INFLUENCE OF PREOXIDATION ON FECRALLOY EFFICACY AS A CATALYST SUPPORT

S.A. Adegbite[‡], M. Barigou[‡], M.J.H. Simmons[‡], A. Wagland[#] and E.H. Stitt[*]

[‡] *School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*
[#] *Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, UK*
[*] *Johnson Matthey Technology Centre, PO Box 1, Belasis Avenue, Billingham, TS23 1LB, UK*

Abstract: The physiochemical transformations caused by thermal pre-oxidation of the surface of Fecralloy® foil, an integral component of metallic monolith catalysts, have been studied to assess their influence on coating adherence. The foil coupons were pre-oxidised at 950 °C for 0, 5, 10 and 30 h and the mass gain was found to fit a hyperbolic model. Measurements were made of surface topography and microstructure using laser profiling interferometry (LPI) and scanning electron microscopy (SEM), with chemical analysis being obtained from X-ray diffraction (XRD). The optimal surface roughness was obtained after 10 h of pre-oxidation, when the surface contained significant amounts of α-alumina arranged as randomly oriented whiskers. Upon coating of the treated foil coupons with a γ-alumina slurry, the sample pre-oxidised for 10 hours gave the best performance in terms of coating loading (7.94 mass %) and adherence (< 10 mass % loss) based on a ultrasonic vibration test.

Keywords: catalyst, Fecralloy®, pre-oxidation, metal, monolith, coating, foil

1. INTRODUCTION

Tightening emissions legislation for vehicles across the world has caused the use of monolith catalysts in automobile emission control to become ubiquitous. Their impact has been considerable, with emission levels from exhaust systems of passenger cars falling by more than 90% since 1975, and with zero emissions now a future target. Environmentally harmful carbon monoxide and oxides of nitrogen in the exhaust stream are converted inside the monolith catalyst into carbon dioxide and nitrogen (Twigg, 2006; Acres and Harrison, 2004).

Monoliths are structures comprised of multiple parallel channels. One method of producing monolith catalysts is to coat the monolith surfaces with γ-alumina slurry containing active species (usually platinum group metals, PGMs, such as Pt, Pd and Rh). Monoliths are generally made from either metallic or ceramic materials, the former from thin metal sheet such as Fecralloy®, the focus of this study, and the latter typically from cordierite (Avila et al., 2005). Fecralloy® is comprised essentially of iron, Fe, chromium, Cr and aluminium, Al. It is well suited for catalyst support applications because of its high mechanical strength, thermal conductivity and ductility which make it easy to process. It clearly outperforms cordierite as a monolith material in all these crucial properties (Hickman and Schmidt, 1992ab).

To ensure adherence of the γ-alumina coatings, Fecralloy® has to be pre-oxidised which changes its surface topography to provide a rough surface (Cybulski and Moulijn, 2006). Pre-oxidation also provides enrichment of the Fecralloy® surface with aluminium, therefore prolonging the product component life (Nicholls and Quadakkers, 2002). Some studies have assessed the effects of pre-oxidation on dip-coated foil coupons, by relating the surface microstructure obtained by scanning electron microscopy (SEM) to the coating adhesion (e.g. Jia et al., 2007; Zhao et al., 2003). However, these comparisons are somewhat qualitative in nature and do not consider a quantitative measure of the surface roughness, nor do they address coating at a controlled shear rate. In this new study, a detailed assessment of Fecralloy® 3D and 2D surface topography by laser profiling interferometry (LPI) was performed as a function of pre-oxidation treatment. In addition, SEM and X-ray diffraction (XRD) techniques have been applied to give a comprehensive description of the physiochemical transformations caused by pre-oxidation. To determine the effect of pre-oxidation on adhesion, a standard γ -alumina slurry was deposited onto the Fecralloy®

foil coupons at a controlled shear rate using an automatic film applicator, and the resulting composites were dried and calcined afterwards. The coating loading and adherence were determined to reveal the optimal pre-oxidation conditions.

2. MATERIALS AND METHODS

2.1. Pre-treatment and assessment of Fecralloy foil

Commercially available Fecralloy® foil of 50 µm thickness with a composition of Fe (72.6 wt%), Cr (22.0 wt%), Al (4.80 wt%), Y (0.30 wt%) and Si (0.30 wt%) (GoodFellow, UK) was used. The foil was cut into 50 mm × 80 mm coupons. The pre-treatment of the coupons consisted of the following steps (Jia et al., 2007):

- *Degreasing*: ultrasonic cleaning at room temperature in acetone bath for 10 min, and then with deionised water at 80 °C for 10 min
- *Pre-oxidation*: oxidation in a furnace (Lenton, UK) at 950 °C for different durations: 0, 5, 10 and 30 h

The specific mass gain of the coupons as a function of pre-oxidation time was determined. The 2D and 3D topography of the coupons were measured by LPI equipped with a 60° conical stylus (Taylor Hobson, UK). The interferometer measured 1000 sampling lengths of 5 µm each, thus, covering a total evaluation length of 5 mm. The surface chemical composition of the coupons was determined by XRD using an X' Pert Pro diffractometer (Phillips, The Netherlands) using Fe-filtered Co Kα radiation and a power of 45 kV × 30 mA, while their microstructure was assessed by using a JEOL 6060 SEM (Oxford Instruments, UK).

2.2. Coating of foils by an automatic film applicator

A γ-alumina slurry of d_{50} = 4.36 µm and solids concentration of 40 wt% was prepared at a pH of 4 using ethanoic acid solution (Fischer Scientific, UK). The slurries were deposited onto the Fecralloy® coupons using a 1132N automatic film applicator (Sheen Instruments, UK) which provided close control of the transverse coating speed. The slurries were drawn across the coupons at a transverse speed of 100 mms^{-1} using a wire-wound bar of 100 µm nominal gap as shown in Fig. 1(a)

The coated coupons were allowed to dry at room temperature, and were then oven dried at 110°C for 1 h and finally calcined at 500°C for 1 h. The surface view of a product coating obtained by SEM is shown in Fig. 1(b).

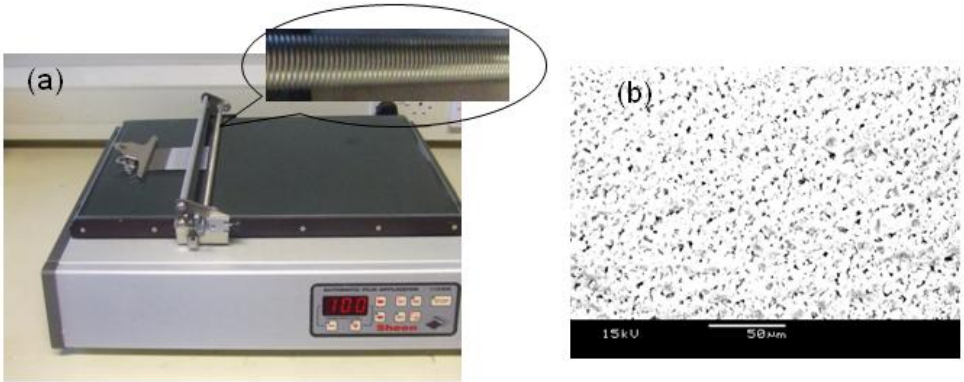


Fig. 1. Coating of Fecralloy® coupons: (a) Coating by an automatic film applicator showing wire-wound bar; (b) SEM micrograph of coating surface.

2.3. *Assessment of coatings*

The loading of slurry on the Fecralloy® surface was calculated by the percentage mass increase of the coupon after coating. To determine coating adherence, the coated foils were soaked into petroleum ether contained inside a sealed beaker for 30 min, then soaked in an ultrasonic bath (300 W and 16 kHz) for 30 min and later dried in an oven at 110°C for 2 h. The percentage mass loss was then calculated. Thus, the lower the mass loss the better the coating adherence.

3. RESULTS AND DISCUSSION

3.1. *Pre-oxidation profile*

The pre-oxidation profile shown in Fig. 2 represents the specific mass gain by foils as a function of pre-oxidation time. The increase in the specific mass gain of the foil with pre-oxidation time arises from the continuous formation of oxide layers on the foil surface. A hyperbolic curve of the following form is shown to describe the pre-oxidation profile very well, with an R value of 0.99:

$$\Delta\overline{m} = \frac{at}{c+t} - \frac{bt}{c+t} \qquad (1)$$

where $\Delta\overline{m}$ is specific mass gain (mgcm^{-2}) and *t* is preoxidation time (h). The constants a, b, c were found to be 12.7, -12.4, and 5.0, respectively. This result is similar to the pre-oxidation profile obtained at 925 °C by Pragnell and Evans (2006).

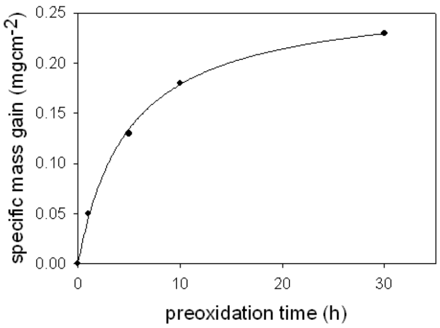


Fig. 2. Pre-oxidation profile of Fecralloy® coupons from 0 to 30 h.

3.2. *Topography characterisation of Fecralloy® coupons by LPI*

The surface topography of the coupons, represented by the 2D and 3D roughness parameters and the textural profiles (Smith, 2002) measured by the interferometer, are shown in Table 1 and Fig. 3. The roughness parameters for the untreated coupon were initially very low, implying negligible efficacy for coating adherence. The roughness parameters increased significantly after 5 h pre-oxidation, peaked at 10 h pre-oxidation and later declined upon prolonged pre-oxidation for 30 h (see Table 1). Clearly, the Fecralloy® coupon pre-oxidised at 950 °C for 10 h had the roughest (optimal) surface; this is supported by the textural profiles shown in Fig. 3. The profiles shown in Fig. 3 also exhibit order in their surface structure, this is particularly evident in the sample shown in Fig. 3(c).

Table 1. 2D and 3D roughness parameters of coupons pre-oxidised at 950 °C for 0 – 30 h

roughness parameters	type	definition	values (μm)			
			0 h	5 h	10 h	30 h
R_a	2D	arithmetic mean	0.06	0.15	0.31	0.23
R_q	2D	root mean square	0.08	0.17	0.36	0.20
S_a	3D	arithmetic mean	0.20	0.35	0.83	0.52
S_q	3D	root mean square	0.24	0.42	1.01	0.69

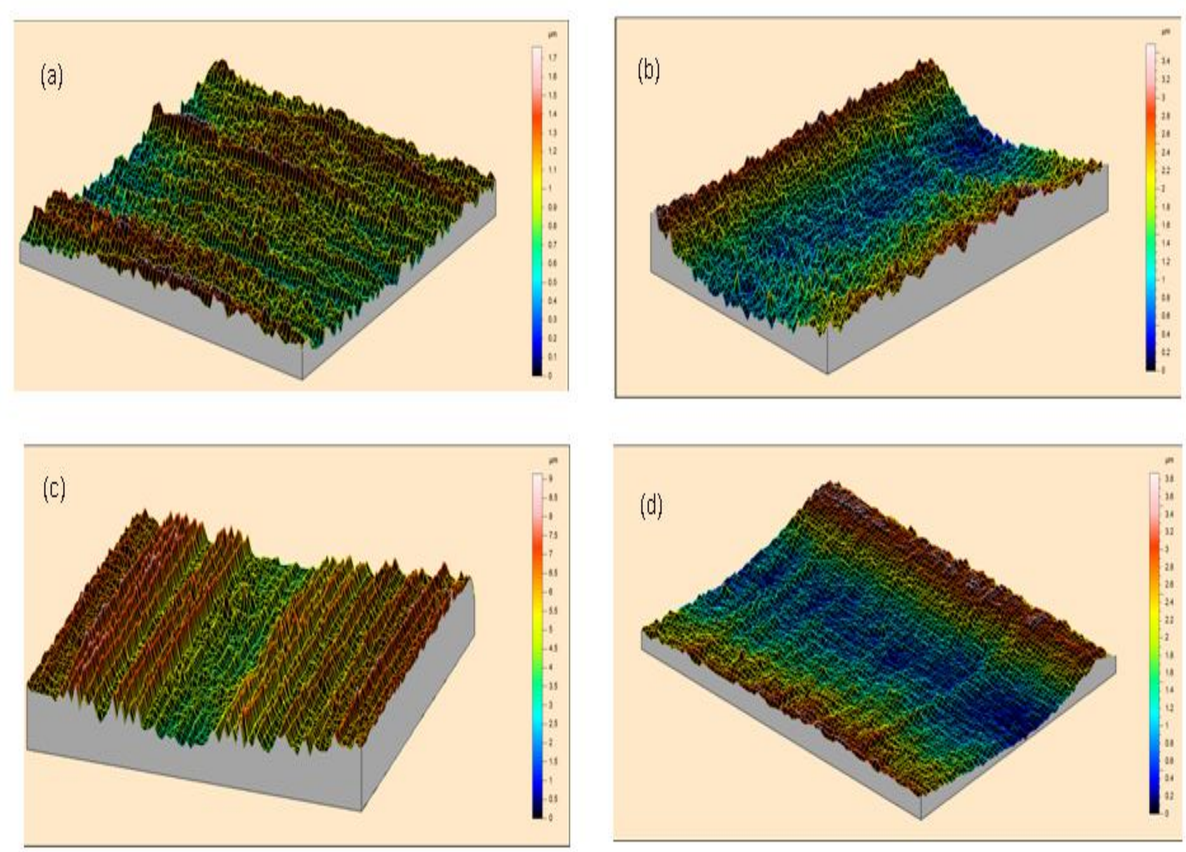
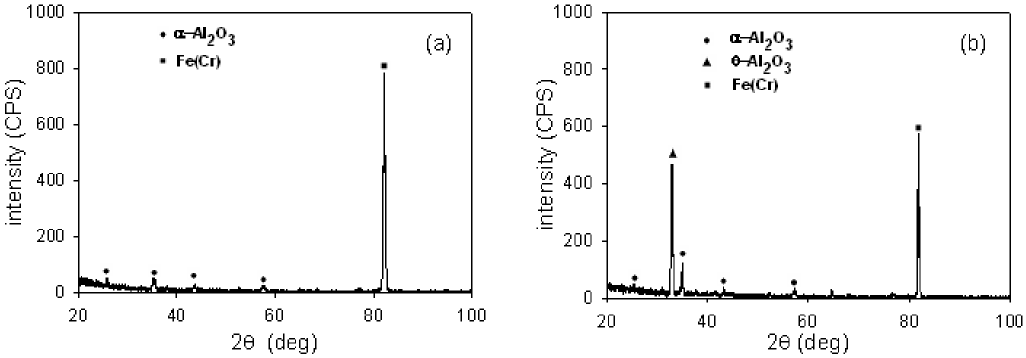


Fig. 3. Textural profiles of Fecralloy® coupons preoxidised at 950^{o}C for (a) 0 h; (b) 5 h; (c) 10 h; and (d) 30 h.

3.3. XRD analysis of Fecralloy® surface

The XRD patterns in Fig. 4 show the surface chemical composition of the coupons pre-oxidised at 950 ^{o}C for 0 – 30 h. The untreated coupon comprises of a Fe(Cr) peak and some α-alumina peaks, which are present in disproportionately small amounts (Fig. 4(a)). Pre-oxidation for 5 h produced substantial amounts of θ-alumina and a small amount of α-alumina (Fig. 4(b)). Increased pre-oxidation to 10 h produced sufficient transformation of θ-alumina into α-alumina, as the peaks of the latter are large and conspicuously visible (Fig. 4(c)). Prolonged pre-oxidation however resulted into formation of α-alumina conglomerates as other alloy elements are spontaneously oxidised; this is characterised by diminishing peaks of α-alumina (Fig. 4(d)). The Fecralloy® surface enrichment by aluminium during pre-treatment is caused by an elemental transport process (Jia et al., 2007; Nicholls and Quadakkers, 2002).



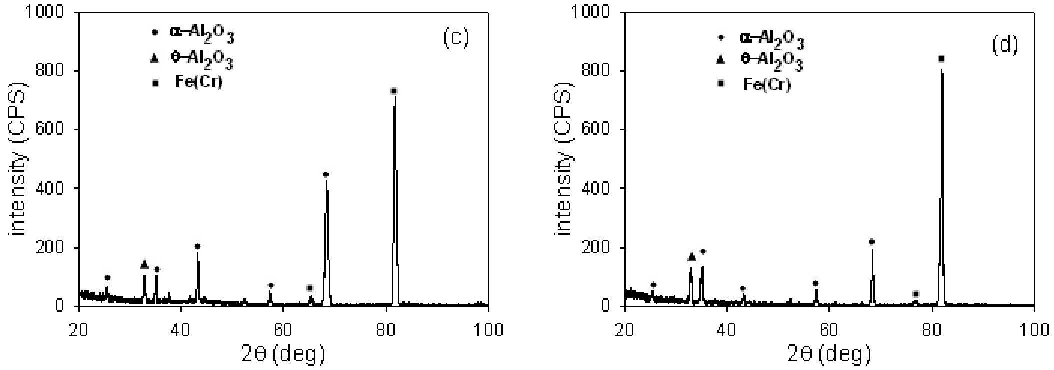


Fig. 4. XRD patterns of Fecralloy® coupons pre-oxidised at 950^{o}C for (a) 0 h; (b) 5 h; (c) 10 h; and (d) 30 h.

3.4. Assessment of Fecralloy® surface microstructure by SEM

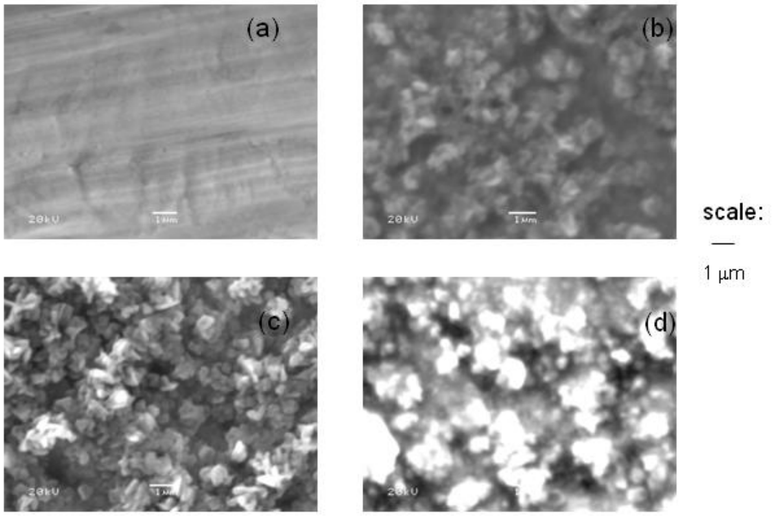


Fig. 5. SEM micrographs of Fecralloy® coupons pre-oxidised at 950^{o}C for (a) 0; (b) 5; (c) 10 and (d) 30 h

The SEM micrographs displayed in Fig. 5 clearly show the distinctions between the surface morphologies of the untreated and pre-oxidised coupons. The untreated coupon (Fig. 5(a)) has no significant microstructure while the pre-oxidised coupons contain α–alumina whiskers (Fig. 5(b) – (d)). After 5 h of pre-oxidation, there exists trace amounts of α-alumina. However, the coupon pre-oxidised for 10 h is characterised by uniform, full, conspicuous and randomly oriented α-alumina whiskers, known for their excellent adhering capability (Avila et al., 2005). The attendant effect of pre-oxidation for up to 30 h was the formation of non-uniform conglomerates of α-alumina. These results show good correlation with the findings of Jia et al. (2007).

3.5. Coating loading and adherence

The coating loading and weight loss from adhesion test are shown in Table 2. Clearly, the duration of pre-oxidation has a major influence on the capability of the foil to perform well as a catalyst support. The results in Table 2 can be explained in the light of the Fecralloy® surface characterisation discussed above in sections 3.2 – 3.4. For the untreated coupon, the coating loading and adherence were unsurprisingly very poor because the foil surface was the least rough. The coupons pre-oxidised for 5 and 30 h showed improved capabilities which is commensurate with their roughness characteristics in section 3.2. The optimal coating loading and adherence were obtained from the coupon with the roughest surface i.e. the sample pre-oxidised for 10 h. This is because of the enhanced surface microstructure brought about by the randomly oriented α-alumina whiskers, thereby creating an ideal topography which is suitable for coating.

Table 2. Coating properties for Fecralloy® coupons pre-oxidised at 950°C for 0 – 30 h.

pre-oxidation time (h)	coating loading[1] (mass %)	mass % loss[1] from adhesion test
0	0.08	99.6
5	5.19	19.4
10	7.94	9.90
30	6.75	16.3

4. CONCLUSIONS

Fecralloy® foils are materials from which metallic monolith catalysts are made. The pre-oxidation condition has been shown to be central to achieving a high degree of performance of Fecralloy® as a catalyst support, in terms of loading and adherence of an alumina coating. A hyperbolic model provided the best fit for specific mass gain by the coupons as a function of pre-oxidation time from 0 – 30 h. The optimal coating loading (7.94 mass %) and adherence (9.90 mass % loss) were obtained from coupons pre-oxidised at 950 °C for 10 h, as these conditions produced the optimal surface topography and microstructure.

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[1] values are averaged over 3 measurements with standard deviation within 2%