

# Morphological studies of coking on heat-resistant alloys

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The deposition of coke from a propylene-hydrogen mixture on to a range of austenitic Fe-Cr-Ni base alloys has been studied. Morphological investigations reveal the formation of a chromium-rich carbide layer on the surface of the alloys. This layer is initially protective, but eventually develops defects from which coke filaments grow. The formation of these filaments is catalysed by the chromium-depleted metal which becomes accessible to the gas following failure of the carbide layer. Once catalytic coke formation commences, it is maintained by the presence within the coke of small metal particles rich in iron and nickel.

## 1. Introduction

The conversion of crude oil to industrially useful chemicals is a complex process involving the separation of various fractions which are then processed in the absence or presence of a catalyst. Many of these reactions must be carried out at high temperatures where the formation of coke is favoured [1]. This coke represents a loss of product and causes problems by depositing on internal surfaces, thereby increasing pressure drops and decreasing heat transfer efficiency. The carbon may also diffuse into the surface, causing internal carburization which leads to equipment failure. As a result, it is of considerable importance to minimize coke formation and carburization, and to maximize coke removal.

Industrially, this is carried out by careful control of operating conditions, by regular decoking and by informed choice of construction materials [2]. Several heat-resistant steels are available, all based on the iron-chromium-nickel alloy system. It is necessary to select an alloy with the desired mechanical properties under reaction conditions, which does not favour coking or carburization and which can perform well over several coking-decoking cycles. The carburization resistance of a range of

alloys has been reported previously [3] and the coking performance of the same alloys is the subject of the present paper.

The kinetics and mechanism of coke formation on pure metals have been studied previously [4, 5]. The catalysed production of carbon has been suggested to involve the adsorption and degradation of hydrocarbons to produce carbonaceous species which may dissolve in the metal, accumulate on the surface or be gasified. Carbon dissolved in the metal will diffuse to grain boundaries and precipitate out, leading to the production of filaments of carbon with metal particles at their tips. Coke remaining on the surface may rearrange to produce an ordered deposit which encapsulates the metal. The observed deposit morphology and the kinetics of deposition were entirely consistent with this model for carbon deposition on a range of metals [5].

The coking and carburization of alloys is more complex, since many minor components present in the alloy can affect significantly both of these processes. Surface concentration of minor components and/or formation of protective scales on the surface can lead to effects entirely disproportionate to the bulk concentration of an additive [2]. As a result, little is

TABLE I Alloy compositions

Alloy	Composition (wt %)*							
	Ni	Cr	C	Nb	W	Si	Mn	Other
HK40	21.6	24.5	0.4	–	–	1.3	0.6	0.8Mo
800	32	20.5	–	–	–	0.5	1.5	0.4Ti
800H	32	20.5	–	–	–	0.5	1.5	0.4Ti
36XS	34.1	25.9	0.43	1.1	1.5	1.6	1.2	–
36XT	44.8	35.5	0.35	1.3	1.7	1.6	0.9	–
G4868	29.7	29.3	0.51	–	–	2.2	1.5	–
PG2535Nb	35.2	25.0	0.45	1.6	–	2.2	1.0	–

\*Balance iron.

known of the behaviour of different alloys, and the present programme was initiated to explore the effect of alloy composition on carburization [3] and on coke deposition from a propylene–hydrogen mixture. Particular attention is focused on morphological changes that occur during coking.

## 2. Experimental procedure

Coke deposition from a propylene–hydrogen mixture was studied using a flow system fitted with a microbalance (C.I. Electronics Mk2B) for the continuous recording of weight gain. Samples of alloy were suspended from one arm of the balance to hang in a Vycor reactor maintained at pre-set temperatures ( $\pm 2^\circ\text{C}$ ). Coke was deposited from a propylene–hydrogen mixture (1:3) flowing through the reactor at  $1\text{ litre min}^{-1}$ : this corresponded to an inlet residence time in the hot zone of 9 sec.

High-temperature alloys were obtained from different sources, their code numbers and compositions being summarized in Table I. Samples were cut as coupons ( $15\text{ mm} \times 15\text{ mm} \times 0.5\text{ mm}$ ), abraded with silicon carbide papers to a 400 grit finish and cleaned ultrasonically in acetone. A small hole was made for suspension purposes, the hole being spark-cut or drilled.

Coupons were suspended from the balance arm with the abrasion marks parallel to the gas flow direction and the Vycor reactor put in place. High-purity hydrogen was then passed over the samples at room temperature (30 min) and at  $700^\circ\text{C}$  (30 min). The propylene–hydrogen mixture was then admitted to the reactor and the weight change followed continuously. At the end of the run, the reactor was cooled in argon and hydrogen and the sample removed for metallographic analysis. This involved X-ray diffractometry together with scanning electron

and optical microscopy. Qualitative analysis of the deposits was performed using energy-dispersive X-ray analysis (EDAX).

## 3. Results

Coke deposition was followed by recording weight gain for long periods of time. Two general types of behaviour were observed. Samples prepared by drilling holes in the coupons by spark-cutting gave the typical weight uptake curves shown in Fig. 1. The kinetics are seen to divide into three regimes: an initial induction period when the coke uptake was low, a subsequent period of linear weight gain, and a final non-linear period during which the deposition rate slowly decreased. Heavy deposits were found to grow near to the hole: on occasion, part of these dropped from the sample causing a step decrease in weight.

Samples prepared by mechanically drilling holes in the coupon were found to perform differently (Fig. 2). The induction period was lengthened and a slow increase in rate of weight uptake with time on line was observed. No major growths of carbon near to the hole were

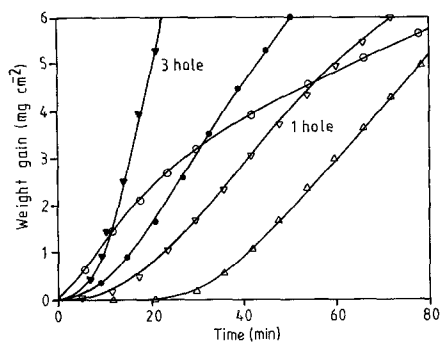


Figure 1 Typical weight uptake curves for coke formation on alloys with spark cut specimen holes. ( $\nabla$ ) 800H (one hole), ( $\blacktriangledown$ ) 800H (3 holes), ( $\circ$ ) nickel, ( $\Delta$ ) 2535Nb.

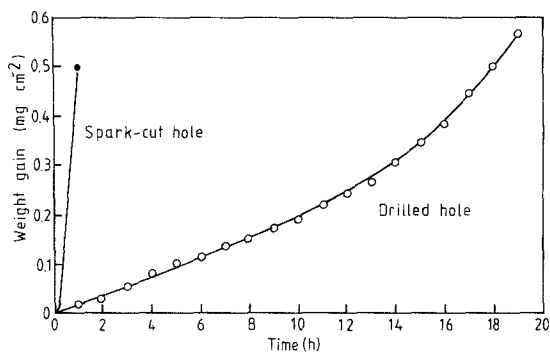


Figure 2 Effect of spark-cut and mechanically drilled holes on the kinetics of coke formation on Alloy 800H.

observed, deposition being spread evenly all over the coupon.

Since it appeared that spark cutting had an adverse effect on coking, three holes were spark-cut in an 800H coupon. Comparison of coking rates with one and three holes (Fig. 1) shows a very significant effect.

Induction periods and weight gained before the onset of linear coking kinetics on spark-cut samples were recorded in Table II for different alloys. The induction period was taken as the time to the point where the extrapolated linear portion of the curve cut the abscissa (Fig. 1).

The morphology of the surface away from the hole during and after the induction period was examined, and a typical sequence of events is shown in Fig. 3. Fine filaments of carbon are seen to develop on the surface and, although the appearance of different deposits varied, similar filaments were developed in all cases. Thus, for example, coke deposits on the different alloys are shown in Figs. 4 and 5 and, when examined at greater magnification, these deposits were found to consist of bundles of interwoven fibres (Fig. 5).

A dense particle was observed at the tip of each fibre and, in some cases, smaller fibres grew from these particles (Fig. 6). The adhesion of

TABLE II Variations in coking parameters associated with nickel and the heat-resistant steels at 700°C

Alloy	Induction period (min)	Weight gain before linear kinetics* (mg cm <sup>-2</sup> )
Nickel	1	0.1
800	7	0.8
800H <sup>†</sup>	15, 5	1.1
HK40	20	0.5
36XT	17	0.3
36XS	43	0.4
4868	29	0.9
2535Nb	29	0.8

\*Values given are the average of 4 to 5 readings.

<sup>†</sup>One and three holes.

these bundles was poor and, if they were dislodged, the surface underneath the bundle was found to be pitted (e.g. HK40, Fig. 4).

In addition, a thin film was formed on the alloy surface. This film was formed in the very early stages of the induction period (Fig. 3c) and persisted throughout the reaction periods examined (Figs. 7, 8 and 9). Examination of these figures reveals that the initially almost perfect film developed cracks and flaws with time, and that filamentary carbon originated from these defects. Analysis by EDAX of this surface film was necessarily qualitative but the results, shown in Table III, indicate that the film is rich in chromium and contains some iron. Enrichment of chromium in the surface film was accompanied by depletion of chromium from the adjacent subsurface region of alloy, as shown in Fig. 9.

*In situ* analysis by X-ray diffraction of the surface showed the presence of graphite, austenite and Cr<sub>23</sub>C<sub>6</sub>. Since the latter two phases are the constituents of the unreacted alloy, it is apparent that the surface film is too thin for successful X-ray diffraction analysis.

Alloys 36XS and G4868 were then coked for 12 h, mounted on edge and examined unetched

TABLE III Uncorrected EDAX analyses of the deposit on alloys 36XS and G4868 after 12 h at 700°C\*

Alloy	Cr/Fe	Fe/Ni	Cr/Ni	Cr/(Ni + Fe)
36XS	1.4	1.6	2.3	0.9
Coke	0.6 to 1.7	0.6 to 8.6	0.4 to 9.0	0.2 to 1.2
Carbide layer	8.1	1.9	16.8	5.4
G4868	1.2	2.5	3.0	0.9
Coke	0.2 to 1.0	1.6 to 2.1	0.3 to 2.0	0.1 to 0.7
Carbide layer	4.0	14.1	57.6	3.8

\*Ratios represent the ratio of integrated K<sub>α</sub> peaks.

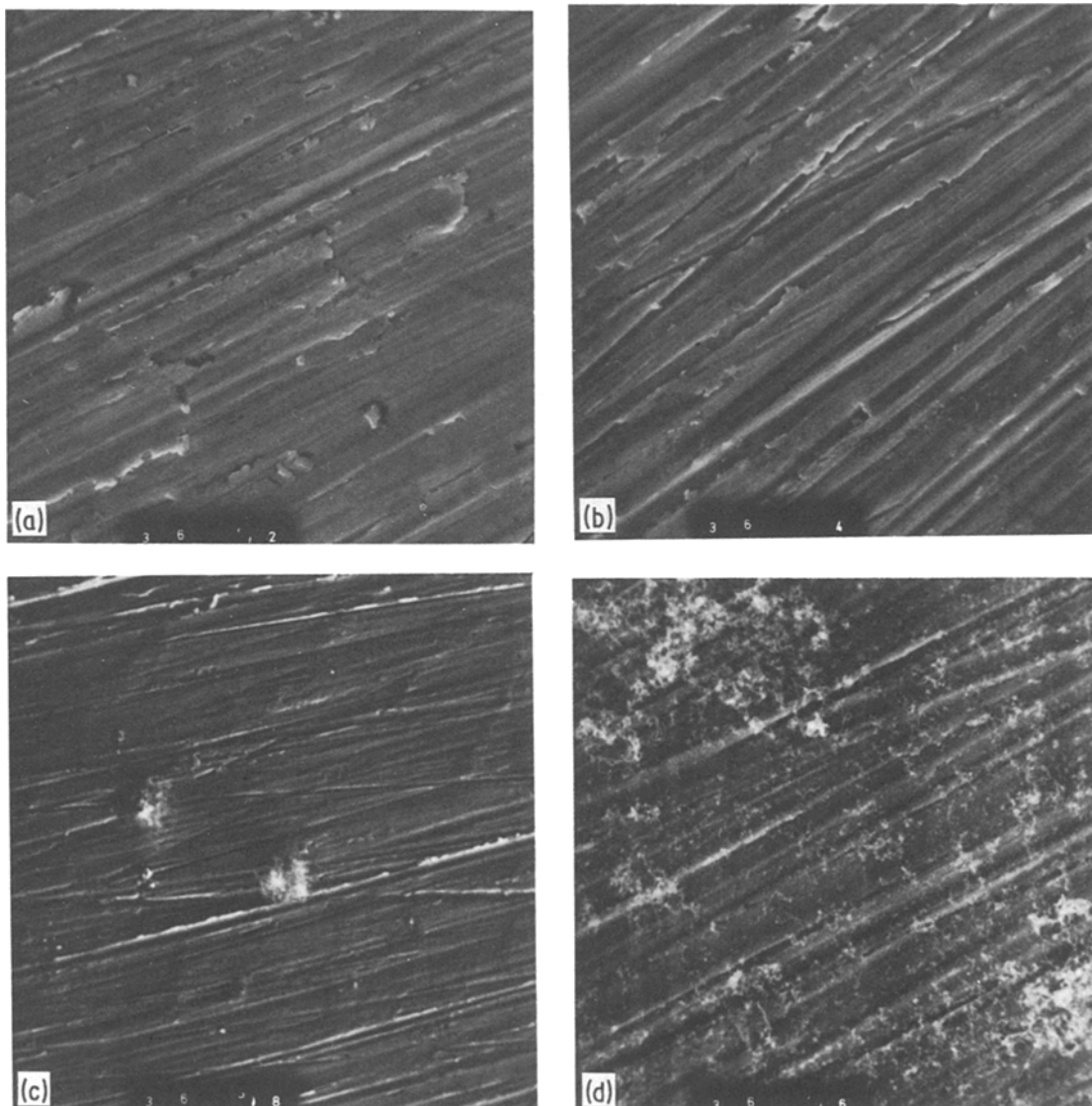


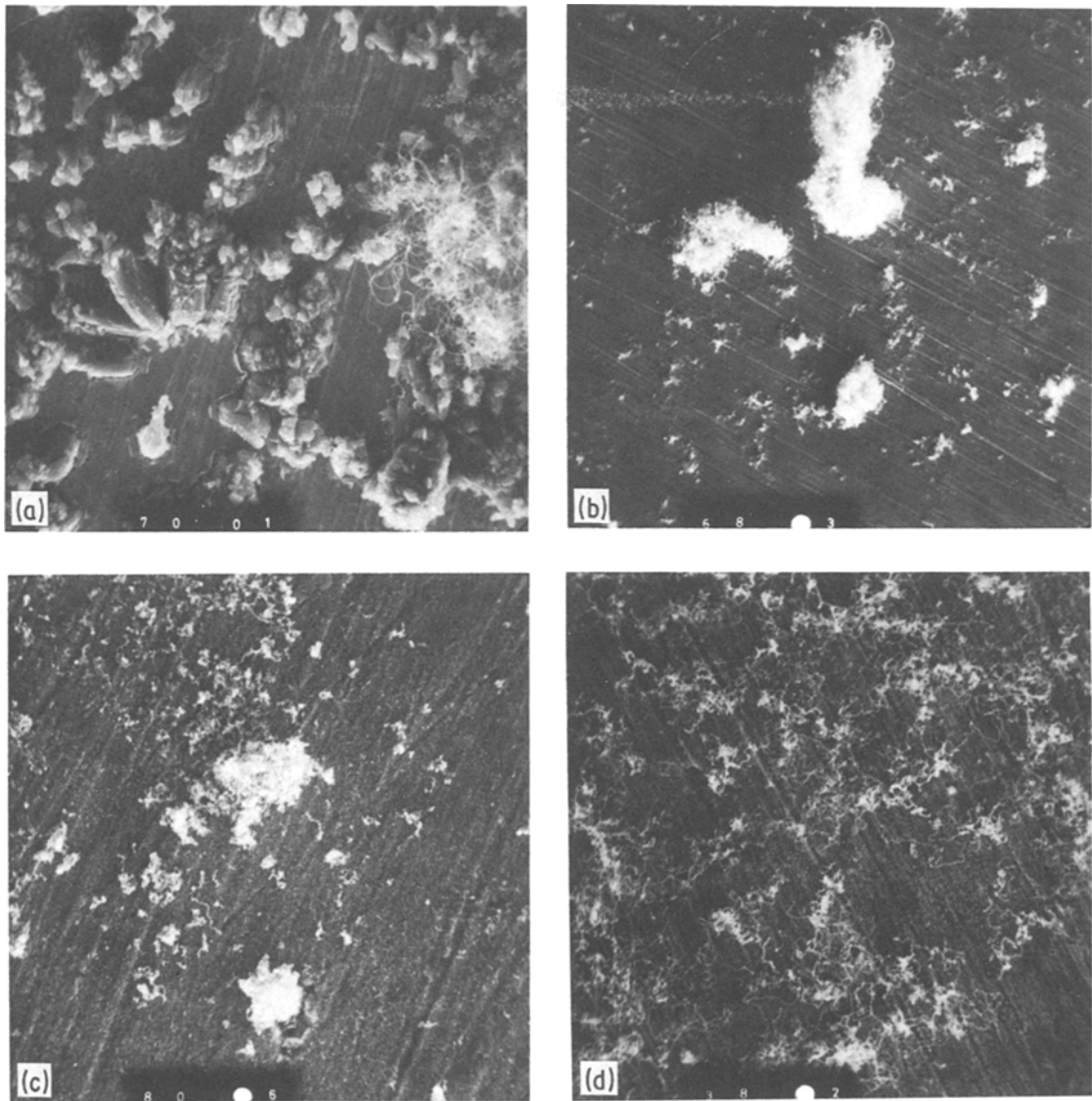
Figure 3 Micrographs of early stages of coke deposition on 36XS: (a) unreacted ( $\times 1116$ ); (b) unreacted but annealed at  $700^{\circ}\text{C}$  in hydrogen for 30 min ( $\times 1116$ ); (c) after 15 min reaction at  $700^{\circ}\text{C}$  with propylene; hydrogen = 1:3 ( $\times 418$ ); (d) after 25 min reaction (end of induction period) ( $\times 1116$ ).

(Fig. 8a) and stain-etched to reveal chromium carbides (Fig. 8b). The surface film is seen to contain carbides. In both alloys, coke growth was associated with surface pitting and this coincided with a grain boundary at which chromium carbide was present.

The coke deposits were found to contain metal and fragmented carbide particles (Fig. 8). Analysis of these particles with EDAX yielded the results shown in Table III. Although subject to error, analysis of large particles in the coke

showed them to be of composition closer to that of the bulk alloy rather than that of the surface carbide film (Table III). These results were obtained by analysis of the larger particles in the deposit (Fig. 8) since errors associated with the analysis of small particles were large.

Coke deposits were removed from the alloy surface and used as substrates over which propylene and hydrogen were passed at  $700^{\circ}\text{C}$ . Further coke formation was observed, even in the absence of alloy.



*Figure 4* Heavier coking with standard gas mixture at 700° C; (a) pure nickel, 120 min reactions ( $\times 349$ ); (b) G4868, 120 min reactions ( $\times 209$ ); (c) 800, 240 min reactions ( $\times 697$ ); (d) 2535 Nb, 180 min reactions ( $\times 697$ ); (e) HK40, 120 min reactions ( $\times 628$ ); (f) G4868, 12 h reactions ( $\times 42$ ).

#### 4. Discussion

Although the deposition of coke on to the alloys was found to be autocatalytic (Figs. 1 and 2), it is obvious that there are major differences between spark-cut samples and drilled samples. This is believed to be due to changes in surface composition during spark-cutting, as discussed below. As a result of this finding, discussion of the kinetics of coking is unrewarding. It was found, however, that studies of the morphological changes occurring during coking are very revealing as to the processes involved.

A thin film was found to be formed on the alloy surface in the very early stages of reaction (Fig. 3). This film remained intact but, eventually, defects developed and carbon filaments were formed. It is clear that the nature and behaviour of this film controls coking, and that coking depends on the film and the nature of the material exposed at a defect.

Exposure of chromium-rich alloys to reducing, carbonaceous atmospheres is known to produce an external film of  $\text{Cr}_3\text{C}_2$  [3] which grows by diffusion of chromium from the under-

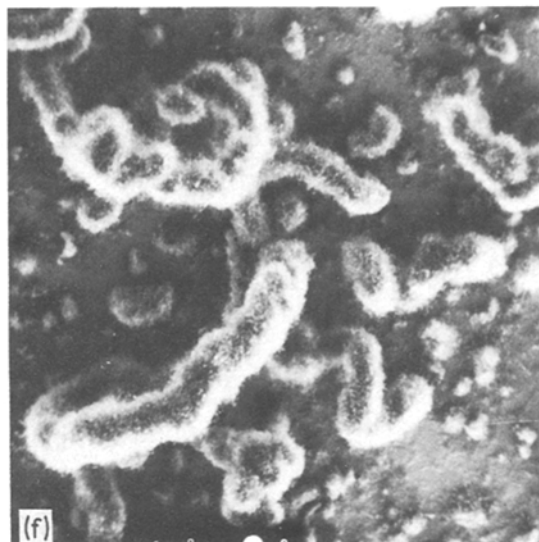
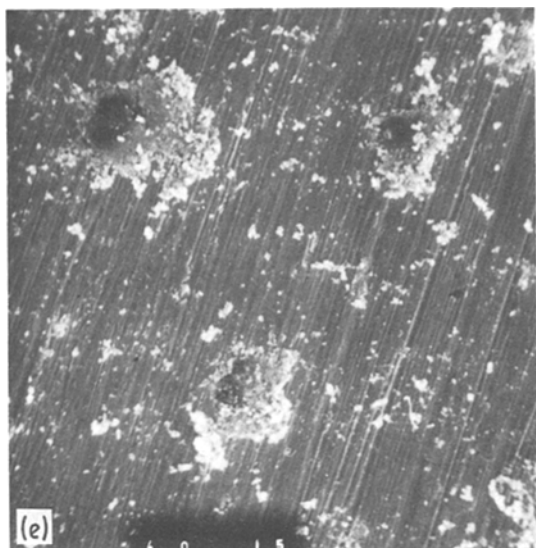


Figure 4 Continued.

lying alloy. The selective reaction of chromium from the alloy is a consequence of the relative thermodynamic stabilities of the various metal carbides. The observation of a chromium-rich external film together with an underlying alloy region depleted of chromium leads to the conclusion that the films formed in the present experiments are mainly  $\text{Cr}_3\text{C}_2$ . The fact that initial reaction leads to carbide film growth and not to coke formation implies that the Fe-Cr-Ni alloys possess very little catalytic activity toward hydrocarbon cracking reactions. Simi-

larly, it must be concluded that  $\text{Cr}_3\text{C}_2$  has negligible catalytic activity to coke formation.

The onset of coking was found to coincide with film failure. When the  $\text{Cr}_3\text{C}_2$  film fails, it allows access of gas to the underlying alloy. The freshly revealed metal surface has a composition quite different from that of the original alloy: it is almost completely depleted of chromium as a result both of selective external  $\text{Cr}_3\text{C}_2$  growth and of internal precipitation of other chromium carbides [6]. The exposed surface is composed essentially of iron and nickel and, as such, is

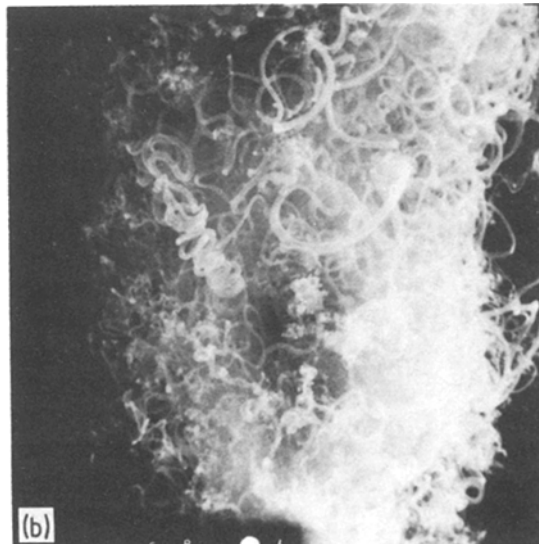
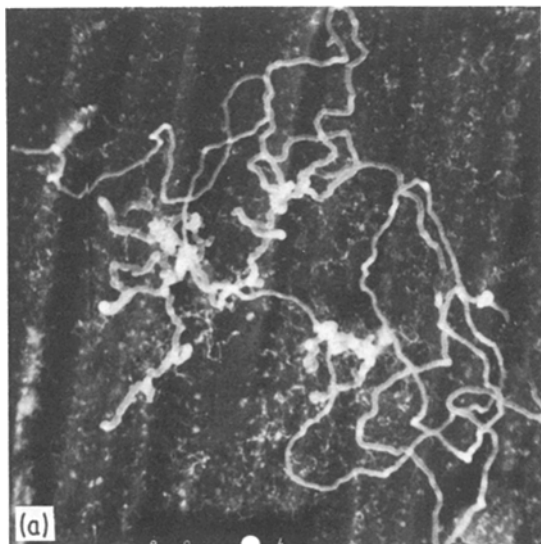
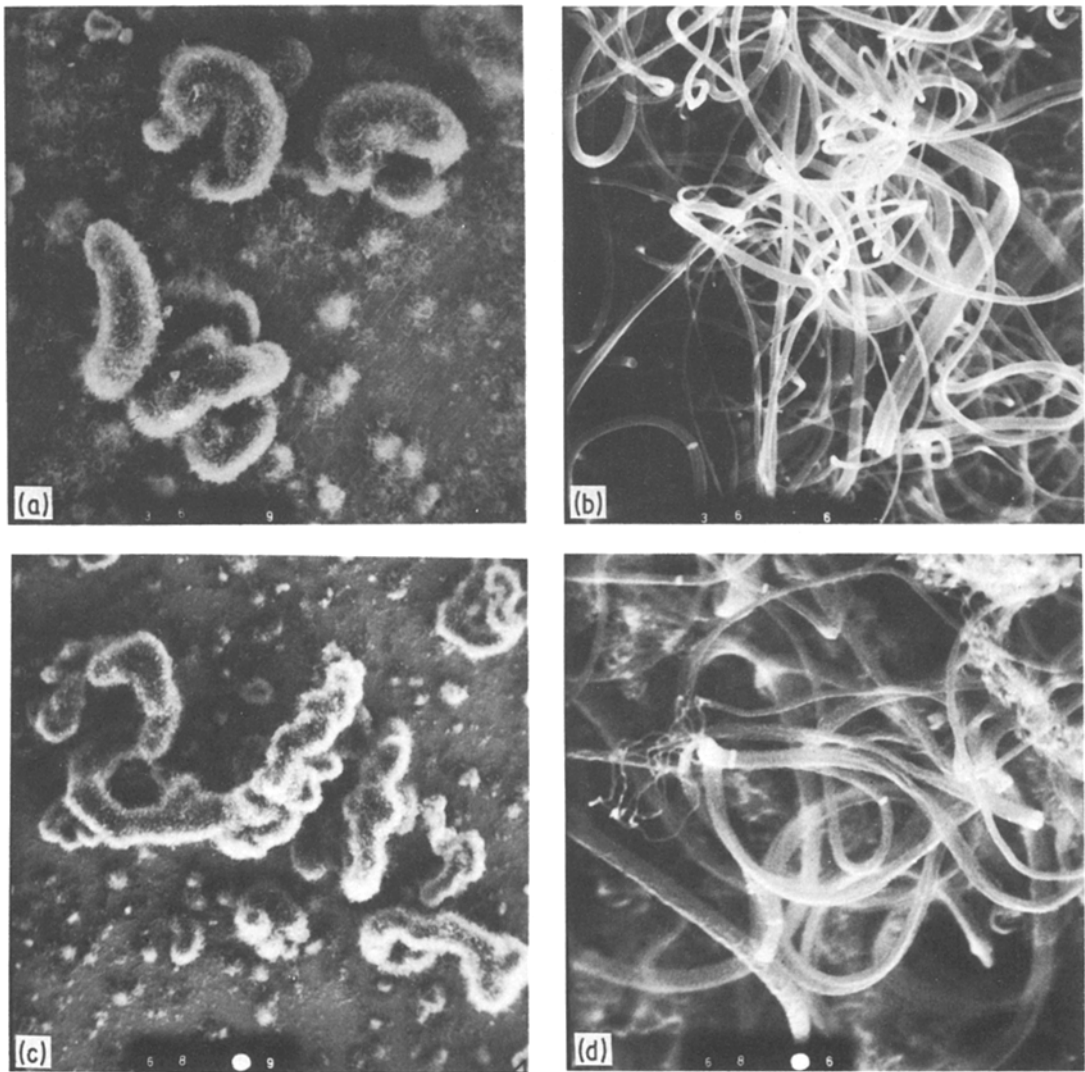


Figure 5 Filament coke formation: (a) on 2535Nb, 180 min ( $\times 3487$ ); (b) on G4868, 120 min ( $\times 1395$ ).



*Figure 6* Coke deposition for 12h on Alloys 36XS and G4868: (a) 36XS ( $\times 46$ ), (b) 36XS ( $\times 1395$ ), (c) G4868 ( $\times 28$ ), (d) G4868 ( $\times 2325$ ).

expected [5] to catalyse coking, as indeed it does. The subsequent substantial growth of carbon leads to a disruption of the carbide film, fragments of which are carried outward with the growing carbon deposit.

Also embedded in the carbon deposit are particles of metal. Analyses of the coke mass were not satisfactory, but did indicate that the particle compositions encompass a considerable range, reflecting the presence of metals and carbides. Chemical analysis of acid-digested metal from the coke deposit [7] showed it to consist essentially of iron and nickel.

These particles should also be catalytically active and their presence throughout the coke

deposit should continue to allow gas-metal contact and to promote coking. This was proved by the fact that coke deposits, separated from the alloy coupons, continued to catalyse coking. A similar conclusion has been arrived at in the case of coking on pure metals, where the coking process was shown to transport catalytic particles into the body of the deposit [4].

The failure of the protective film could result from two causes. It is evident that, even during the initial period, some filamentous carbon is formed at grain boundaries/discontinuities in the film (Fig. 3 and 8). As this carbon grows, the protective film could be dislodged, leading to the exposure of more catalytic metal and to enhanced

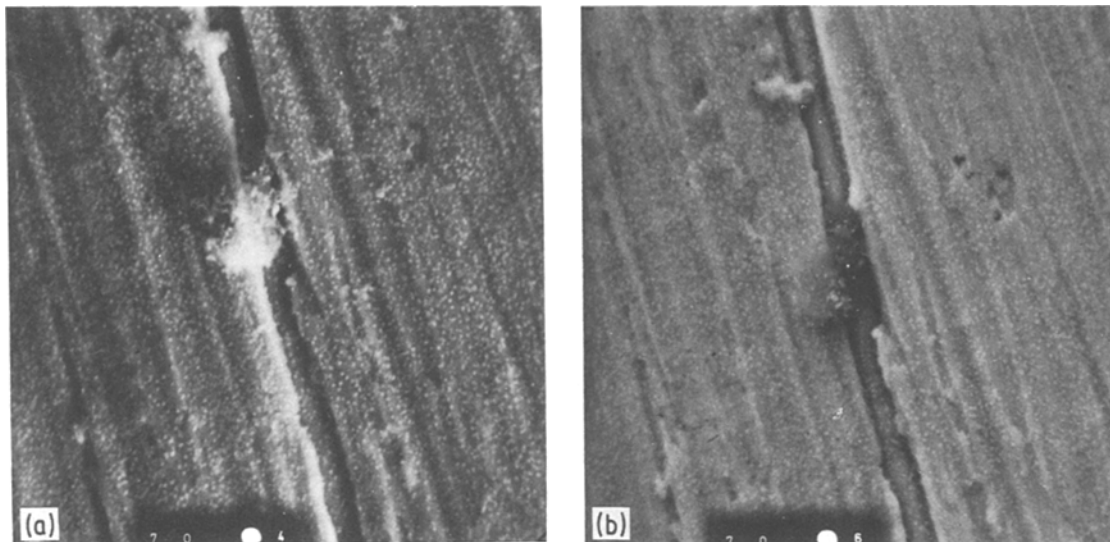


Figure 7 Thin film formation during coking on Alloy 800H, 240 min ( $\times 2092$ ): (a) SEM. micrograph, (b) back-scattered electron image.

growth of filaments. Not every grain boundary would be associated with a discontinuity, but the higher the density of grain boundaries the more the chance of finding a discontinuity and a site for growth of filaments. In support of this, it was found that alloys with larger grain sizes tended to have longer induction periods.

Secondly, it is apparent that reaction of chromium in the alloy to form carbides involves a considerable change in volume ( $6.8 \text{ cm}^3$  of chromium per mole of chromium in the alloy compared to  $9.0 \text{ cm}^3$  of  $\text{Cr}_3\text{C}_2$  per mole of chromium). Accommodating volume expansion

which accompanies the formation of a  $\text{Cr}_3\text{C}_2$  film and  $\text{Cr}_7\text{C}_3$  within the alloy will lead to the accumulation of lateral stresses within the film, which may result in failure after relatively short times. This tendency will be exacerbated by any minor excursion in temperature as a result of the difference in coefficients of thermal expansion between carbide and alloy. Film separation, if it occurs, might well originate at grain boundaries, and a correlation between grain-boundary density and length of induction period would be predicted.

Thus it appears that carbon uptake initially

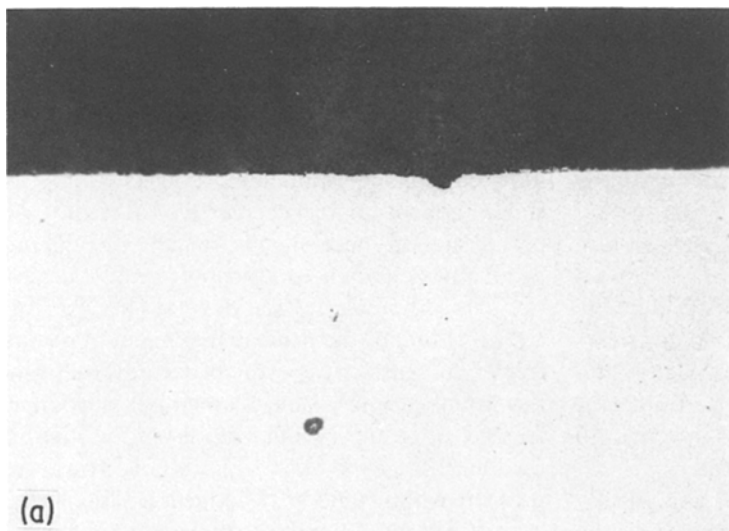
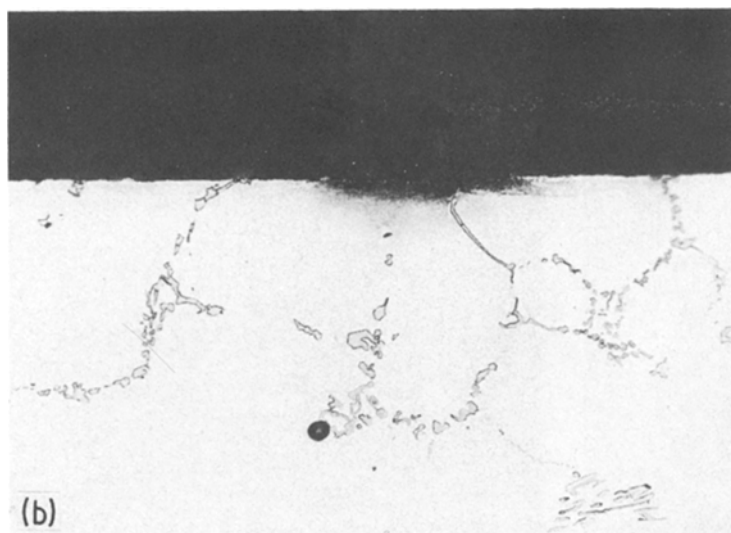


Figure 8 Cross-section of Alloy G4868 after 12 h of reaction ( $\times 415$ ): (a) cross-section showing coke growth, (b) etched cross-section showing carbide formation.





depends on the rate of external carbide formation together with dissolution of carbon in the alloy, and that coking begins when the surface film is disrupted, exposing alloy of different composition. The early onset of coking at the site of spark-machining presumably reflects an alteration in alloy surface chemistry at this location. The effect is so large as to obscure the variation of coking behaviour with bulk alloy composition. Nonetheless, it can be concluded from the present studies that the

resistance of these materials to coking depends on the formation and continued integrity of a superficial, chromium-rich carbide layer.

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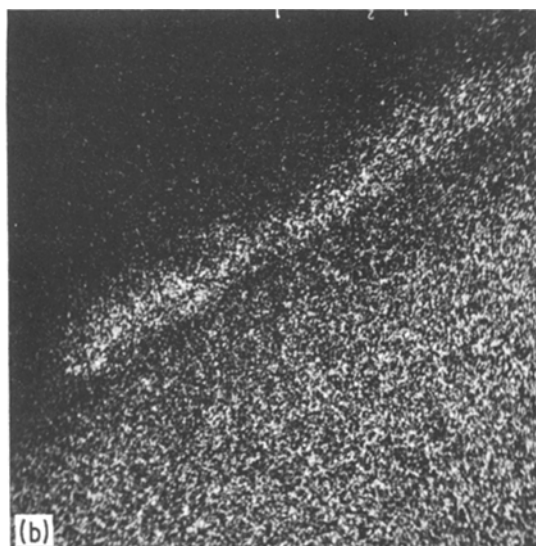
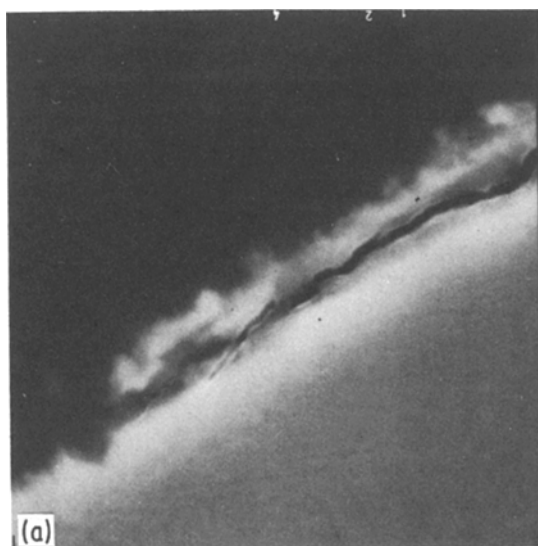


Figure 9 EDAX images of Alloy G4868 after 12 h reaction: (a) general SEM. micrograph ( $\times 6975$ ), (b) chromium content, (c) iron content, (d) nickel content.

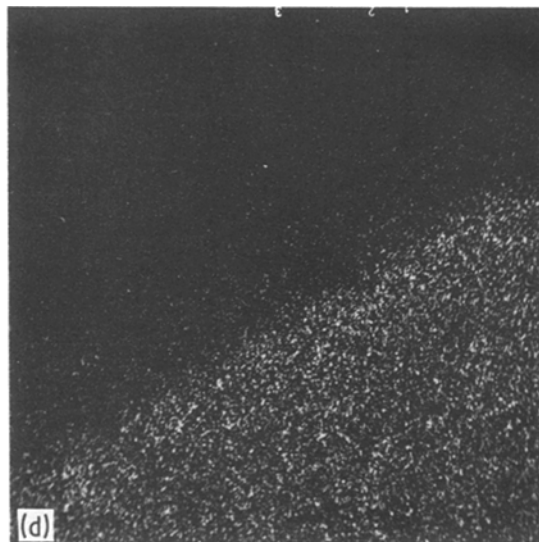
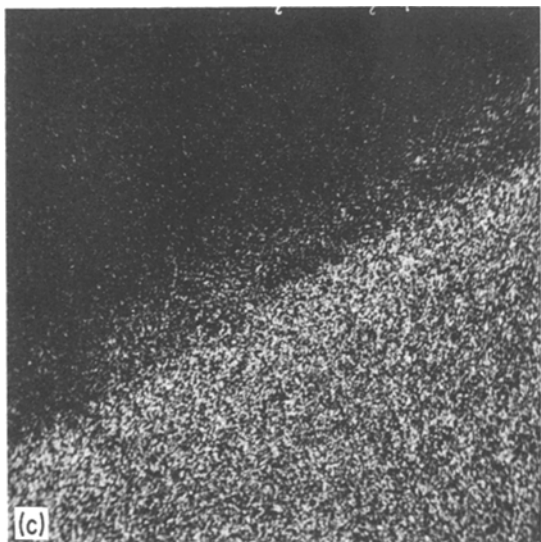


Figure 9 Continued.

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