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Role of surface chemistry on the nature of passive oxide film growth on Fe–Cr (low and high) steels at high temperatures

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High temperature materials degradation or protection of Fe–Cr alloys are often related to the nature of their oxide scale formation. Breakdown of passive oxide films lead to localized corrosion. Various alloying elements are often incorporated in these alloys to prevent high temperature oxidation. The addition of selected alloying elements is cumbersome and not always cost effective. In this article, we investigate the role of rare earth oxide coatings on high temperature corrosion prevention of both low and high Cr steel. An *in situ* high temperature oxidation setup has been built to study the oxidation kinetics of both coated and uncoated low and high Cr steels under ambient pressure and dry air. Reduction in scale growth kinetics is observed in the presence of coating. While scanning electron microscopy and x-ray diffraction are employed to study the structure and morphology of the oxide films, x-ray photoelectron spectroscopy and Auger electron spectroscopy are used to study the surface chemistry of the oxide layer. This article relates some of these data to explain the nature of scale growth kinetics (linear or logarithmic or parabolic) observed in both low and high Cr steels. © 1999 American Vacuum Society. [S0734-2101(99)11304-6]

I. INTRODUCTION

The effect of addition of rare earth elements such as Y, Ce, Sc, La, etc., in their oxide form to both Cr₂O₃ and Al₂O₃ forming alloys for improving their high temperature oxidation behavior has been reviewed in a great detail.^{1–4} Several mechanisms have been proposed to explain the beneficial effects of rare earth additions to high temperature alloys.^{5–9} However any conclusive single mechanism is yet to evolve to explain such effects, i.e., reduction in scale growth kinetics.

The high temperature material degradation or protection shown by Fe–Cr alloys are often related to the nature of their oxide scale formation. Breakdown of passive oxide films often lead to localized corrosion. The surface oxides and hydroxides are of wide importance and can exist in varying oxidation states. In order to understand the high temperature oxidation and corrosion of Fe–Cr alloys, the surface chemistry of the oxides needs to be examined in detail. A particular interest to us is to extend the use of x-ray photoelectron spectroscopy [(XPS) or often known as ESCA] to distinguish between various oxides formed in both coated and uncoated steel during oxidation. This investigation presents the results on the isothermal oxidation behavior for Fe–Cr alloys (low and high Cr) in dry air with and without superficially coated CeO₂ coatings. While x-ray diffraction (XRD) and scanning electron microscopy (SEM) investigates the structure and scale morphology, XPS provides detailed surface chemical studies of both coated and uncoated Fe–Cr alloys at elevated temperature. Moreover, the application of the cerium oxide

coatings is considered to be the most practical procedure for ensuring high local concentration of the active element within the scale and thus preventing the material degradation and failure.

II. EXPERIMENT

A. Materials used

The spectrographic analysis of the low and high Cr steel samples used in this study is listed in Table I. Cerium oxide powder and reagent grade ethyl alcohol were purchased from Aldrich Chemicals, USA.

B. Sample preparation

All the steel samples were mechanically rough polished using 600 SiC grit paper followed by cleaning in methanol. Some specimens were coated with cerium oxide from a slurry of CeO₂ powder dispersed in ethyl alcohol. The calculated coating thickness was in the range of 2–5 μm .

C. Arrangement for oxidation studies

The oxidation method and the details of the oxidation setup were the same as reported elsewhere.⁶ An electronic microbalance (Sartorius MP8; accuracy of ± 0.1 mg) attached to a computer was used to record the continuous mass change for various time-temperature programs. Experiments were carried out at 923 K in dry air for 24 h to examine the improvement if any with regard to scale adherence and suppression in scale growth rate in the presence of rare earth oxide coatings.

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TABLE I. Typical spectrographic analysis composition of low and high Cr steels.

Steel %	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Al	N	Fe
Low Cr	0.08	0.6	0.015	0.03	0.02	0.06	0.04	0.06	0.05	0.1		rest
High Cr	0.025	1	0.04	0.03	1		0.6	17–20	1.75–2.25		0.03	rest

D. Oxide scale characterization

At the termination of each oxidation run, each sample with its oxide layer was examined visually, optically, and by SEM attached with an energy dispersive spectroscopy (EDS) to access the scale composition, morphology, and the nature of various oxide phases formed on the steel substrate.

Oxide surface chemical analysis was performed using a 5400 PHI ESCA (XPS) spectrometer having a base pressure of 10^{-10} Torr using Al $K\alpha$ X radiation (1486 eV, line width 0.7 eV) with a power of 350 W. Survey and individual high-resolution spectra were recorded with a pass energy of 44 and 17 eV to achieve the maximum instrument resolution. Data were collected with at least 1 (in survey mode) and 0.1 eV/step (in high-resolution mode) to be sure to identify the subtle features in the XPS spectrum. The spectrometer scale was calibrated using gold ($4f_{7/2}$) = 84 ± 0.2 eV. The charging shifts produced by the insulating oxide samples were removed by using a binding energy scale by fixing the C(1s) binding energy of the hydrocarbon part of the adventitious carbon line at 284.6 eV.¹⁰ Nonlinear backgrounds were removed from the spectra using a method described by Sherwood.¹¹ XPS data were smoothed to remove incidental noise spikes using a Savitsky and Golay smoothing program. This program allowed us to deconvolute peaks by specifying the peak's position, height, width, and shape. Nonlinear least square curve fitting was performed using a Gaussian/Lorentzian peak shape,^{11,12} which include x-radiation satellites in the fitting routine. The shape parameters include the peak's Gaussian/Lorentzian ratio and tail characteristics such as height, slope, and exponential to linear tail mix. In addition spectra were analyzed using an automated incremental peak deconvolution program which varied the peak height within an envelope over a complete range to determine the best fit, checked by using the χ -squared value to the smoothed data.

Sputter depth profiling was carried out using a PHI 600 scanning Auger microprobe by sputtering an area of 5 mm² of the oxide films by high purity (99.999%) argon ions and simultaneously analyzing a small part of the area by scanning auger multiprobe. The following ion gun parameters were used during etching: ion beam energy 3 keV, emission current 25 mA.

III. RESULTS AND DISCUSSION

A. Kinetics

The oxidation kinetic plots for both ceria coated and uncoated low and high Cr steel at 923 K under isothermal exposure are presented in Fig. 1. Coated samples in the case of high Cr steel showed marked reduction in the rate of scale

growth as compared to the low Cr coated steel. The lack of Cr in the latter sample seems to allow the oxidation to continue at a significant rate. It is the reduction in the rate due to coating that is of interest in the low Cr steel. It is observed that the high Cr coated steel after 24 h of exposure registered 20 times less mass gain than that of the uncoated one. In both cases the kinetics of the oxide scale growth follows a logarithmic behavior and not the parabolic law. These kinetic results seemed to be valid at this temperature.¹³ Such improved performance in the coated high Cr steel is attributed to enhanced Cr diffusion through a distorted lattice as well as through grain boundaries to the alloy surface, thus facilitating an early establishment of protective external Fe doped Cr₂O₃ or a Cr-rich spinel layer. This is reported in the section of XPS results later.

B. SEM and XRD

Figure 2 represents the selected top-surface SEM morphology of the oxide scales formed on uncoated and CeO₂ coated high and low Cr steels. The uncoated sample clearly demonstrates both cracks and oxide spallation [Fig. 2(a)]. The EDS analysis (not shown) on the top scale surface shows mainly iron oxides in low Cr steel and Cr₂O₃, Fe₂O₃ (Cr, Fe, and O peaks) in high Cr steel. Figure 2(b) shows a uniform coating on the high Cr steel surface with cerium oxide particles whose presence is further confirmed from the EDS results. The amount of Cr and Si is suppressed. Si is believed to be taking part in the internal oxidation,⁶ (also found to form silica from XPS studies) as well as surface

FIG. 1. Mass gain/unit area vs time for uncoated and CeO₂ coated low and high Cr steel during isothermal oxidation at 923 K.

FIG. 2. SEM micrographs (SEI) of the top scale surface formed on: (a) uncoated high Cr steel, (b) CeO_2 coated high Cr steel, and (c) CeO_2 low Cr steel. XRD spectra for high Cr steel (A) uncoated oxidized and (B) coated-oxidized peak identification: (i) Fe–Cr, (ii) Cr_2O_3 , (iii) Fe_2O_3 , (iii)' FeCr_2O_4 , (iv) CeO_2 , (v) $\text{CeO}_2 \cdot \text{Cr}_2\text{O}_3$.

oxide formation. Similar results were found in the coated low Cr steel [uniform coating with some scale spallations: Fig. 2(c)], except that there was no Cr and the Fe signal is suppressed due to the presence of cerium oxide. The reduction in scale growth kinetics is very much dependent on the Cr content of the steel which is responsible for the formation of the protective Cr_2O_3 layer.

XRD analysis of the oxide scales on bare low Cr steel indicates the presence of Fe_2O_3 . The Fe_2O_3 peaks in coated steel are suppressed drastically by CeO_2 peaks (in coated steel), thus indicating the formation of barrier that can suppress the corrosion to a certain extent. Some mixed $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ peaks are also detected. A typical XRD pattern [Fig. 2(d)] of the top scales formed on bare and coated high Cr oxidized steel showed the formation of the following compounds: Fe_2O_3 , Cr_2O_3 , and possibly FeCr_2O_4 in uncoated steel and $\text{CeO}_2 \cdot \text{Cr}_2\text{O}_3$ with CeO_2 in coated steel sample. The main Fe–Cr (001) peak is further depressed in the coated sample with no Ce_2O_3 present, which was later confirmed by XPS. The formation of Ce_2O_3 (more thermodynamically stable) needs much higher temperature and is

reported in the study of Fe-20%Cr alloy with Ce additions.¹⁴ The presence of cerium oxide suppresses the scale growth and prevents material degradation.

C. XPS results

1. XPS survey spectra

The surface chemistry and (%) atomic concentration of the oxide layer are studied using x-ray photoelectron spectroscopy (XPS). Figures 3 and 4 represent the XPS survey spectra of bare and coated low and high Cr steel under selected oxidizing conditions. Table II lists the atomic surface concentration of selected steels. In Fig. 3(b), the oxidized low Cr steel shows an increase in surface Fe and O concentration indicating the migration of cations to the surface. In this case, the band gap is reduced to 1.5 eV as compared to 2.2 eV in the uncoated sample showing the presence of transition metal species on the surface. The coated oxidized steel [Fig. 3(c)] shows a marked decrease in Fe (i.e., reduction in outward cation migration) and O concentration and the surface is mostly coated with CeO_2 . An increase in the band gap

FIG. 3. XPS 0–1200 eV survey spectra for (a) low Cr steel, (b) low Cr steel-oxidized (c) low Cr steel coated and oxidized.

to 2.9 eV indicates the insulating nature of the oxide scale. Corresponding XPS Fe(2p) and O(1s) spectra (not shown) of the bare low Cr steel sample reveal the presence of Fe⁺² (B.E. 709.6 eV), Fe⁺³ (B.E. 710.9 eV), and physisorbed OH species [O(1s) B.E. 531.9 eV] on the surface due to low temperature oxidation (LTO).¹⁵

The survey spectra of bare, oxidized, and coated high Cr steel, [Figs. 4(a)–4(c)] indicate the definitive presence of carbonaceous species [Fig. 4(a)] along with surface hydroxides (from Cr, O, and Fe high resolution XPS spectra) in the bare alloy. The relative Cr/Fe ratio increases from 0.94 (bare) to 3.5 during oxidation, an indication of Cr cation migration, and it decreases to 2.5 in the coated oxidized steel. This indicates the early passivation of the steel surface due to ceria-based rare earth oxide coating. The relative Cr/O ratio is 0.09 in coated-oxidized steel with respect to 0.026 in the uncoated-oxidized steel, indicating a change in the relative presence of Cr cations versus O anions. Thus in the presence of a coating, the formation of an early chromia layer might have changed the oxidation from outward cation migration to inward anion ingress and thereby decreasing the oxidation rate as observed from the oxidation kinetics data. This effect is well documented in the case of 316 and 321 steels as reported in the literature.^{4–7}

FIG. 4. XPS 0–1200 eV survey spectra for (a) high Cr steel, (b) high Cr steel-oxidized (c) high Cr steel coated and oxidized.

2. XPS Cr(2p) for high Cr steel

The relative Cr content in steel plays an important role in Cr₂O₃ oxide formation in high temperature material degradation. In the case of low Cr steel, Cr content is very low to be detected by XPS and this Cr did not play any significant role in the surface protective chromia formation. Thus this article is focused on the Cr chemistry of the high Cr steel. Figures 5(a)–5(c) represents the Cr(2p_{3/2}) XPS spectrum for bare, oxidized, and coated oxidized steel at 923 K for 24 h. The bare steel [Fig. 5(a)] shows a main peak at 576.2 eV along with two small shoulder peaks at 574.3 and 578.0 eV, representing the presence of Cr₂O₃, Cr⁰, and Cr-hydroxide type species, respectively.¹⁶ The surface oxide and hydroxide formation is due to the natural passivation (LTO) and physisorbed OH from air exposure.¹⁵ The full-width at half-maximum (FWHM) of Cr(2p_{3/2}) in Figs. 5(b) and 5(c) increases to 2.7 and 3 eV as compared to the Cr(2p) line in the bare sample, indicating the presence of multiple Cr-containing oxide species due to high temperature exposure. The decrease in Cr(2p) B.E. (575.5 ± 0.2 eV) in Cr₂O₃ is due to formation of possible Cr–Fe–Mn transition metal mixed oxides (also revealed from XRD analysis). A further decrease in Cr(2p) B.E. to 577.4 eV in Fig. 5(c) is due to the

TABLE II. Surface atomic concentration of key elements calculated from XPS survey spectrum.

	Cr	Fe	Mn	Si	O	Ce	C
High Cr steel							
Bare	1.2	1.6	0.43	5.1	31.3		63
Oxidized	1.4	0.4	1.3	17	54.2		23
Ceria coated-oxidized	5.6	2.6	2.2	12.6	60.0	1.8	15
Low Cr steel							
Bare		0.8			16		77
Oxidized		10			58		24
Ceria coated-oxidized		3.0			45	4.0	45

FIG. 5. XPS Cr(2p) spectra for (a) high Cr steel, (b) high Cr steel-oxidized (c) oxidized ceria coated high Cr steel. Experimental core level spectra (····), and the result of computer fitted spectra (—). Suggested peak identification: (1) Cr^0 , (2) Cr_2O_3 , (3) Cr-OH (4) Fe-Mn-Chromates , (5) Cr-Ce-O type.

possible formation of Cr-Ce-O type oxides. Insertion of a more ionic Ce-O type bond in the Cr-O lattice makes the Cr-O bond more covalent. A similar type of compound has been observed in the CeO_2 coated chromia.¹⁷ Formation of

FIG. 6. XPS Ce(3d) spectrum for high Cr steel coated and oxidized. Experimental core level spectra (····), and the result of computer fitted spectra (—). Suggested peak identification: [see the text and Table III(a)].

chromia in the presence of ceria is responsible for preventing the material degradation and is consistent with the suppression in oxide growth kinetics (Fig. 1).

3. Cerium surface chemistry

Table III lists the Ce(3d) binding energy values of both high and low Cr (samples 1 and 2) coated oxidized steel. Figure 6 shows a typical Ce(3d) XPS spectra of ceria coated high Cr oxidized steel. The twelve peaks consists of main Ce core level lines and it's associated satellites for both CeO_2 and $\text{Ce}_{1+x}\text{O}_{2-x}$. The ratio between the core and the satellite lines (derived from the control CeO_2 sample and also present in the existing literature¹⁸) is maintained during the peak fitting. The complex multi-peaked Ce(3d) spectra are due to the hybridization of Ce(4f) with ligand orbitals and frac-

TABLE III. (a) XPS binding energies (accuracy ± 0.2 eV) of Ce (3d) for CeO_2 oxidized coated low and high Cr steel. (b) Auger depth profile analysis for CeO_2 coated oxidized high Cr steel.

(a) CeO_2 coated and oxidized high Cr steel (1)						
	$\text{Ce } 3d_{5/2}$			$\text{Ce } 3d_{3/2}$		
B.E. (eV)	883.7(X)	889.8(X')	900.1(X'')	902.63(Y)	908.8(Y')	918(Y'')
B.E. (eV)	883.0(x)	889.3(x')	899.2(x'')	901.6(y)	907.5(y')	917(y'')
± 0.2 eV		$\Delta_{X'-X} 6.1$	$\Delta_{X''-X} 16.4$	$\Delta_{Y-X} 18.9$	$\Delta_{Y'-Y} 6.17$	$\Delta_{Y''-Y} 15.4$
CeO_2 coated oxidized low Cr steel (2)						
	$\text{Ce } 3d_{5/2}$			$\text{Ce } 3d_{3/2}$		
B.E. (eV)	883(x)	889.3(x')	899.2(x'')	901.5(y)	907.5(y')	918.5(y'')
± 0.1 eV		$\Delta_{x'-x} 6.2$	$\Delta_{x''-x} 16.2$	$\Delta_{y-x} 18.5$	$\Delta_{y'-y} 6.0$	$\Delta_{y''-y} 17.0$
(b) Top surface mostly Ce and O						
	Si	C	O	Cr	Fe	
Sputtering						
Beneath the coating	35.5	11.1	19.7	18.0	15.5	
4 min	18.0	5.00	46.0	19.0	12.0	
8 min	6.00	...	60.8	22.6	10.2	
10 min	...	...	66.5	24.0	9.4	

Note: x' , x'' , y , y'' and X' , X'' , Y , Y'' are satellite lines of Ce (3d).

tional occupancy of the valence 4*f* orbitals.^{19–21} The CeO₂ XPS spectrum reveals the nature of passivation of steel underneath the cerium oxide coating. The Ce(3*d*_{5/2}) and Ce(3*d*_{3/2}) lines for both steels showed a spin orbit splitting of 18.7±0.2 eV (for example, see Fig. 6 for high Cr steel) and is consistent with the literature data for CeO₂.^{16,18} Both low and high Cr coated oxidized steels do not show formation of any Ce₂O₃ type compounds (also evident from earlier XRD data), instead the later shows both CeO₂ (883.0 eV) and Ce_{1+x}O_{2-x} (883.7 eV) species on the surface. A particular 3*d*_{3/2} multielectron satellite at 918 eV is present in both the samples indicating the presence of Ce (+4) species only and not Ce (+3), although the presence of Ce (+3) formation is being suggested in the literature.¹⁷

The Ce(3*d*) spectrum contains mainly 3*d*_{5/2} features at binding energies 883.0, 883.7(*X*), 889.8(*X'*), 900.1(*X''*) and 883.0(*x*), 889.3(*x'*), 899.2(*x''*) for both high and low Cr coated and oxidized steel, respectively. The similar 3*d*_{3/2} features for both the coated steels appeared to be at 902.63(*Y*), 908.8(*Y'*), 918(*Y''*) and 901.6(*y*), 907.5(*y'*), 918.5(*y''*) eV, respectively. The peaks at 883.7 and 889.8 eV have generally been assigned for final states with strong mixing of 4*f*¹ and 4*f*² configuration. These states arise from the core hole potential in the final state and the 4*f* hybridization in the initial state.^{19–21}

The low Cr steel shows the presence of CeO₂ on the surface and the reduction in the scale growth is not as prominent as in high Cr coated steel (see kinetics data in Fig. 1). The high Cr steel in the presence of ceria coating showed the presence of both CeO₂ and Ce_{1+x}O_{2-x} phases at binding energies 883.0 and 883.7 eV, respectively. The increase in the binding energy of the latter is attributed to the excess charge transfer from cerium to oxygen. The presence of oxygen deficient cerium oxide layer allows the inward ingress of oxygen and enhances early formation of Cr₂O₃ scales and thus prevents high temperature oxidation and is consistent with kinetics plot (Fig. 1), where the mass gain is 20 times less in the coated high Cr steel. The increase in the Ce(3*d*) binding energies as compared to the existing literature¹⁸ is due to the fact that in the presence of transition metal oxides, Ce in CeO₂ is more ionic, i.e., high B.E. and thus the former experiences a decrease in their binding energies.

Relative movement of anions and cations during the oxidation process are further investigated using Auger electron spectroscopy. Auger depth profile analysis [data shown in Table III(b)] has revealed the top surface layer to be composed of CeO₂ and a small presence of Cr oxides (along with other oxides). With sputtering, an increase in oxygen content towards the oxide—metal interface indicates the change in the oxidation mechanism from outward cation migration to inward anion ingress. A relative increase in Cr content reveals an early Cr₂O₃ layer formation at the scale/metal interface, thus preventing high temperature degradation.

4. Valence band studies

A detailed understanding of the surface chemistry associated with oxidation and prevention is needed to tackle more

FIG. 7. XPS valence band spectra: (a) low Cr steel oxidized, (b) low Cr steel-CeO₂ coated and oxidized, (c) high Cr steel-CeO₂ coated and oxidized.

complex problems associated with corrosion. XPS displays valuable core level chemical shifts, which allows one to identify various chemical species on the corroded surface, but there often remain difficulties in distinguishing subtle chemical differences. A number of studies on application of valence band photoemission in oxidation and corrosion are reported in the literature.^{22–24} This article presents the valence band spectra of oxidized and coated low Cr steels [Figs. 7(a) and 7(b)] and high Cr coated steel [Fig. 7(c)]. Figure 7(a) shows the valence band region of oxidized low Cr steel, where the broad hump between 4 and 8 eV represents the hybridization of O(2*s*) and Fe(3*d*) density of states with a band gap of 1.5 eV, indicating the outward cation migration, also seen from both XPS survey and XRD data. The band gap increases to 3 eV in Fig. 7(b) indicating

the presence of CeO_2 and the region between 4 and 7 eV indicates the interaction of $\text{Ce}(4f)$ and $\text{O}(2s)$ shells (broad feature) in the valence shell. Hardly any transition metal oxides (Fe_2O_3) are observed thus indicating the suppression of cation migration. Figure 7(c) shows the valence band region of ceria coated high Cr steel. The cerium oxide presence is prominent, and the presence of small transition metal oxides is also evident from the peaks at 0.5–2.3 eV. This is consistent with the core level XPS data. In particular, it is sufficient to note that the part of the transition metal oxide metal band structures dominated by $\text{O}(2p)$ remains relatively fixed (at 5–6 eV below E_F , the pseudo Fermi energy) for a series of third period $3d$ oxides.¹⁵ One should also note that the valence band region gives information from a greater depth than the core region due to significantly greater kinetic energies (thus escape depths) of the photoelectrons involved. The relative amount of oxide to metal is very high in the valence band region than in the core region due to greater depth probed by this region.

So it is postulated from the XPS, AES, XRD, and SEM results that at the beginning of the exposure of the steel to high temperature, a ceria modified chromia oxide film is favored by outward Cr^{+3} diffusion. In the transition stage, growth of Cr_2O_3 layer occurs above and beneath the ceria modified layer by outward Cr^{+3} diffusion and inward O^{-2} ingress through the initially formed defect oxide lattice as evident from the XPS results. Table III(b) shows the auger depth profile analysis for CeO_2 coated oxidized high Cr steel. At longer oxidation times, anion transport becomes dominant and the surface shows less oxygen [see Table III(b)] and increases with depth (i.e., inward O^{-2} ingress is favored in presence of ceria coating). Similar phenomenon studied by SEM, EDS, and x-ray mapping is sited in the case of 316, 321, and 304 steels.^{6,7} Postoxidation (and also Auger) analysis reveals the presence of cerium oxide particles at the scale/air interface [Table III(b)] and acted not only as heterogeneous nucleation sites at the alloy surface but also as sources of active element ionic segregation to block faster diffusion paths such as grain boundaries within the scale.⁶ In the case of low Cr steel, the presence of CeO_2 prevents the scale growth to lesser extent by suppressing the formation of iron oxides. Cr concentration is very small to be detected by the XPS. Thus a critical Cr content is required to observe the beneficial effects of rare earth oxide coatings in high temperature degradation of steels.

IV. CONCLUSIONS

The presence of superficially applied rare earth oxide CeO_2 coating has shown improvement in high temperature oxidation behavior of Fe–Cr alloys. Although the presence of Ce alone has improved the oxidation behavior of both low and high Cr steels, the best improvement was achieved with the high Cr steels. In the presence of Ce, the oxidation rate has been reduced by a factor of 20 in the latter case. Without the coating, the surface layer of the steel is shown to be a mixture of principally Cr_2O_3 and Fe_2O_3 and in cases Mn in form of MnO_2 . The application of Ce on the surface acts as

a reactive ionic element, which facilitates the formation of an early Cr_2O_3 protective layer. Thus, the ion migration has shifted from outward cation migration to inward anion ingress (from Auger analysis). The presence of Ce suppresses the formation of Fe_2O_3 allowing the Cr_2O_3 layer to form uninhibitedly and uniformly. The XPS data also seem to indicate that the presence of Ce allows transition metal oxides to be more covalent and thus protective. These covalent structures are speculated to have a polymer type nature, which improves the oxide layer's ability for slower oxygen uptake to provide a more protective barrier.

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