



Performance of Cr oxide coatings on 304 steel against metal dusting

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ARTICLE INFO

Available online 29 August 2013

Keywords:

Metal dusting

Protective thin films

Reactive magnetron sputtering

304L steel

ABSTRACT

The response to metal dusting of Cr/Cr₂O₃ thin films deposited on 304L stainless steel substrates by reactive magnetron sputtering (RMS) under various deposition conditions was investigated. Selected coated samples and bare substrates were exposed to an atmosphere of CH₄ + H₂ + residual oxygen at 800 °C for up to 20 h via thermogravimetric analysis (TGA). The results indicate that the presence of the Cr/Cr oxide film resulted in a clear improvement in resistance against metal dusting of the 304L steel. The protective behavior of the Cr/Cr oxide coatings arises from several effects: decrease of catalytic deposition of carbon on the Cr oxide surface (and expected prevention of inward diffusion of carbon through the Cr oxide), and hindrance of outward Cr and Fe diffusion which were identified as important events in the metal dusting of the bare 304L steel. The structural differences among the various Cr/Cr oxide films prepared in the present conditions played a lesser role in their protective behavior than the presence of the outer Cr oxide layer.

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1. Introduction

Metal dusting is a high temperature corrosion phenomenon that occurs in carbon supersaturated environments in a range of temperatures between 400 and 800 °C and affects iron, cobalt and nickel based materials. As a result of exposure to metal dusting conditions, materials deteriorate and eventually disintegrate generating important economic losses in various industries such as petrochemical, ore reduction, and metal processing among others. A very complete review of metal dusting has been provided by Young et al. [1].

The search of solutions to this problem relies on an understanding of the corrosion mechanism that applies for metal dusting. In particular, for the case of Cr-containing steels, the mechanisms proposed have evolved from those in the early studies of Grabke et al. [2–4] and Pippel et al. [5] to the currently more widely accepted findings of Zhang et al. [6], Szakalos et al. [7,8], and Natesan et al. [9]. The earlier works recognized that the formation of the surface native chromia (Cr₂O₃) layer protected these alloys by preventing inward diffusion of carbon as long as it remained intact. However, once this layer was disrupted or could not reform, ingress of carbon led to the formation of cementite which eventually decomposed and led to dusting of the alloy. More recent evidence presented in [6–9] have demonstrated that the presence of cementite is not central to the metal dusting mechanism for these alloys. These studies indicate that upon failure of the surface Cr₂O₃ layer,

the progress of metal dusting is not only associated to C inward diffusion, but also to that of oxygen. Zhang et al. [6] recognized the effect of the composition of atmosphere and alloy surface condition during exposure of 304 stainless steel to metal dusting. For low oxygen potentials that prevented the formation of Fe and Ni oxides, ingress of C and O led to the formation of oxides and C-rich phases whose nature depended on the atmosphere composition, but nevertheless ended in material disintegration.

Szakalos and coworkers [7,8] on the other hand have put forward a metal dusting mechanism which starts with inward diffusion of both C and O, formation of Cr carbides, followed by their dissolution by oxidation which results in the formation of austenite particles and graphite channels. The austenite particles catalyze further C deposition as nanotubes.

The most important point from the information above for the present paper is that metal dusting attack of alloys such as 304 L stainless steel initiates when carbon and/or oxygen deposit on the surface and migrate into the alloy through disruptions in the surface chromia layer. Based on these facts, several approaches to protect materials against metal dusting have been proposed. These include alloy development [9–12], modification of the corrosive atmosphere [13,14], application of coatings [15,16], and surface modification of alloys [17,18]. All these methods have produced varying degrees of success especially the alloy modification proposed by Natesan et al. [9] and the Ni–Sn coatings applied by Geers et al. [16] have provided outstanding results. The search for protective methods against metal dusting however is still open and we have proposed an alternative approach. It basically involves the deposition of oxide thin films on the surface of commercial

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alloys. Oxides such as Cr_2O_3 , Al_2O_3 , SiO_2 , not only are impermeable to C ingress [19], but also are non-catalytic to carbon deposition [20]. RMS has been selected as the deposition technique mainly due to its versatility in terms of processing-structure-property combinations. It is a physical vapor thin film deposition technique that basically involves sputtering of atoms by energetic ions, typically from a weakly ionized plasma, in a reactive atmosphere to produce the required compound on the surface of a substrate. The protective nature of Cr and Al-oxide based thin film coatings deposited on HK40 steel substrates by RMS has already been investigated [21,22] with encouraging results. Based on the knowledge gained from these investigations, in the present study we further explored the process-structure relationship during film deposition by RMS of Cr/Cr oxide coatings and its effect on their protective performance against metal dusting conditions on a different substrate material, 304L stainless steel. This steel is also widely used in applications where metal dusting represents a serious problem and as it will be described in the present investigation, it can benefit even more than the HK40 steel from the use of Cr/Cr oxide thin films as protective coatings.

In addition to the analysis of the role of the Cr/Cr oxide as a protective coating, comparison of the performance of the films against that of bare 304L substrates in the metal dusting atmosphere provided further insight into the evolution of the attack of this material in this environment.

2. Experimental procedure

2.1. Deposition experiments

The coating architecture, which consisted of a pure Cr adhesion layer followed by a layer of Cr oxide, was deposited by reactive magnetron sputtering of a Cr target in an Ar and $\text{O}_2 + \text{Ar}$ atmosphere. The details of the deposition system used have been published elsewhere [21,22]. The substrates were thin samples 10 mm long, 6 mm wide and 1.5 mm thick cut from a 304L steel bar (0.019%C, 1.570%Mn, 0.32%Si, 18%Cr, 8.05%Ni and 0.033%P, Fe balance). Prior to the deposition experiments, the samples were ground up to 800 grids in SiC papers, polished to a mirror finish, and ultrasonically cleaned in ethanol for 5 min. The samples were then placed in the RMS reactor hanging 30 mm from the target surface.

The deposition process was carried out in two steps: first the adhesion layer of pure Cr was produced and then Cr was sputtered in an $\text{O}_2 + \text{Ar}$ to deposit the oxide layer. The process variables investigated included: mode of oxygen flow (constant vs. graded at various rates), applied power, substrate cleaning and application of a negative bias voltage on the substrate. Six different coatings were thus produced (S1 to S6) and their deposition conditions are presented in Table 1. In all the experiments the reactor chamber was first evacuated to reach a pressure of about 6.6×10^{-3} Pa, then Ar was introduced at a flow rate of 20 sccm and a power of 50 W was applied to the magnetron to initiate the plasma and the chamber pressure increased then to around 3.2 Pa. At this point, in the cases where substrate cleaning was considered (S5 and S6), a voltage of -420 V was applied to the substrates for 10 min to perform the cleaning, then the bias voltage was turned off

and the sample was moved away from the vicinity of the magnetron. The target was then sputtered clean for about 5 min at 50 W. Upon cleaning, pressure was adjusted to reach 1.7 Pa and the pure Cr adhesion layer around 500 nm thick was deposited on the substrate in the conditions indicated in Table 1. Next, the atmosphere was switched to $\text{Ar} + \text{O}_2$ to deposit the Cr oxide layer, where the flow of O_2 was fed at various rates. The deposition details are presented in Table 1. The flow of Ar was kept constant at 20 sccm. The deposition temperature, as measured by a thermocouple attached to the sample (except in S6) varied between 33 °C and 90 °C. Upon deposition of the coating architecture, the samples were left to cool inside the chamber and then taken to out to perform the TGA runs.

2.2. Thermogravimetric analysis (TGA) experiments

Evaluation of the response of the coated and uncoated 304L substrates to a metal dusting atmosphere was carried out by thermogravimetric analysis. The dimensions and preparation of the uncoated samples were the same as those indicated for the substrates to be coated. After preparation, the samples were introduced in a SETARAM Setsys Evolution thermobalance heated in an Ar atmosphere up to the reaction temperature (1073 K), then exposed to a pre-mixed commercial gas mixture of $\text{CH}_4 + \text{H}_2 + \text{Ar}$ at this temperature for the prescribed carburization time. $\text{CH}_4 + \text{H}_2$ was introduced into the furnace at 0.266 sccm and Ar at 0.093 sccm. The composition of the $\text{CH}_4 + \text{H}_2$ gas was: 10.1 vol.% H_2 , 15.0 ppm O_2 , 5.0 ppm H_2O , and balance CH_4 . The pressure registered during the experiments was 0.725 atm. The exposure times were: 2.5, 5, and 20 h for the uncoated samples and 20 h for selected coated substrates (S3-S6) based on their microstructural characterization. The sample weight change was monitored and data acquisition was carried out with the Setsoft 2000 software included in the TGA equipment.

2.3. Characterization of samples

The microstructure of the samples was characterized in the as-deposited state and after the TGA experiments. Phase identification was performed by X-ray diffraction (XRD) using a D8 FOCUS apparatus operated at 25 kV and 25 mA with $\text{Cu-K}\alpha$ radiation. The composition, morphology, size and distribution of the various microstructural constituents were characterized by conventional scanning electron microscopy plus energy dispersive analysis (SEM + EDS) in a JEOL 6360LV equipment.

Selected samples (S1-S3) were subjected to nanoindentation experiments. These were performed using a Nanoindenter XP (MTS) with a Berkovich indenter tip with the area function calibrated using fused silica. A set of sixteen indentations with 12 loading/unloading cycles was done on each sample surface. The maximum applied load was 400 mN and the holding time at each load step was 15 s. The hardness and elastic modulus profiles were determined by the Oliver & Pharr method [23].

Adhesion was evaluated through scratch testing. For these tests, additional films were prepared on 25 mm diameter, and 1.5 mm thick 304L disks. The tests were conducted in a scratch tester ST-30 applying a maximum load of 20 N with inclination of 1° and a speed of 25 mm/min. The

Table 1
Experimental details for the deposition runs.

Sample	Cr adhesion layer	Plasma cleaning (min)	Oxide layer			ΔO_2 flow/time (sccm/min)	Pressure (Pa)	Bias voltage (V)	Coating thickness (μm)
			Ar flow (sccm)	O_2 flow (sccm)	Power (W)				
1	Power: 50 W Ar flow: 20 sccm Pressure: 1.7 Pa Time: 5 min	0	20	5	50	Constant.	1.72–3.03	0	1.2
2				0–5		0.1	1.79–3.03		1
3						0.2	1.71–2.64		1.3
4					45		1.7–2.75		0.5
5		10			50		1.72–2.89	-300	1.25
6							1.68–2.74		0.8

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