and (often) $Cr_{23}C_6$ were identified among the deposits formed on all alloys. As reaction times and temperatures increased, the ratio of the Cr_3C_2 line intensities to those of Cr_2O_3 was found to increase.

Although identified by XRD, Cr_2O_3 and Cr_3C_2 produced at 700 and 800° C could not be found on the alloy surfaces either metallographically or with the SEM. Scales formed on the alloys after relatively short times at 900° C could be seen using the SEM (Fig. 13) and the optical microscope. Their grey appearance, as opposed to the highly reflective appearance of chromium carbides, suggested that the scale consisted mainly of oxides. Scales formed after long reaction times at the same temperature contained at least two phases, the white Cr_3C_2 and the grey Cr_2O_3, as shown in Fig. 9.

Similar scales were obtained after relatively short reaction times at 1000° C, but the scale contained higher proportions of Cr_3C_2 and a third, dark grey coloured phase at the alloy–scale interface (Fig. 12). This latter phase intruded into the parent alloy. EDAX analysis across the scale formed on 36XS (Fig. 12a) revealed silicon enrichment at the alloy–scale interface and the presence of low concentations of iron in the Cr_3C_2 scale. The EDAX results are shown in Fig. 14, where the results have been scaled to 100% omitting non-metals. Electron microprobe analysis of the dark grey phase confirmed that silicon enrichment had occurred in this region.

No alloy carburization of any significance occurred in these experiments. However, precipitation of fine

TABLE III Phases identified on coked alloys by *in situ* X-ray diffraction*

Material	Temperature (° C)		
	700	900	1000
Copper			G
Nickel	G	G	G
36XT	Cr_2O_3, Cr_3C_2, $Cr_{23}C_6$	Cr_2O_3, Cr_3C_2, $Cr_{23}C_6$	G, Cr_3C_2, Cr_2O_3
36XS	Cr_2O_3, Cr_3C_2, $Cr_{23}C_6$	Cr_2O_3, Cr_3C_2, $Cr_{23}C_6$	G, Cr_3C_2, Cr_2O_3, $Cr_{23}C_6$
2535Nb	Cr_2O_3, Cr_3C_2, $Cr_{23}C_6$	Cr_3C_2, $Cr_{23}C_6$	G, Cr_3C_2, Cr_2O_3
800H	Cr_2O_3, Cr_3C_2	Cr_2O_3, Cr_3C_2	G, Cr_3C_2, Cr_2O_3, $Cr_{23}C_6$
HK40	Cr_2O_3, Cr_3C_2, $Cr_{23}C_6$	Cr_2O_3, Cr_3C_2, $Cr_{23}C_6$	G, Cr_3C_2, Cr_2O_3

*G = graphite.

TABLE IV Steady-state rate of formation and gasification of coke formed at 800° C on nickel and HK40 specimens

Material	T (°C)	Gas atmosphere*	P_{O_2} (atm)	Rate of formation (mg cm^{-2} min^{-1})	Rate of gasification (mg cm^{-2} min^{-1})
Nickel	800	A[†]	–	1.3×10^{-1}	–
	800	B	–	1.3×10^{-2}	–
	800	C	1×10^{-20}	8.0×10^{-3}	–
	800	D	8×10^{-14}	–	8.8
	800	E	1×10^{-20}	–	4.8
HK40	1000	A	–	8.7×10^{-2}	–
	1000	B	–	7.0×10^{-2}	–
	1000	C	5×10^{-16}	4.5×10^{-2}	–
	800	D	8×10^{-19}	–	0

* Gas atmosphere A, 3:1 $H_2:C_3H_6$; B, 3:1:4 $H_2:C_3H_6:Ar$; C, 3:1:4 $H_2:C_3H_6:H_2O$ ($P_{H_2O} = 0.50$ atm); D, 3:1:4 $H_2:Ar:H_2O$ ($P_{H_2O} = 0.50$ atm); E, 6. 6:1 $H_2:H_2O$ ($P_{H_2O} = 0.13$ atm).

[†] Results for this atmosphere taken from a previous study [6].

carbides within the alloy was evident at temperatures above 800° C as shown for the cast alloy 2535Nb in Fig. 11.

3.2. Coke formation and gasification

It would be expected that the gasification of filamentous coke (catalyst present) and of layered coke (catalyst absent) would proceed at different rates. Accordingly, cokes of different morphologies were prepared and gasified.

Filamentous coke (deposit weight ca. 10 mg) was produced by passing hydrogen–propylene–steam over nickel at 800° C and by passing hydrogen–propylene–argon over nickel at the same temperature. The amount of coke produced was essentially the same in each case (Table IV).

Coke produced from hydrogen–propylene–steam was then gasified at 800° C using a 3 : 1 : 4 hydrogen : argon : steam mixture (partial pressure of oxygen = 8×10^{-19} atm). A second sample was prepared and gasified using a 6.6 : 1 hydrogen : steam mixture (partial pressure of oxygen = 1×10^{-20} atm). After an initial period, a constant and fast rate of weight loss was observed until ca. 70 to 80% of the carbon had been gasified. The rates of gasification for the two atmospheres are reported in Table IV.

Layer-like carbon was produced from 3 : 1 : 4 hydrogen : propylene : argon atmospheres at 1000° C on Alloy HK40. This coke was gasified using the 3 : 1 : 4 hydrogen : argon : steam mixture at 800° C. Gasification was much slower, with only ca. 25% of the coke being removed. No steady-state rate was observed and gasification stopped after ca. 2 h.

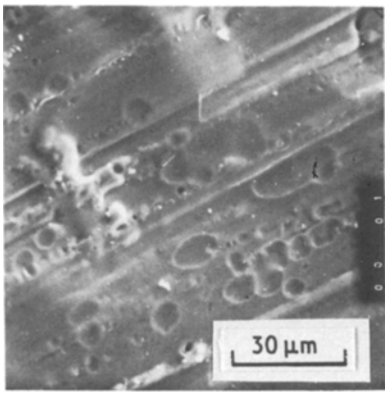


Figure 5 Surface of copper coked for 60 min at 900° C.

4. Discussion

It is now well established that the formation of coke in pyrolysis systems is complex, with interactions occurring between metal-catalysed processes and coking originating mainly in the gas phase [2, 6]. Nickel is known to be a good catalyst, producing catalytic coke at low temperatures and being covered in gas-phase coke at high temperatures [6]. Copper is non-catalytic, and coke produced on its surface originates mainly in the gas phase [9].

The coking behaviour of nickel and copper, as studied in the present investigation, is fully in accord with results reported in the literature [6, 9]. Both the kinetics of the reaction and the morphologies of the deposits agree with previous studies.

Alloys which contain both catalytic and non-catalytic elements may be expected to show coking characteristics somewhere between the limits set by nickel and copper. Surprisingly, in view of the composition of the alloys (Table I), catalytic coking was found to be minimal. Thus, for example, the kinetics of coking on alloys (Fig. 1) were found to approximate to those observed on copper, the apparent activation energy (270 ± 30 kJ mol^{-1}) being positive in all cases. The morphology of the cokes produced at lower temperatures showed little evidence of filamentous carbon (Fig. 6) and "filaments" produced at higher temperatures were coarser than filaments of catalytic carbon produced on nickel. This is readily seen by comparing Fig. 7 with Figs 8 and 9.

The reasons for this behaviour become clear from examination of cross-sections of the deposit (Figs 9, 11 and 12). It is seen that scales are produced on most alloys even after only short reaction times, and these scales form a non-catalytic coating on the surface of the alloy [3, 4, 8]. The nature of the scale depends on the composition of the alloy and on the reaction conditions. The predominant phases present in the scale were Cr_3C_2 and Cr_2O_3, the relative amount of the carbide increasing with increasing severity of reaction conditions, i.e. increasing time-on-line or increasing temperature. This can be understood from a consideration of the equilibrium

$$3Cr_2O_3 + 4C = 2Cr_3C_2 + \tfrac{9}{2}O_2$$

For the gas mixture 3 : 1 : 4 hydrogen : propylene : steam the stability limits of the oxide and carbide are

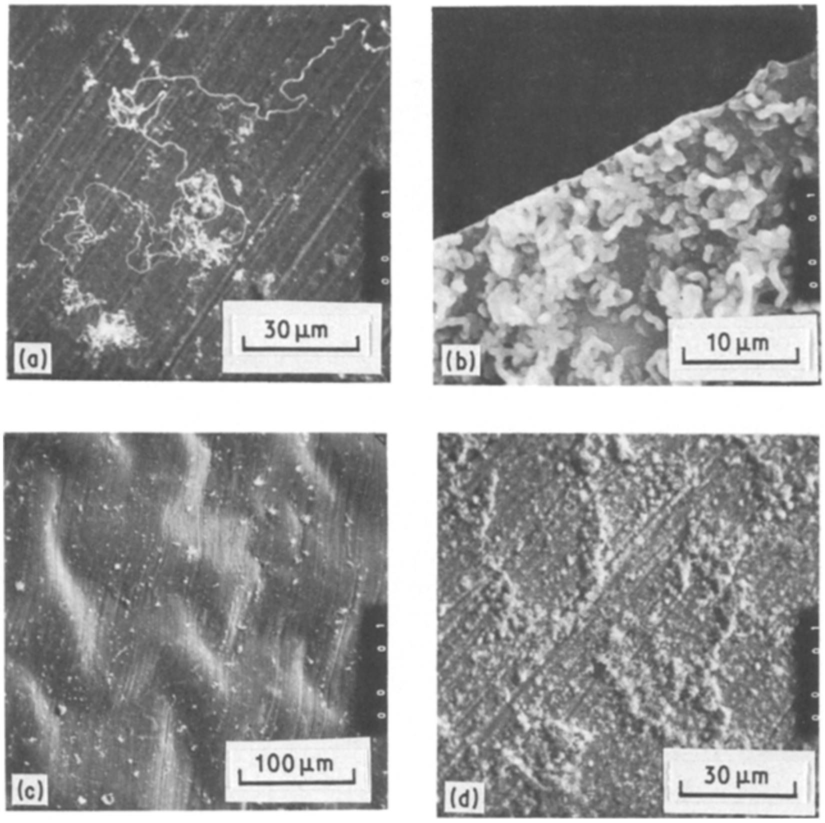


Figure 6 Surface morphologies of coked deposits formed on alloy at 800° C: (a) HK40, 150 min reaction; (b) 800H, 1200 min; (c) HK40, 1200 min; (d) 2535Nb, 300 min.

shown in Fig. 15. From this diagram, Cr_2O_3 would be expected to form at the gas–alloy interface. However, the deposition of a continuous coke layer above the scale would be expected to lower the oxygen potential and to result, eventually, in the conversion of the oxide to carbide.

As noted above, the scale serves to separate the metal surface from the gas stream. Since the scale is formed essentially of chromium-based compounds [4, 8] and since diffusion of chromium within the alloy is slow, a thin layer of chromium-depleted metal forms at the alloy surface immediately below the scale. This layer is therefore rich in iron and nickel. When the scale cracks, gas access to catalytic metal occurs and filamentous coke formation is expected and found. This explains the formation of localized regions of filamentary coke on alloy surfaces which appear otherwise to be non-catalytic to coking.

It was also surprising to find that carburization of the alloys was minimal (Fig. 11). Chromium carbide scales are known [10] to afford little protection against carburization, the rate of which is controlled by the solubility and diffusivity of carbon within the alloy. However, carburization has been reported to be minimal under conditions where Cr_2O_3 is stable [10], apparently due to the concurrent formation of continuous sub-surface layers of SiO_2. Silica is much more stable than Cr_2O_3 and about 2 wt % is considered to be sufficient to form an effectively protective layer. Limited evidence of silica enrichment near the surface of the alloys used was obtained in the present work, but the results were not quantitative.

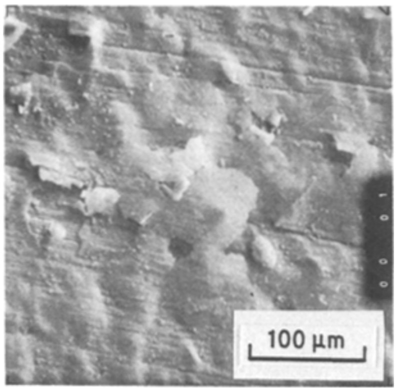


Figure 7 Typical low-magnification surface appearance of alloys coked at 900° C (HK40, 150 min).

The formation of scale on the surface of alloys cannot be expected to remain continuous, in view of the conditions under which the industrial process operates. In agreement with this, the localized growth of masses of coke filaments on alloys has been attributed to the exposure of catalytic metal at sites where scale failure occurs [4].

At higher temperatures, the rate of coke formation in the gas phase accelerates and the deposition of encapsulating coke increases [11]. At the same time, the coke deposit is expected to be more compact. In agreement with this, filamentous carbon was found to be less important and, when formed, the filaments tended to become encapsulated by gas-phase coke (Fig. 9).

The role of steam in the reaction was investigated by comparing coke formation from gas mixtures with and without steam on nickel and on HK40 (Table IV) and by comparing these with previous results in 3 : 1 hydrogen–propylene atmospheres [8] (open symbols in Fig. 1). The general behaviour of all materials at most temperatures was similar. In the presence of steam, coking rates were reduced by the same factor as was the partial pressure of propylene. It is therefore concluded that so far as the coking reaction is

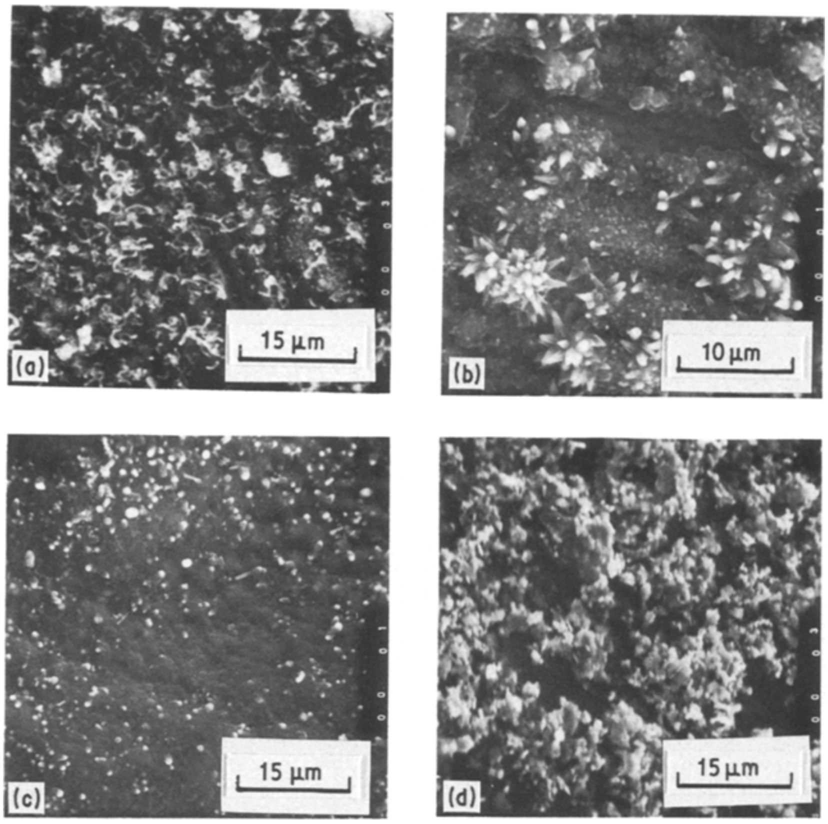


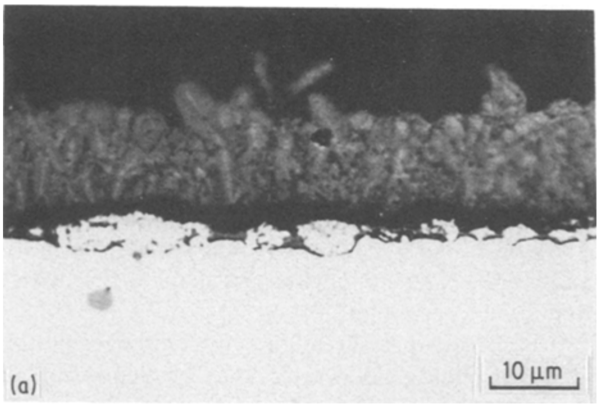
Figure 8 Surfaces of alloys after coking at 900° C: (a) 36XT, 80 min; (b) 36XT, 240 min; (c) 800H, 90 min; (d) HK40, 150 min.

concerned, the steam functions merely as a gas-phase diluent. Surprisingly, steam had little if any direct effect on coke formation. As a result, studies of the gasification of coke by steam were undertaken.

Gasification of coke produced on nickel at 800° C (catalytic coke) was extremely rapid (Table IV) and most of the coke was removed. On HK40, gasification was slow and only ca. 25% of the coke could be removed. This finding is in complete agreement with the known rates of gasification of catalytic and non-catalytic carbon [1, 12].

In the case of nickel, it might be argued that gasification involves either steam or the small amounts of oxygen that are generated from the reaction mixture under reaction conditions. Two results were compared where the steam and oxygen partial pressures were varied (Table IV). Comparison of the steam ratios (3.8 : 1), the oxygen partial pressure ratios (80 : 1) and the rates of gasification (1.8 : 1) suggests that steam is responsible for gasification. This result agrees with the findings of other workers [6, 13, 14].

These results fail to explain one observation – that the rate of coking on nickel was approximately the same in a 3 : 1 : 4 hydrogen : propylene : steam



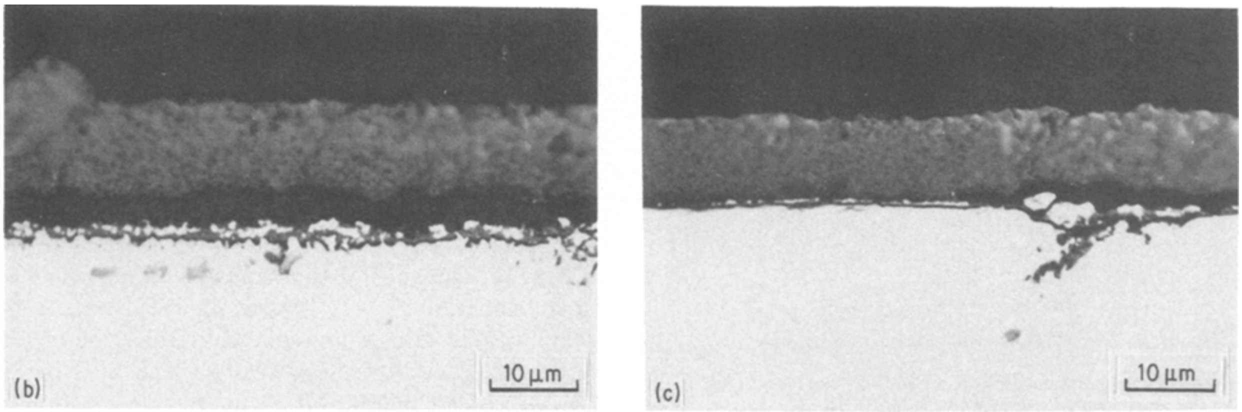


Figure 9 Metallographic cross-sections of coke deposits formed after extended periods at 900° C: (a) 36XT, 1400 min; (b) 800H, 2200 min; (c) HK40, 1600 min.

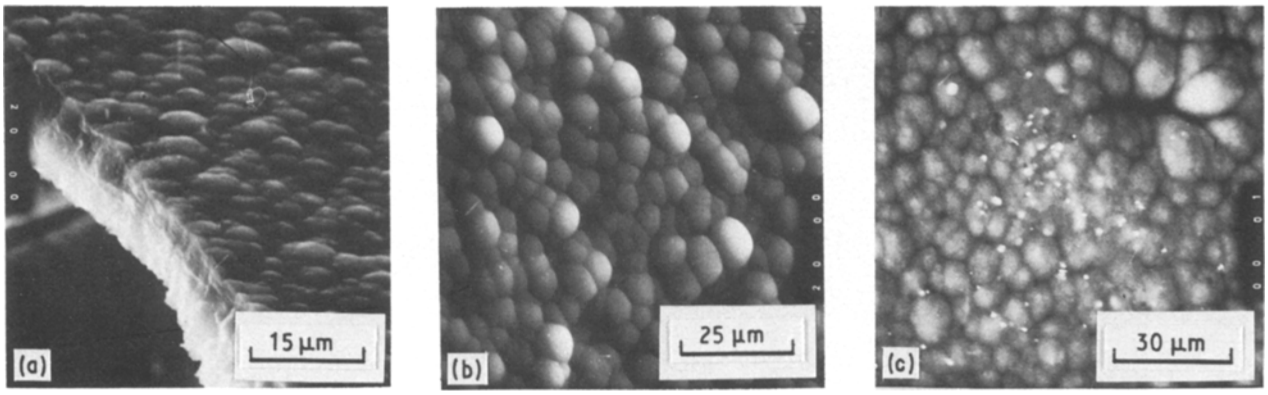


Figure 10 (a) Fractured coke deposit formed on 800H after 90 min at 900° C. (b) Coke deposit formed on HK40 after 180 min at 1000° C. (c) Backscattered electron micrograph of coke deposit formed on nickel after 120 min at 1000° C.

atmosphere as in a 3 : 1 : 4 hydrogen : propylene : argon atmosphere. If coke gasification is so rapid, why is the coke deposition rate the same in the absence and presence of steam? The only possible explanation would seem to be that gasification requires adsorption of steam and that hydrocarbon, if present, preferentially adsorbs on the surface, favouring coke production rather than coke removal. If this is the case, then the extent of coke deposition/gasification will depend on the relative strengths of adsorption of different hydrocarbons and steam. As the spectra of gas-phase species produced from a wide range of feedstocks are broadly similar, the deposition of coke may not vary greatly with the ratio of the feed.

The large variations in coking behaviour of alloys in atmospheres with and without steam below 900° C may be attributed to the varying effectiveness of their

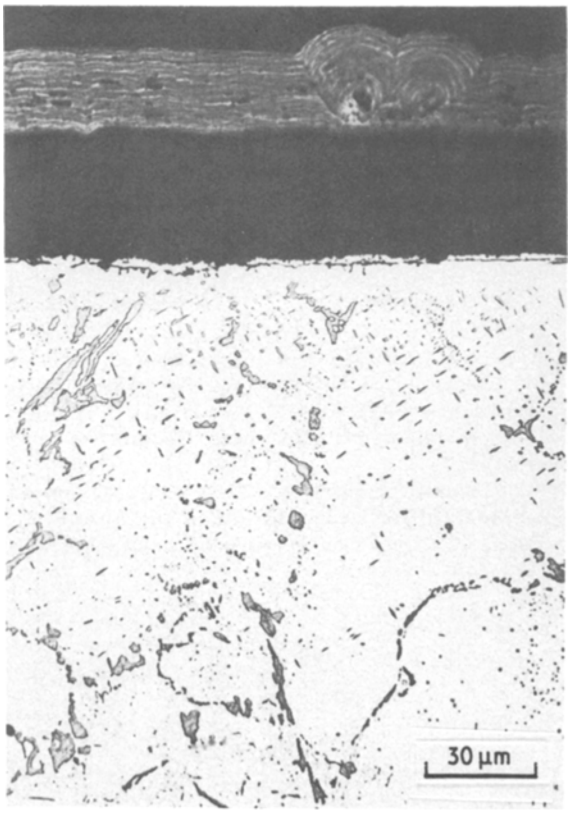


Figure 11 Etched cross-section of 2535 Nb coked for 120 min at 1000° C, showing layered structure of the coke deposit.

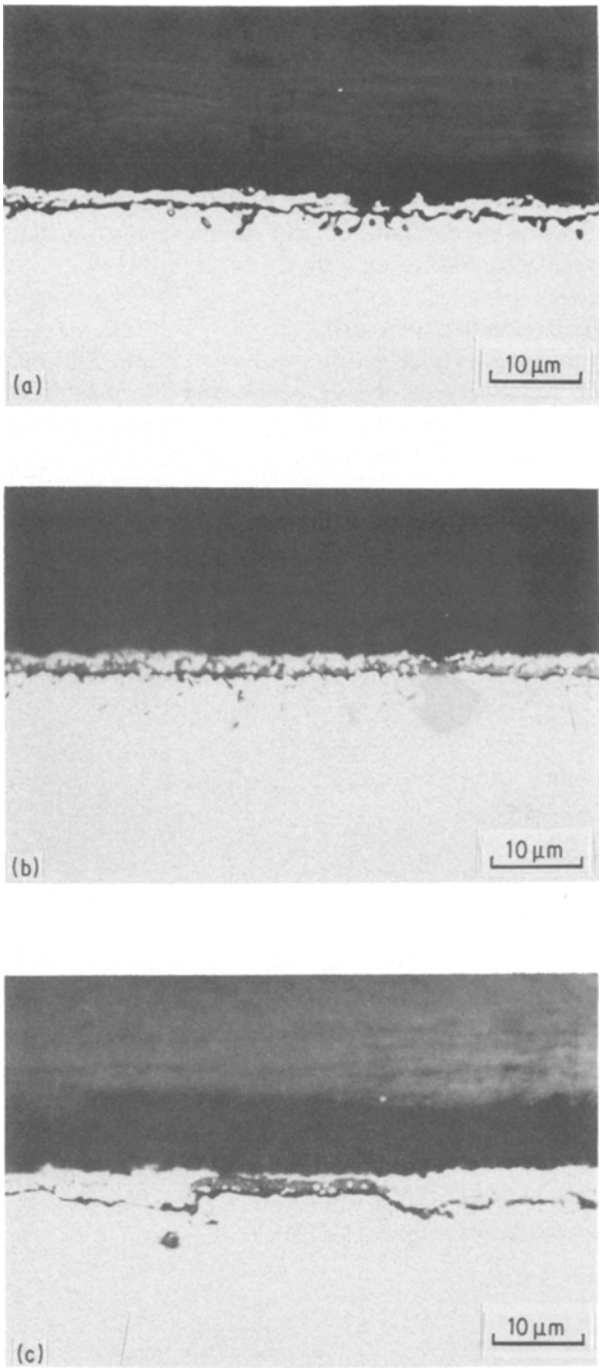


Figure 12 Metallographic cross-sections of scales formed on alloys reacted at 1000° C: (a) 36XS, 150 min; (b) 800H, 120 min; (c) 36XT, 240 min.

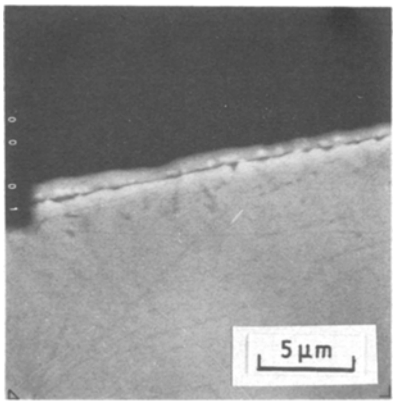


Figure 13 Cross-section of scale formed on 800H after 90 min at 900° C.

carbide/oxide scales in excluding the gases from the underlying metal. By comparision, scales formed in steam-containing atmospheres acted as highly effective barriers in excluding hydrocarbon gases from contact with catalytic metal beneath. Consequently, carburization and formation of filamentous coke deposits were minimized and similar deposition rates were observed for all alloys.

Acknowledgement

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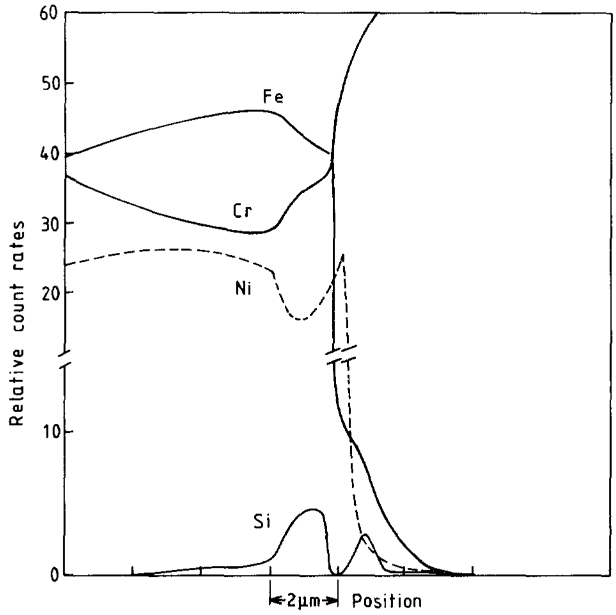

Figure 14 EDAX analysis in the region of the alloy–scale interface of 36XS reacted at 1000° C for 150 min.

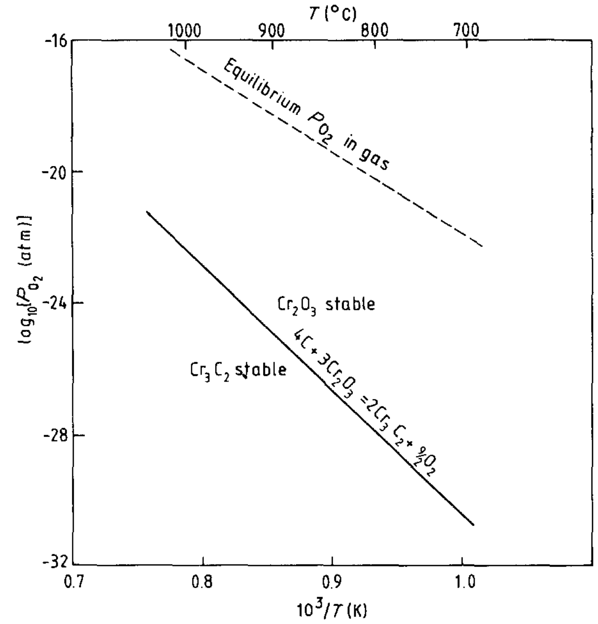

Figure 15 Equilibrium oxygen potential of 3 : 1 : 4 H_2–C_3H_6–H_2O atmosphere and the Cr_3C_2/Cr_2O_3 equilibrium unit carbon activity.

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