A study of metal dusting corrosion on Fe- and Ni-based alloys

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Synopsis

Behaviour studies of metal dusting processes and associated filamentous carbon formation were undertaken on Alloys 600, 601, and 800 using a simulated metal dusting environment of 25CO-70H_2-5H_2O (vol.%) at 650°C.

These samples were studied visually and by optical microscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy with energy-dispersive X-ray spectroscopy (TEM-EDX) and X-ray diffraction (XRD). Visual examination and SEM surface observation showed that Alloy 800 suffered metal dusting attack at an early exposure reaction period. The coke deposit amounts increased significantly with reaction time from 168 hours to 336 hours in Alloys 600, 601, and 800. Alloy 800 showed pitting after 168 hours' exposure, and the degree of pitting increased after 336 hours. XRD showed all these alloys had a common austenitic phase, with Alloy 800 also having ferritic metal particles. Alloy 800 after 168 hours' exposure had a complex phase mixture on the surface, consisting of ferritic Fe and austenitic FeNi phases. For coke deposit, there were also Fe_3O_4, Fe_3C and graphitic carbon. The existence of Fe, Ni, and Cr metal particles, and also graphitic carbon in coke deposits, was confirmed by EDX analyses.

Keywords

metal dusting, Alloy 600, Alloy 601, Alloy 800, SEM, TEM, XRD.

Introduction

Metal dusting is a corrosion phenomenon in which iron, steels, and Ni- and Co-based alloys disintegrate into metal or carbide particles in a coke deposit when exposed to strongly carburizing gases (carbon activity a_C>1) at elevated temperatures (400–800°C)[1]. Chromium-containing alloys can form a protective chromia (Cr_2O_3) scale to resist metal dusting. However, extensive chromium carbide (Cr_3C_2, $Cr_{23}C_6$) precipitation results in the depletion of chromium to such an extent that the protective chromia scale is not maintained, and therefore metal dusting occurs. The dusting of these alloys is normally in the form of pitting, where the original material transforms into a dust of coke or graphite and nanocrystalline-sized oxide particles. The mechanisms leading to metal dusting depend on the substrate material (e.g. Fe, Ni, Ni-based alloys, and austenitic and ferritic steels)[2]. The metal dusting phenomenon occurs in many petrochemical processes and is thus of great significance because of cost of replacement of the metal-dusted plant components and the associated downtime.

Metal dusting occurs in environments where carbon activity, a_C > 1, and the gaseous reactions that lead to or cause metal dusting are[3]:

$$\begin{aligned} &CO + H_2 = C + H_2O \\ &a_c = K_1.P_{CO}.P_{H2} / P_{H2O} \end{aligned} \qquad [1]$$

$$\begin{aligned} &2CO = C + CO_2 \\ &a_c = K_2.P^2{}_{CO} / P_{CO2} \end{aligned} \qquad [2]$$

$$\begin{aligned} &CH_4 = C + 2H_2 \\ &a_c = K_3.P_{CH4} / P^2{}_{H2} \end{aligned} \qquad [3]$$

In this study, a simulated metal dusting gas mixture of 25CO–70H_2–5 H_2O (vol.%) at 650°C was fed into the system, and using Equation [1], the carbon activity, a_C, was 5.50, and oxygen partial pressure, p_{O2}, was 3.47 × 10^{-25} atmospheres.

Investigational procedure

The behaviour studies of metal dusting were carried out on Alloys 600, 601, and 800. These alloys were cut to 20 x 20 mm

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dimensions with a 5 mm hole in the centre for holding a coupon on an alumina ceramic boat. Coupons were ground to a 320 grit finish with silicon carbide (SiC) paper before exposure in the simulated metal dusting atmosphere in the especially designed rig. Table I shows the nominal compositions of Alloys 600, 601, and 800 (wt%).

For metallographic evaluation, the reacted specimens were first copper-plated to avoid removal of the surface during preparation, and then mounted on edge for viewing the cross-section in a polyfast conductive resin for optical microscopy and SEM analysis. Mounted specimens were successively ground to 1200 grit using SiC paper, and then polished to 1 μm finish using diamond slurry. Reaction kinetics and product characterizations of the alloys were studied by visual examination, optical microscopy, SEM-EDX, TEM-EDX, and XRD.

Experimental results

Investigation of Alloy 600

Figure 1a shows a photograph of Alloy 600 before exposure. After 24 hours' exposure the alloy turned goldish in colour, as seen in Figure 1b. Figure 1c shows that after 96 hours' exposure it became a brownish colour, with no sign of metal degradation. After 168 hours' exposure, the sample had small amounts of coke deposit on the surface (Figure 1d). Figure 1e shows the sample after 336 hours' exposure with coke deposits on the surface, and Figure 1f shows it after coke removal, indicating no sign of major metal degradation, although fine pits were seen on the edges and surfaces.

The surface of Alloy 600 before exposure is shown in Figure 2a. There was not much change on the surface after 24 hours' exposure (Figure 2b). After 96 hours (Figure 2c) there were uniform platelets on the surface with a dark phase between. Figure 2d shows light platelets on the surface with a grey phase after 168 hours. After 336 hours (Figure 2e), there were coke deposits and some white precipitates, and carbon filaments (Figure 2f). EDX analysis confirmed the presence of carbon filaments.

Figure 3a shows a grey oxide layer on Alloy 600 after 24 hours' exposure. The prepared cross-sections were then compared. Figure 3b shows a thicker dark layer along the edges after 96 hours. After 168 hours there were coke deposits on the edge, with some penetration into the alloy. XRD confirmed only the FeNi (γ) phase after 24, 96, and 168 hours' exposure, but after 336 hours there was γ, α-CrFe, Cr_2O_3 and graphite on the surface. The coke deposit contained graphite-2H; C, α-CrNi, and Fe_3O_4 (Figure 4).

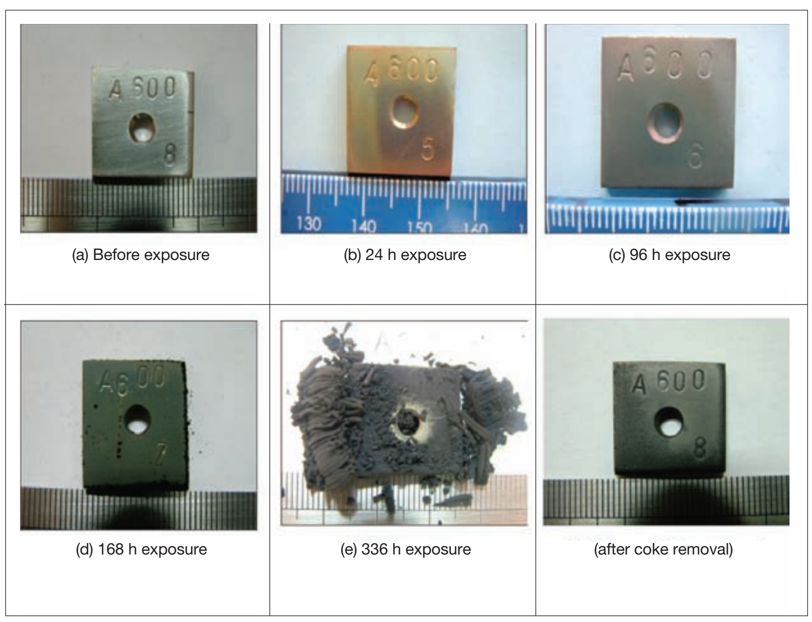
Investigation of Alloy 601

Figure 5a shows Alloy 601 before exposure. After 24 hours' exposure there was a bluish colour on the surface, and a brownish colour on the edges of the coupon, as shown in Figure 5b. The bluish colour remained visible on the surface after 96 hours' exposure(Figure 5c). After 168 hours' exposure the sample had some coke deposits on the edges (Figure 5d), and these had increased after 336 hours (Figure 5e). After removal of the coke, there was no sign of major metal degradation, although there were fine pits present (Figure 5f).

Table I

Nominal compositions of Alloys 600, 601, and 800 (wt%)[4]

Alloy	C	Cr	Ni	Fe	Al	Ti
600	0.08	15.5	Bal.	8.0	-	-
601	0.10	23.0	Bal.	14.4	1.4	-
800	0.05	21.0	32.5	Bal.	0.3	0.3



(a) Before exposure (b) 24 h exposure (c) 96 h exposure

(d) 168 h exposure (e) 336 h exposure (after coke removal)

Figure 1—Photographs of Alloy 600 coupons after different exposure times

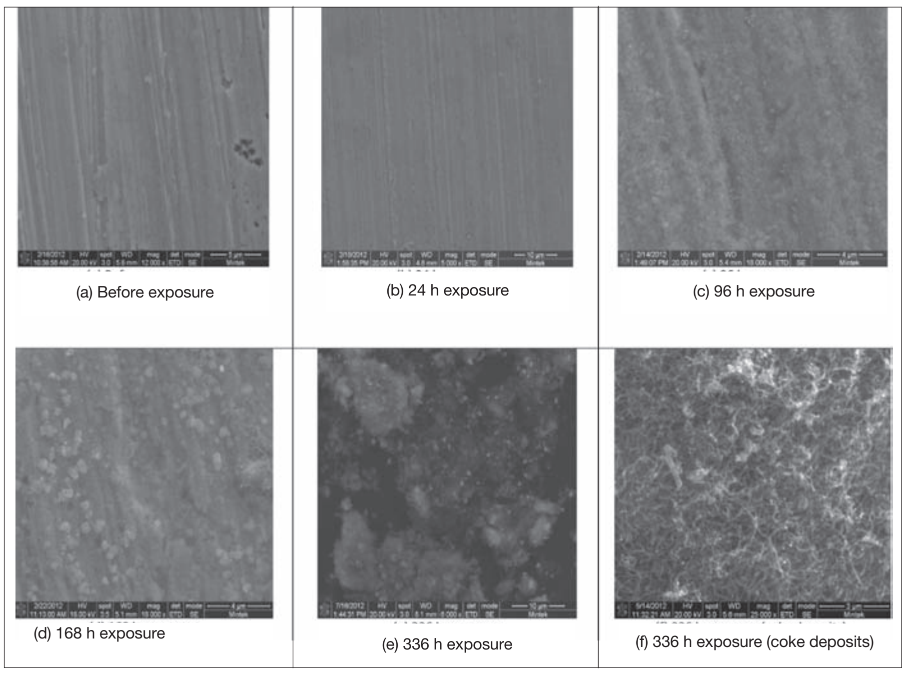


Figure 2—SEM-SE images showing the surfaces of Alloy 600 after different exposure times

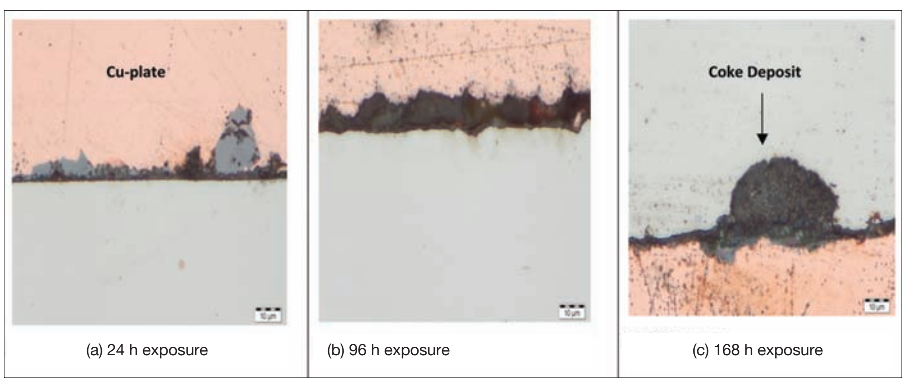


Figure 3—Optical micrographs of cross-sections of Alloy 600 after different exposure times

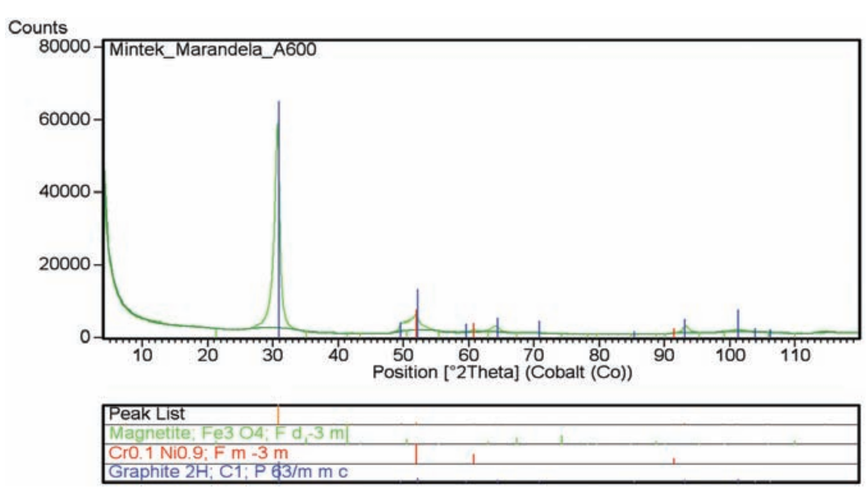
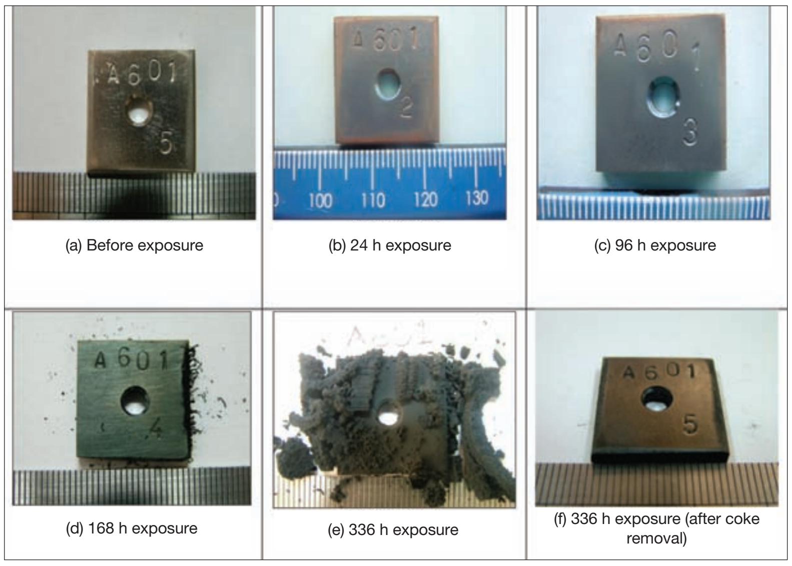
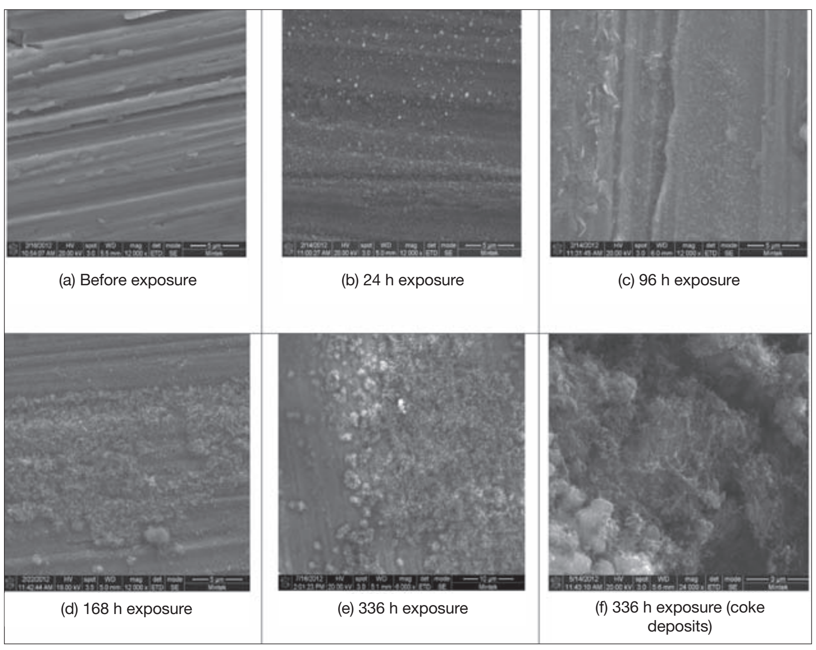


Figure 4—XRD pattern of coke deposits from Alloy 600 after 336 h exposure



(a) Before exposure (b) 24 h exposure (c) 96 h exposure (d) 168 h exposure (e) 336 h exposure (f) 336 h exposure (after coke removal)

Figure 5—Photographs of Alloy 601 coupons after different exposure times



(a) Before exposure (b) 24 h exposure (c) 96 h exposure (d) 168 h exposure (e) 336 h exposure (f) 336 h exposure (coke deposits)

Figure 6—SEM-SE images showing the surfaces of Alloy 601 after different exposure times

The surface of Alloy 601 before exposure is shown in Figure 6a. Figure 6b shows the surface after 24 hours' exposure, exhibiting fine platelets on the surface with some white precipitates. Figure 6c shows a fine deposit on the surface. After 168 hours' exposure, there were grey protrusions on the surface, as shown in Figure 6d. These had increased in number after 336 hours' exposure (Figure 6e). There were also carbon filaments (Figure 6f), which were confirmed by EDX.

The cross-sections of Alloy 601 were compared. After 24 hours' exposure (Figure 7a) there was a thin deposit. Figure 7b shows a cross-section optical micrograph after 96 hours' exposure showing some slight attack on the edges progressing internally in the alloy. The optical micrograph after 168 hours' exposure (Figure 7c) shows slight attack on the edges of the alloy. XRD showed the presence of γ, α-CrFe, and graphite on the surface, whereas the coke deposit contained Fe_3O_4, α-CrNi and graphite-2H; C, as shown in Figure 8.

Investigation of Alloy 800

The coupons of Alloy 800 were compared after different exposure times. There was very little difference between the unexposed sample and that exposed for 24 hours (Figure 9a and 9b), whereas the film had darkened and become duller after 96 hours (Figure 9c). Both samples at 168 hours' and 336 hours' exposure had coking on the surface. Once the coke had been removed, pitting could be seen, with larger pits for the longer exposure.

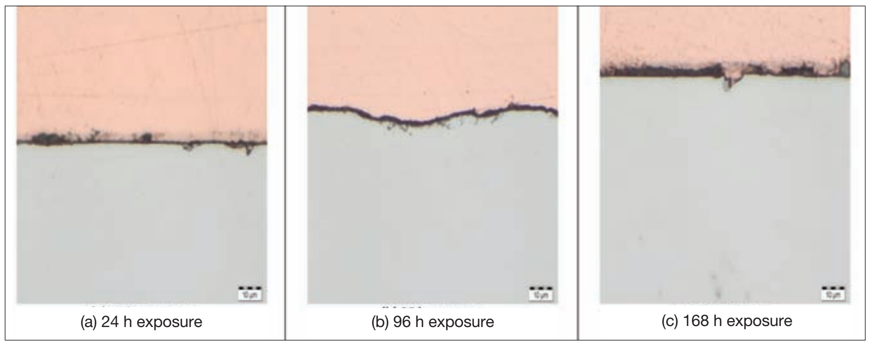


Figure 7—Optical micrographs of cross-sections of Alloy 601 after different exposure times

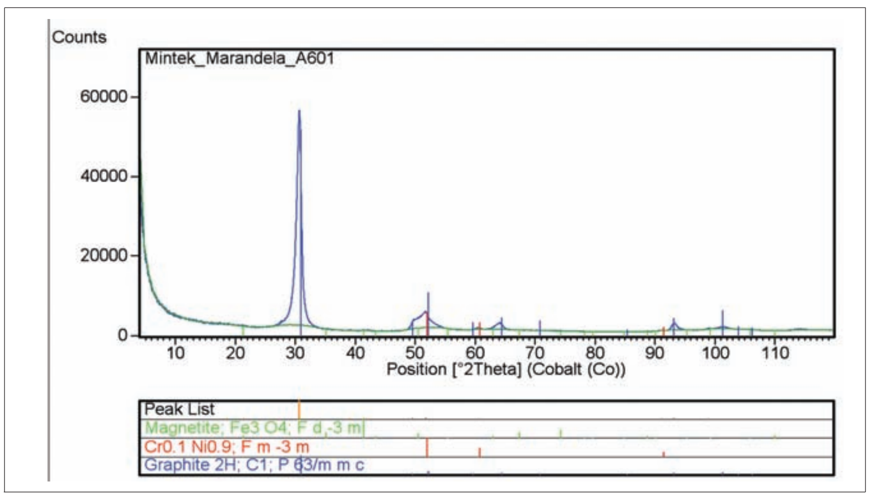


Figure 8—XRD pattern of coke deposits from Alloy 601 after 336 h exposure

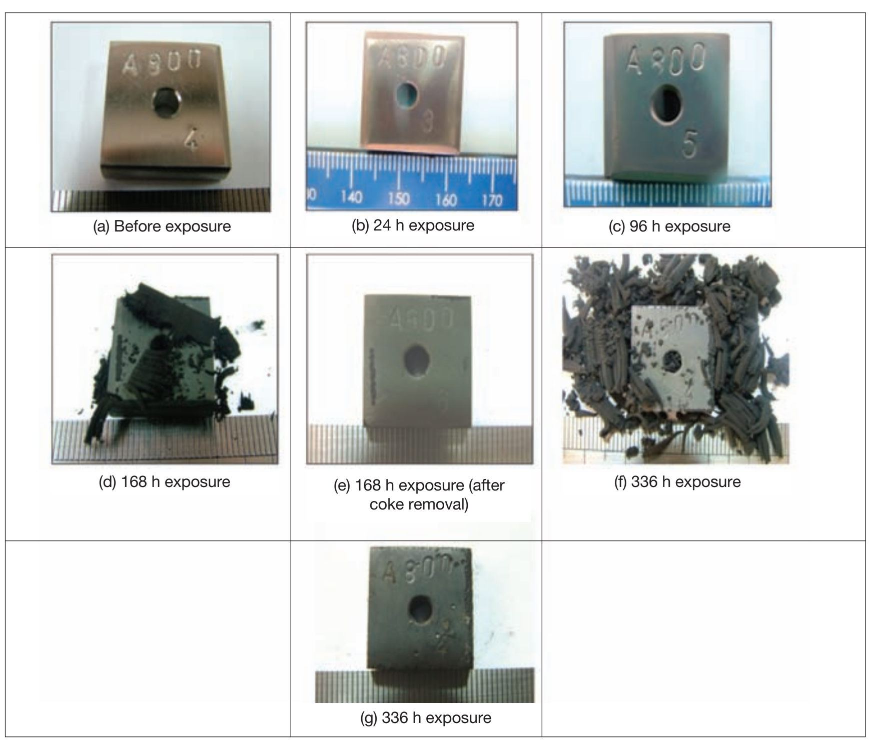


Figure 9—Photographs of Alloy 800 coupons after different exposure times

The surface of Alloy 800 before exposure is shown in Figure 10a. After 24 hours' exposure, there were fine and uniformly distributed platelets (Figure 10b). Figure 10c shows that the uniformly distributed platelets which had increased in size after 96 hours. After 168 hours' exposure, the platelets remained and the coke deposit was discernable. EDX identified C, Fe, Ni, and Cr on the surface. After 336 hours, the deposits had increased further. The surface in Figure 10f also shows uniform platelets, and Figure 10g shows coke deposits with carbon filaments. The presence of C was confirmed by EDX analysis.

The prepared cross-sections were compared. Figure 11a shows a cross-section of Alloy 800 after 24 hours' exposure, exhibiting a uniformly distributed grey oxide layer along the edge, with some penetration. After 96 hours' exposure, the cross-section shows the edge of the alloy without any attack (Figure 11b). Figure 11c shows the coke deposit layer deposited on the edge after 168 hours' exposure. The XRD

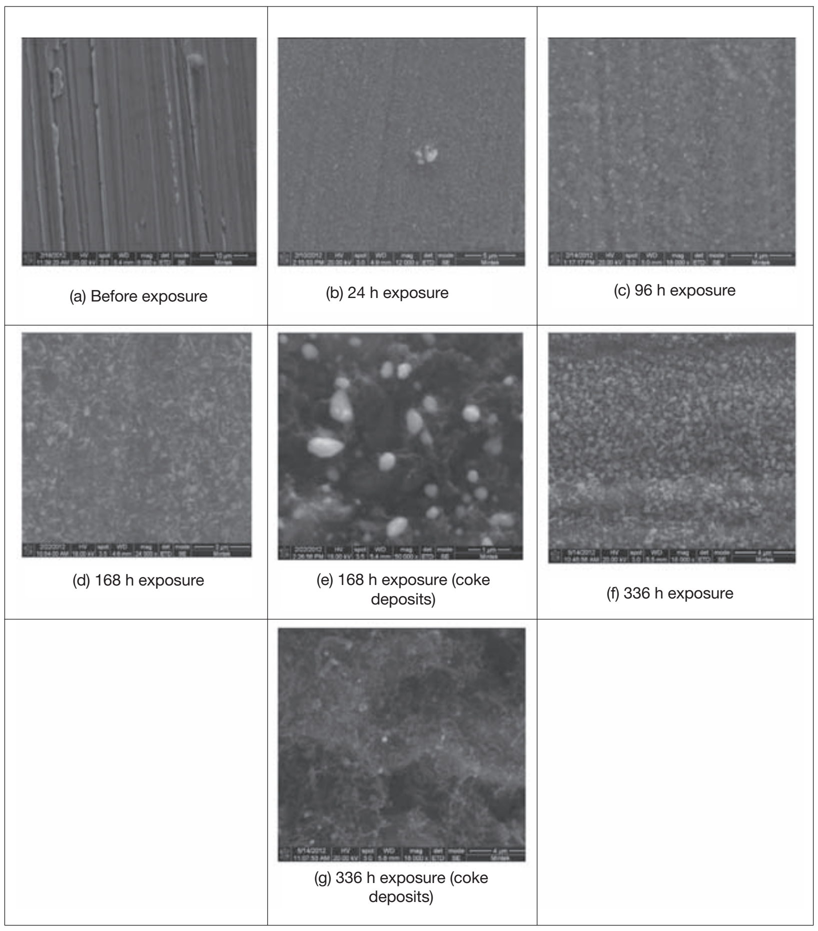


Figure 10—SEM-SE images showing the surfaces of Alloy 800 after different exposure times

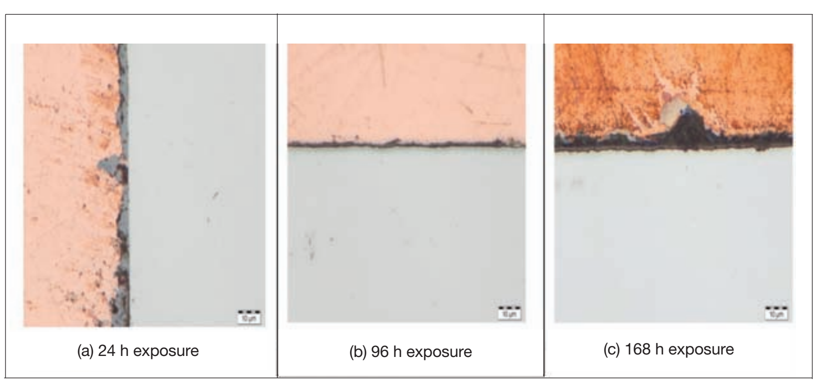


Figure 11—Optical micrographs of cross-sections of Alloy 800 after different exposure times

spectrum revealed the existence of α-Fe and γ phases after 24 and 96 hours' exposure. The coke deposit after 168 hours comprised graphite-2H; C, γ, Fe_3C, and Fe_3O_4, as shown in Figure 12. XRD identified Fe_3O_4 and graphite-2H; C in the coke deposits, as can be seen in Figure 13, and also γ, α-CrFe, and $Cr_{23}C_6$ after 336 hours' exposure.

Reaction kinetics

Figure 14 shows the reaction kinetics of Alloys 600, 601, and 800 for mass change and coke deposits after exposure. There was no metal loss from Alloys 600 and 601 until after 168 hours. Alloy 800 experienced metal losses after 96 hours due to pitting, with increased loss after 336 hours' exposure. Coke deposits increased with increased exposure time, but become noticeable only after 168 hours. Alloys 800 and 600 had high amounts of coke deposits. There are no error bars in Figure 14 as only individual measurements were taken.

Discussion

Ni-based alloys (Alloy 600 and 601) had better metal dusting resistance than the Fe-based alloy (Alloy 800). Alloy 601 suffered less metal loss, which can be attributed to its potential to form a double barrier Cr_2O_3 and Al_2O_3 protective oxide layer due to the high Cr and Al contents. Alloys 800 and 600 depend mostly on Cr content for protection by Cr_2O_3, which was attacked after longer exposure, then allowing metal degradation to take place. Extensive chromium carbide ($Cr_{23}C_6$) precipitation resulted in the depletion of chromium to such an extent that the protective chromia scale was not maintained, and therefore metal dusting occurred[2]. Metal attack on Alloy 800 occurred by pitting from about 168 hours' exposure, and increased at 336 hours. Ni-based alloys (Alloys 600 and 601) had fine pits at the edges after 336 hours, which caused metal loss. Coke deposited on the alloys contained carbon filaments, with Fe, Ni, and Cr metal particles.

Conclusions

From visual examination, optical microscopy, SEM-EDX, TEM-EDX, and XRD analysis, the following conclusions were drawn:

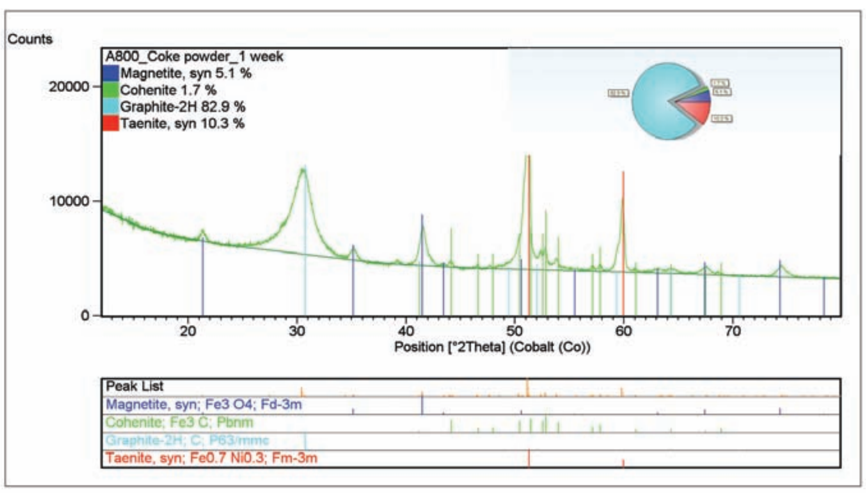


Figure 12—XRD pattern of coke deposits from Alloy 800 after 168 h exposure

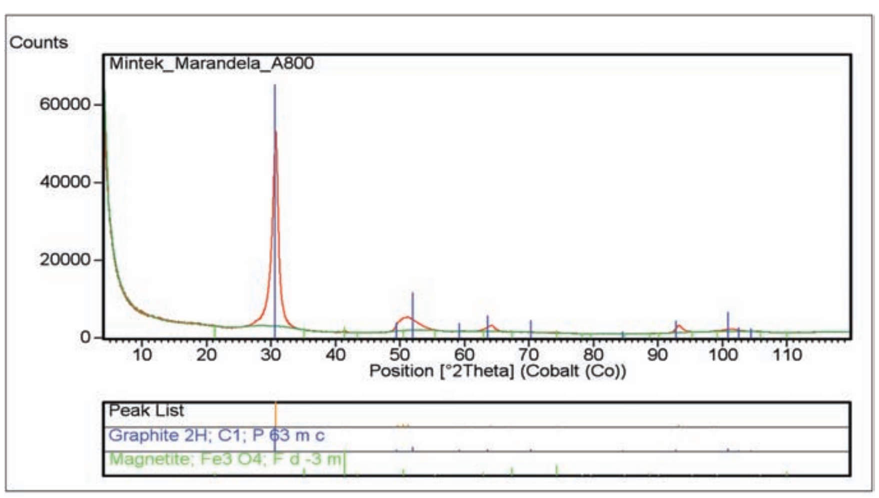


Figure 13—XRD pattern of coke deposits from Alloy 800 after 336 h exposure

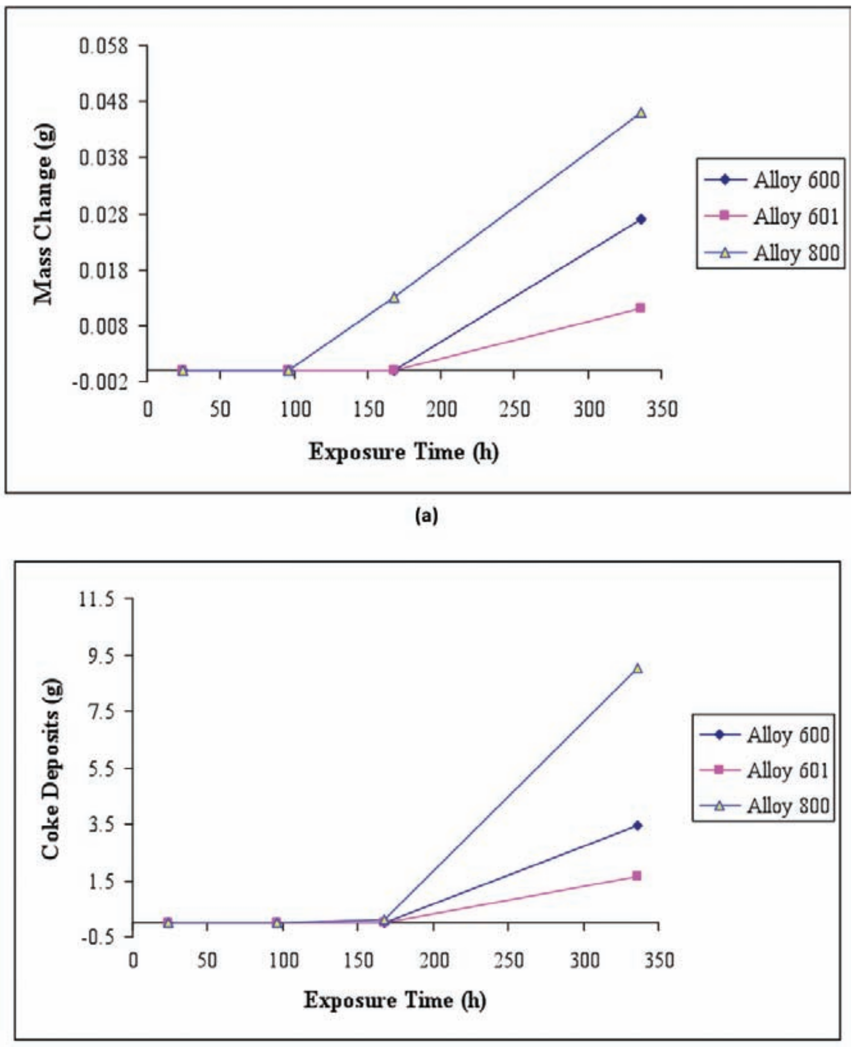


Figure 14—Reaction kinetics on Alloys 600, 601 and 800: a) mass change, and b) coke deposition

- Alloys 600 and 601 had better metal dusting resistance than Alloy 800, with Alloy 601 suffering less metal loss
- Alloys 600 and 601 had only fine pits at the edges after 336 hours
- Alloy 800 suffered major metal dusting attack from 168 hours due to pitting, which increased with exposure time
- The coke deposits increased on all alloys with increased exposure
- SEM-EDX and TEM-EDX confirmed the presence of coke deposits, which comprised carbon filaments and metal particles
- XRD showed Alloys 600 and 601 to have γ, α-CrFe, and also Cr_2O_3 and graphite after 336 hours, whereas the coke deposits contained Fe_3O_4, α-CrNi and graphite-2H; C
- XRD showed Alloy 800 to have γ, Fe_3O_4, Fe_3C, $Cr_{23}C_6$ and graphite-2H; C phases.

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