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Preparation of Protective Coating Film on Metal Alloy

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***Abstract*—**A novel chromium-free protective coating films based on a zeolite coating was growing onto a FeCrAlloy metal using in – situ hydrothermal method. The zeolite film was obtained using in-situ crystallization process that is capable of coating large surfaces with complex shape and in confined spaces has been developed. The zeolite coating offers an advantage of a high mechanical stability and thermal stability. The physicochemical properties were investigated using X-ray diffraction (XRD), Electron Microscopy (SEM), Energy Dispersive X–ray Analysis (EDX) and Thermogravimetric Analysis (TGA). The transition from oxide-on-alloy wires to hydrothermally synthesised uniformly zeolite coated surfaces was followed using SEM and XRD. In addition, the robustness of the prepared coating was confirmed by subjecting these to thermal cycling (ambient to 550^{o}C).

***Keywords*—**FeCrAlloy, Zeolite ZSM-5. Zeolite coating.

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I. Introduction

METAL corrosion is a universal problem and generally resulting losses each year are in hundreds of billions of dollars. Developing of satisfactory protective coating continues to be of great importance. A chromium hexavalent (C^{+6}) are widely used on aluminium and its alloys for corrosion protection, which is a proven carcinogen, and known to cause many serious health problems [1], [2]. Use of C^{+6} become increasingly strict by health and safety regulations, essentially a novel chromium-free surface finishing process will have to be developed so that pollution is avoided at the source [3].

Zeolite coatings have been an increasing interest in to be used as a novel chromium-free protective coatings on aluminium alloys. Attachment of zeolite crystals on a metal surface can be achieved using different methods with varying success. These methods can be classified into; firstly, a dip coating uses a binder to attach already synthesised zeolite crystals to a (metal) surface. Secondly, in-situ growth method which is a method of growing zeolite crystals onto the metal using the alumina formed on the metal surface as a part source of Al required for the zeolite preparation [4]. The pre-treatment step is crucial as it requires the formation of a uniform thin aluminium oxide layer on the metal surface. This film then increases the wetting of the support by the synthesis gel mixture and/or promotes the nucleation of zeolite crystals [5]-[7]. Hence, it is essentially to understand the factors that affect the growth of the zeolite films on the metal surface.

Zeolite synthesis is attributed to the conversation of amorphous reactants containing silicon and aluminium which are mixed together with a cation source and water to form a microporous crystalline aluminosilicate via a series of complex chemical reactions. High-silica zeolites are known for their thermal stability up to 1400°C without losing their crystalline structure and also for their stability to the most mineral acids (react only with hydrofluoric acids).

The growth and adherence of zeolites layers on the metallic surface is difficult [7]. An interesting metallic substrate is FeCrA alloy (FeCrAlloy). The FeCrAlloy, a high temperature steel alloy, is used as a support metal because of its special properties. This steel alloy has high thermal resistance and stability 1400^{o}C [6]. After oxidation at high temperature, an Al_2O_3 layer can be seen on the FeCrAlloy surface. This layer is beneficial during the coating process of zeolite because it helps to adherence between metallic support and catalyst [8].

Preparation of zeolite coatings is desired for a variety of potential area of applications such as catalysis, adsorptions, separation, chromatography, membranes, corrosion protection, medical, optics, electronics and sensors [4]. Some of applications are related to the membrane in separation process that requires the zeolite coating to be synthesised as a very thin film on the support [3]. We have been investigating the preparation of chromium-free protective coatings of ZSM-5 zeolite and have studied the effect of the both the FeCrAlloy pre-treatment and in-situ zeolite gel crystallisation times on the growing of ZSM-5 zeolite films onto FeCrAlloy metal.

II. Experimental

A. Support Pre-Treatment

FeCrAlloy annealed wires (0.5 mm diameter) were supplied by GoodFellows with a pre-determined chemical composition by weight of Fe 72.8%, Cr 22%, Al 5%, Y 0.1%, and Zr 0.1%.

The pre-treatment process was as follows; Oxide removeal using No.100 glass paper; immersion in 0.1M KOH at 25^{o}C for 10 minutes, followed by 0.1M HNO_3 solution at 80◦C for 5 min [6]. The wires were then rinsed with de-ionised water, placed in acetone and ultrasonicated for 10 minutes (Cam sonix C080T) and finally placed in de-ionised water and ultrasonicated for 10 minutes.

The wires were heated in a muffle furnace (Progen Scientific) to 1000^{o}C in air at a heating rate of 10 ^{o}C/ min and held at 1000^{o}C for between 3–24 h. The wire samples were hung over a stainless steel support to ensure even oxidation of the surfaces and when removed from the furnace rapidly cooled to ambient temperature.

B. ZSM-5 Coating Films

The pre-treated FeCrAlloy support wires were cut into lengths (2.5 cm) and inserted vertically into a PTFE- lined autoclave and the hydrothermal zeolite synthesis performed.

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ZSM–5 was synthesised using a seeding and feedstock gel [8], where a seeding gel with a molar composition of $4.5Na_2O:3.0TPAOH:60SiO_2:1200H_2O$ was prepared using colloidal silica (Ludox AS–40 from Sigma–Aldrich), sodium hydroxide (Sigma–Aldrich) and tetrapropylammonium hydroxide (1M, Sigma–Aldrich). The seeding gel was aged overnight at 100°C and then 3.2 g of the seeding gel was added to a feedstock with a molar composition of $6.5Na_2O:2Al_2O_3:60SiO_2:1916H_2O$. This was prepared by dissolving sodium aluminate (Fisher Scientific) and sodium hydroxide (Sigma–Aldrich) in deionised water and adding colloidal silica (Ludox AS–40). The gel was then poured into a PTFE-lined autoclave, heated to 180°C in an oven and held at temperature for between 4–48 h. Then, the zeolite precipitated in the autoclave and the coated wires were removed, rinsed and then ultrasonicated in de-ionised water for 10 min.

III. Characterisation

A Philips X' Pert PRO X–ray diffraction scanning the crystal growth of the zeolite on the wire surface was characterised using 0.000832 o/min using slit widths 1/8° and 1/4° over a 2θ range of 3°–52°.

The calcination and adhesion of the zeolite layers for all samples was studied using a thermogravimetric analyzer (Q5000-IR TA Instruments). Calcination was carried out by heating in air (25 ml/min) from ambient at a rate of 1°C/min to 550°C and held at this temperature for 480 min. The adhesion of the zeolite layers was tested by thermal cycling selected wires between ambient to 550°C at 10°C/ min. The wires were held at both the high and low temperatures for 30 minutes and the process was repeated five times.

Surface morphology and chemical analysis were carried out on gold–coated wires samples under high vacuum using the Quanta200 FEI scanning electron microscopy and the Genesis software.

Energy Dispersive Spectrometry EDS spectroscopy was used to identify elements and count the impinging X–rays based upon their characteristic energy levels [9]. Since, a well-polished surface is required for quantitative/qualitative analysis and concentration maps, two techniques were used. Firstly the external surface of the wire was analysed directly using X–ray spot analysis on carbon or gold–coated samples. Secondly the analysis of the elements dispersed across different layers of the metal, oxide layer and coated zeolite was carried out. Wires samples were prepared by immersion vertically in a resin and then sectioned with diamond saw to obtain a clean surface. This surface was then ground with SiC sandpaper and polished with Al_2O_3 to get a smooth flat surface. The samples were then rinsed with alcohol to remove contamination and finally carbon or gold–coated.

IV. Results

A. Optimisation of Wire Oxidation Time and Zeolite ZSM-5 Coating

Wires oxidised at 1000°C for between 3 – 24 h were then immersed in aged zeolite ZSM–5 gel and heated. A uniform layer of ZSM-5 covered the oxidised wires (SEM analysis Fig. 1). All coated wires were calcined and thermal cycled in a TGA to determine adhesivity of zeolite film on the metal surface and the zeolite coverage (g/m^2) was estimated by taking the increase in the mass of the wire due to the growth of the zeolite film and dividing by the surface area of the wires (Table I).

All wires lost weight on heating to 550°C due to the breakdown of structure-directing template, TPAOH. Thermal cycling of the wires which had been oxidised for 3 – 5 h showed very little weight loss (0.1%). However, wires oxidised for 6 h showed a 10-fold increase in weight loss and wires oxidised for 9 hours or more showed significant peeling of the zeolite layer. A significant increase in coverage and excellent adherence on thermal cycling suggest the wire oxidation time at 1000°C is optimum at 4 hours.

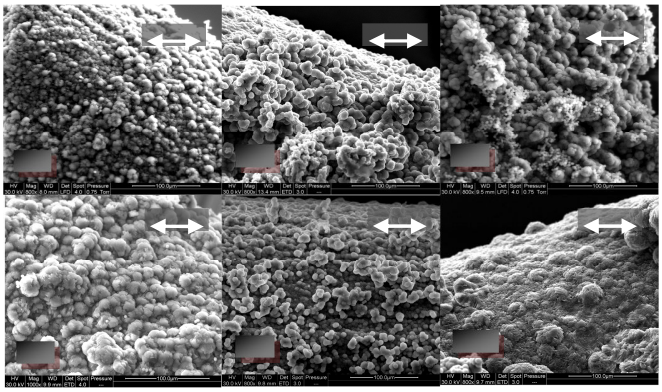


Fig. 1 SEM images showing the morphology of ZSM–5 grown on wires oxidised for between 3 –24 hours.

TABLE I
THE CHANGE IN ZSM–5 COVERAGE OF WIRES OXIDISED BETWEEN 3 – 24H AND THE WEIGHT CHANGE AFTER CALCINATION AND THERMAL CYCLING OF THE WIRE SURFACE AT DIFFERENT OXIDATION TIMES

Wires	3h	4h	5h	6h	9h	24h
Zeolite coverage (g/m^2)	192	317	161	151	142	102
Weight loss on calcination (%)	3.4	3.2	2.5	2.0	1.9	1.8
Weight loss after thermal cycling×5 (%)	0.1	0.1	0.1	1.0	7.8	10.9
Thickness Layer (μm)	130	150	125	120	80	51

The morphology of ZSM–5 on the oxidised wires was investigated after calcination (Fig. 1) and found to be similar for all wire oxidation timescales however evidence of slower growth of ZSM–5 can be seen when the oxide layer has a much lower surface area (i.e. > 6 h). Thermal cycling had little obvious effect on morphology but the zeolite layer began to peel off wires oxidised for 6 h or more. The damaged ZSM–5 surface grown on the 24 h oxidised wire is highlighted in Fig. 2.

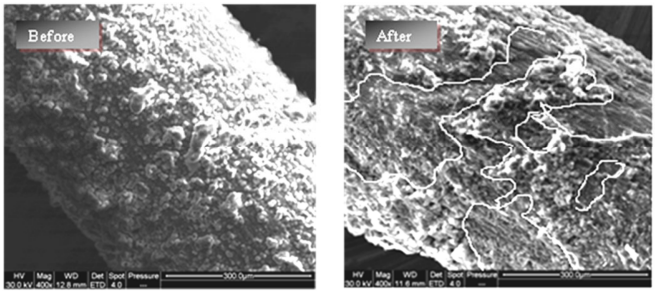


Fig. 2 SEM images before and after thermal cycling for ZSM–5 coated wires oxidised for 24 h. Note the highlighted area where peeling has occurred

B. Optimisation of the Zeolite Crystallisation Time ZSM–Coating Film

The hydrothermal synthesis of ZSM–5 was carried out at different crystallisation times by immersing the FeCrAlloy wires oxidised for 4 h. In order to study the growth of the zeolite on the metal surface, the analyses were performed on the zeolite in the bulk phase and on the zeolite grown on the metal surface.

XRD was performed to study the crystal growth of the zeolite on the wire surface and compared with the crystal growth in the bulk phase. These analyses confirm that the increase in crystallisation time leads to an increase in the intensity of the XRD peaks of ZSM–5. It is worth noting that ZSM–5 crystallisation starts earlier on the alumina-rich metal surface (12 h) whilst forming slower in the bulk (typically 20 h, Fig. 3). This suggests that the crystallisation is assisted by the alumina layer formed on the FeCrAlloy surface. The crystallisation was complete by 48 h for both the bulk powder and the FeCrAlloy wires.

SEM images were taken of the wires surface at different crystallisation times (Fig. 4) and revealed differences in the zeolite coverage as well as crystal size. Initially growth was on FeCrAlloy wire surface then the crystals subsequently grow on other crystals already present. Good coverage at crystallisation times of 12, 20 and 48 h showed spherical crystals with twining. As might be expected as the crystallisation time increased so did the surface coverage and the typical Si/Al ratio achieved was 11 (Table II). A similar Si/Al ratio was found for the bulk ZSM-5 powder

Element mapping for ZSM-5 film after 48 h crystallisation time is shown in Fig. 5. Fe and Cr mapping clearly showed the elements present in the body of the wire and Si and Al clearly show the zeolite grown on the wire. The Al mapping showed a very sharp increase in Al concentration at the surface of the wire (bright red line signifying the boundary between the wire and the zeolite). This is also highlighted in the line scan of the cross-section of the wire on Fig. 6. The Kα signals plotted of Si, Al, Fe and Cr started where the EDAX elemental line scan was made on the chosen range to show the zeolite film (substrate, aluminum oxide layer, zeolite layer). The Cr and Fe from the FeCrAlloy wire is not zero due to the background signal. The sharp peak in Al Kα signals plotted indicated the aluminum oxide layer on the metal surface then the signal decreases

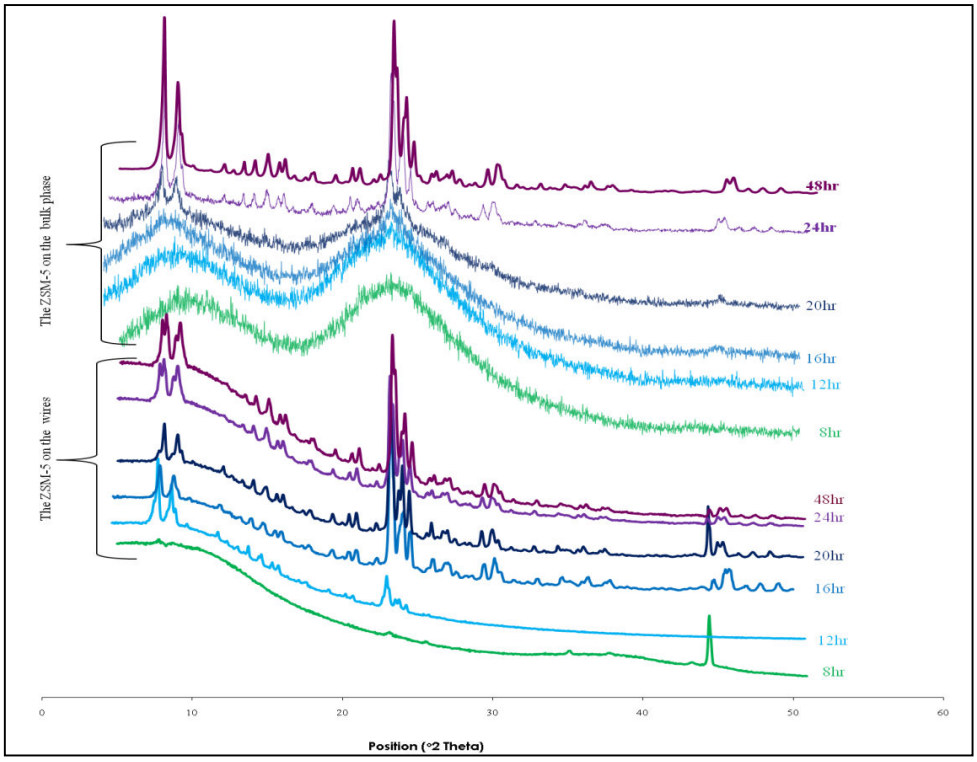


Fig. 3 XRD patterns as ZSM–5 is crystallised on the metal surface and in the bulk phase

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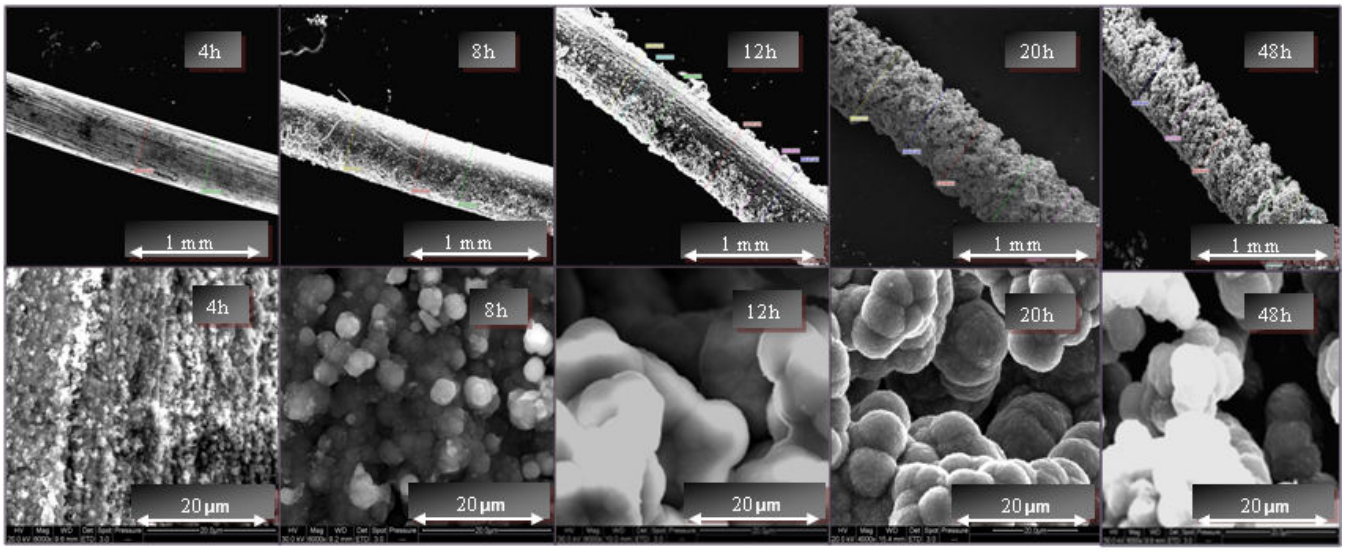


Fig. 4 SEM images of ZSM5 on the surface of wires oxidised for different times

TABLE II
ZSM-5 WEIGHT GAIN, LAYER THICKNESS AND SI/AL RATIO AT DIFFERENT CRYSTALLISATION TIMES

Time (h)	Zeolite (%)	Layer thickness (µm)	Coverage (g/m^2)	Si/Al
4	0.03	5	0.25	0.03
8	1.8	10	16	8.00
12	11.3	50	100	11.21
16	15	100	151	11.15
20	18	120	152	11.04
24	23	134	212	11.02
48	35	146	317	11.00

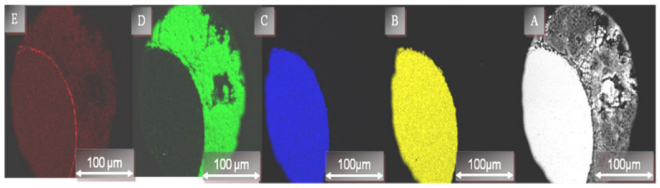


Fig. 5 SEM-EDAX micrograph of the Na-ZSM-5 structured catalyst after 48 h crystallisation time: A) BSE image, (B, C, D and E) element mapping for Fe, Cr, Si and Al respectively

The element mapping through the cross-section also highlights defects such as cracks and one large cavity within the zeolite phase. Overall the zeolite phase is continuous and attached but further improvements in synthetic method will improve homogeneity of the zeolite coating.

V. DISCUSSION AND CONCLUSIONS

Coatings grown on physically pre-treated wires oxidised at 1000°C for a time of 3 – 5 hours were optimal. ZSM–5 (48 hours at 180°C, Si/Al = 11) was successfully synthesised on FeCrAlloy wires that had been oxidised for 4 hours. A continuous zeolite layer was successfully anchored to the alumina grown on the surface of the wire during oxidation. Repeated thermal cycling of the coated wires showed the zeolite coatings to be stable with little loss of zeolite layer. However, the synthesis of zeolites on wires oxidised for greater than 5 hours were prone to flaking and loss of layer integrity.

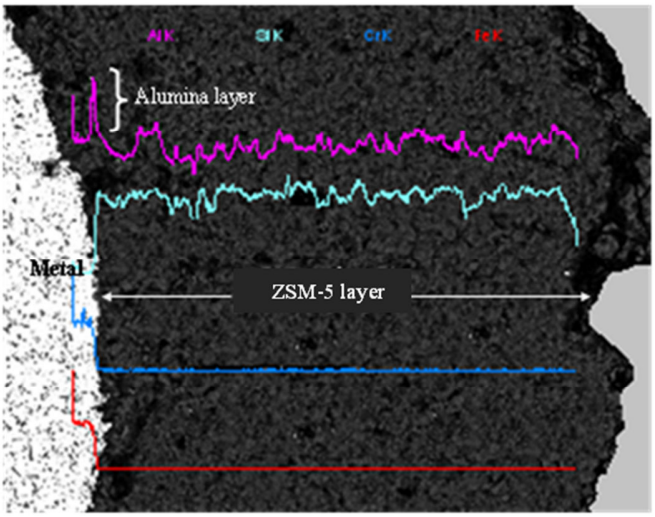


Fig. 6 Line scan of cross-section through the wire, alumina and zeolite phase; purple line, light blue line, blue line, and red line represent the Al, Si, Cr, and Fe, respectively (after 48 h crystallisation time)

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