PROTECTION OF STAINLESS-STEELS AGAINST CORROSION IN SULPHIDIZING ENVIRONMENTS BY Ce OXIDE COATINGS: X-RAY ABSORPTION AND THERMOGRAVIMETRIC STUDIES

T. FRANSEN and P.J. GELLINGS

Laboratory for Inorganic Chemistry and Materials Science, Twente University of Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands

J.C. FUGGLE

Laboratory for Molecular Spectroscopy, Katholieke Universiteit, Toernooiveld, 6525 ED Nijmegen, The Netherlands

G. VAN DER LAAN

Materials Science Centre, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

and

J.-M. ESTEVA and R.C. KARNATAK

Laboratoire pour l'Utilization du Rayonnement Electromagnétique, Bâtiment 350, Université de Paris, F-91405 Orsay Cedex, France

In this paper a study is reported concerning ceramic coatings containing cerium oxide, prepared by the sol-gel method, used to protect Incoloy 800H against sulphidation. When the coating is sintered in air at 850°C good protection is obtained. In an X-ray absorption spectroscopic study of the coatings it was observed that the best protective coating contains all cerium as Ce^{IV} after pretreatment. After sulphidizing cerium was reduced to Ce^{III}. Possible mechanisms to explain the protective properties are discussed.

1. Introduction

Stainless steels give excellent protection against corrosion in oxidizing environments. However, there is an increasing need for materials resistant to the reducing, sulphidizing environments present in the plants for gasification of coal or heavy oils as well as many areas of the (petro)chemical industry. At present many plants in these areas must be based on metallic components with a short lifetime if cooling of the components is not possible [1].

Because of the high temperatures involved coating procedures must rely on metallic or ceramic layers, of which the latter hold most promise. The use of protective "ceramic" layers is quite a recent development even for oxidizing environments [1,4] and until now very little has been done on protection against sulphidation.

For oxidizing environments Ecer et al. [2], found that a very good resistance could be obtained by dipping Ni- or Fe-base alloys in a slurry of CeO_2 in ethanol, followed by drying and sintering in air. Bennett et al. [3], using the so-called sol-gel method, were also able to obtain a greatly improved oxidation resistance.

The mechanism of this improvement has been suggested to be the adsorption of Ce^{4+} ions on the grain boundaries of the oxide layer, thus effectively blocking fast diffusion pathways. In addition it was suggested that adsorption of Ce hindered grain growth, resulting in a better adherence to the substrate due to enhanced plasticity of the oxide [3]. However, there is no direct evidence supporting these mechanisms.

In this paper we show that coating stainless steels with Ce oxide by means of the sol-gel method improves the sulphidation resistance by several orders of magnitude, and that its effectivity depends on the pretreatment of the coated material [4]. In addition we report upon an XAS-study to give some evidence for the mechanism for such protection.

As it is expected that the state of the cerium ions present in the coating plays a significant role it was decided to try to establish this by spectroscopic means. In principle, several spectroscopic methods can be used to distinguish the chemical valence of Ce, including electron and X-ray spectroscopies at the 3d and 2p edges. For the particular problem in hand X-ray absorption at the 3d edges in the photoyield mode is most appropriate because of its intermediate probing depth. In electron spectroscopies like ESCA, the inelastic mean free path of the electrons is only about 1 nm. Thus the signal from the ceriated layer is strongly influenced by a miscellaneous layer of hydrocarbons, strongly bound water, and other contaminants which coats any "real" surface and even the Ce contribution to the signals is only characteristic of the extreme surface. Sputtering methods are useful but ambiguous because the sputtering ions damage the sample to a depth comparable to the probing depth of electron spectroscopy. This is not a problem in X-ray absorption in the photoyield mode where the characteristic probing depth is some tens of nanometers.

The principle of this method relies on the fact that the electron photocurrent from a sample is proportional to the number of photons absorbed in the surface layer. If only the elastic (no-loss) photocurrent is detected, then the photocurrent is proportional to the number of photons absorbed within one inelastic mean free pathlength of the surface. It is more usual to collect electrons from the entire photoelectron spectrum including the secondaries. In

this case the current is proportional to the number of photons absorbed in a surface layer of the order of tens of nanometers thick because even electrons that have been scattered many times, can escape the surface. The characteristic absorption length for soft X-rays, being typically hundreds of nanometers, is long even by comparison with the escape depth of secondary electrons. Consequently, the photoyield spectrum in total yield mode is exactly equivalent to the absorption spectrum in transmission mode. Whilst still not a "bulk" method, X-ray absorption can "see through" surface contamination and thus has potential as a tool for the study of technologically interesting "dirty" samples which has been underexploited until now.

X-ray absorption and emission are well known as quantitative analytical tools, but is less well known that they may also be useful tools for qualitative analysis, e.g., to determine the valence of an element. Ce is a case where XAS should work rather well because of the localized f-electrons. Ce^{III} compounds have nominally one 4f-electron, Ce^{IV} compounds have nominally none. Hybridization of the f-electrons with the other valence states only slightly changes the simple picture for Ce^{III} compounds [5–8]. Thus the 3d absorption "edges" have strong peaks which can be interpreted as due to transitions from the initial state to the $3d^94f^2$ or $3d^94f^1$ final states [4–8]. The spectra themselves contain complicated multiplet and many-body effects whose interpretation is not trivial [5–7], but this does not hinder the use of the spectra as a fingerprint for Ce^{III} and Ce^{IV}. The salient point here is simply that the spectra are distinct and the $3d \rightarrow 4f$ transitions are at different energies in Ce^{III} and Ce^{IV} compounds. For CeO_2 the position is more complicated but the spectrum is still quite distinct [9].

2. Experimental

2.1. Material

The composition of Incoloy 800H which has been investigated in this work was (in wt%): Cr 19.9, Ni 31.7, C 0.08, Mn 0.7, Si 0.5, Ti 0.4, Fe balance.

The material was annealed for 1 h at 1350 K, water quenched, annealed for 1 h at 1230 K and water quenched again. Samples of $10 \times 8 \times 3$ mm^3 were always cut from the stock material with good cooling. The final surface finish was grinding with 500 grit SiC paper. All test specimens were ultrasonically cleaned with hexane and ethanol prior to coating and/or sulphidation.

2.2. Preparation of the sols

Cerium hydroxide ($Ce(OH)_3$) was prepared from cerium nitrate, $Ce(NO_3)_3 \cdot 6H_2O$ and NH_4OH. The $Ce(OH)_3$ was stirred in dilute HNO_3 at 60°C, yielding a sol with pH = 0.3.

2.3. Application of the coatings

The coatings were applied by immersing (dipping) the test pieces in the sol and withdrawing them from the liquid at a speed of 0.7 mm s^{-1}, followed by drying for 16 h in air at 20°C.

2.4. Pretreatment of coatings

The ceria deposits were sintered in air or in argon at 1 atm by heating the specimens to 850°C at a rate of 30°C h^{-1} and directly after reaching the maximum temperature cooling at a rate of 30°C h^{-1} to 20°C. For comparative purposes non-coated specimens were also included in the test. These were subjected, both without further pretreatment and after 2 h exposure to HNO_3 (pH = 0.3), to the same heat treatment procedure prior to sulphidation.

2.5. Sulphidation tests

Thermogravimetric measurements were performed in a Cahn-1000 balance. The test pieces were suspended in the balance which was first flushed for 16 h with argon at a flow rate of 180 ml min^{-1}. Subsequently the temperature was increased. As soon as the desired temperature (550°C in this study) was reached a flow of 50 ml min^{-1} of hydrogen containing 5% H_2S was introduced. This yields a sulphur partial pressure of approximately 10^{-7} kPa. After exposure all specimens were examined using conventional optical and scanning electron microscopy. In some cases electron microprobe analyses were performed with a JEM200CX electron microscope equipped with an ASID3D and a LINK860 quantitative EDS analyzer. The spot size was 40 nm resulting in a lateral resolution of 100–200 nm.

2.6. X-ray absorption spectroscopy

The observations were carried out using the background continuum emitted by the Anneau de Collisions d'Orsay (ACO) storage ring at Orsay as a source of synchroton radiation. A double crystal monochromator equipped with beryl single crystals gave a tunable X-ray beam with about 0.37 eV resolution in this energy region [10]. An open channeltron was used as the electron detector. Checks were made on the light flux using an Al sample which has a flat absorption in the energy region of interest. The only structure is due do a "glitch", or anomalous reflection at 898 eV for which we corrected using the Al reference. The energy scale was calibrated using the Ni $2p_{3/2}$, Cu $2p_{3/2}$ and Mg 1s edges and the corresponding XPS binding energies [11], as well as previously determined structures in the spectrum of Ce itself [12].

After pretreatment and/or sulphidation the specimens were exposed to air at room temperature for some weeks. They were then inserted in the vacuum system and baked (150°C for 10 h) to reach ultra-high vacuum and remove lightly bound contamination from the surface).

3. Results

3.1. Sulphidation tests

Best and reproducible results were obtained for evenly distributed films on a smooth surface. In fig. 1 some typical thermogravimetric results are shown. it is observed that the test pieces with a Ce oxide layer (containing about 0.3 mg ceria/cm^2) show by far the best resistance against sulphidation under the circumstances used in this study. Pretreating in argon leads to a significantly lower protective effect than pretreating in air.

Microscopic investigation after sulphidation was in complete agreement with the thermogravimetric results. The attack was severe only on uncoated specimens where it started in the form of sulphide nodules at random points on the surface [4].

It was shown with the electron microprobe that the product layer formed during sulphidation, which on coated specimens pretreated in air had a thickness of approximately 0.5 μm, consisted of a chromium-rich inner and an iron-rich outer layer. the distribution of the alloy constituents in these layers was comparable for coated and uncoated Incoloy 800H. Electron microprobe
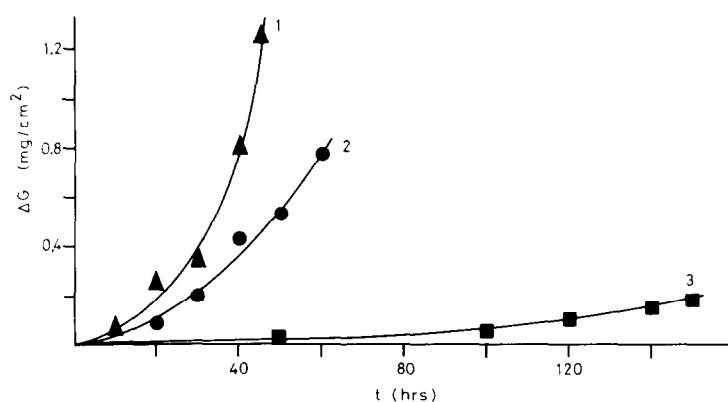

Fig. 1. Thermogravimetric results for Incoloy 800H in an Ar/H$_2$/H$_2$S atmosphere at 550°C after various pretreatments: (1) uncoated, pretreated in air at 850°C; (2) coated with ceria, pretreated in Ar at 850°C; (3) coated with ceria, pretreated in air at 850°C.

analysis of the layer showed the cerium to be incorporated both in the inner and in the outer layer, similar to the findings of Bennett et al. [3] after *oxidation* in CO_2. On the basis of the weight change by coating and by sulphidation it can be concluded that the layers contain a maximum of about 20% Ce oxide.

3.2. X-ray absorption

The normalized spectra recorded in the manner described above are reproduced in fig. 2. The spectrum shown in fig. 2a. is that of the specimen pretreated in air and then exposed to $Ar/H_2/H_2S$ for 160 h at 550°C. The spectrum of the sample pretreated in argon and exposed to $Ar/H_2/H_2S$ under the same conditions shows no significant structural differences, but the signal to noise ratio was poorer. This is consistent with a lower Ce concentration in the thicker sulphide film. These spectra are typical of those found for materials containing Ce^{III} [6–8] and show structure due to the $3d^94f^2$ multiplet. In principle about 20 lines should contribute appreciable weight to the
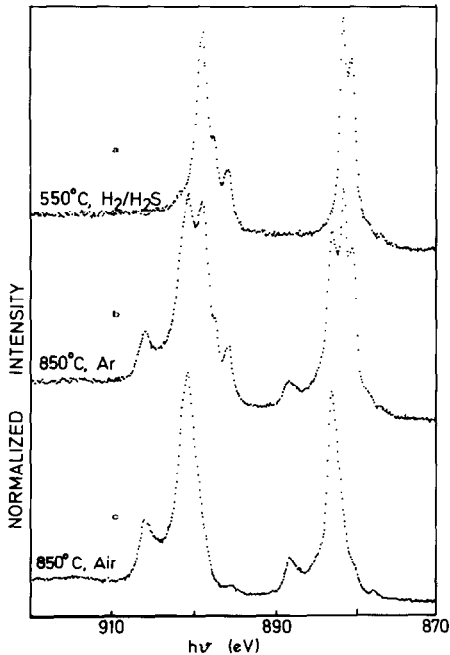

Fig. 2. XAS spectra of Incoloy 800H surfaces coated with ceria: (a) pretreated in air at 850°C and subsequently exposed at 550°C to an $Ar/H_2/H_2S$ mixture for 160 h; (b) pretreated in Ar at 850°C; (c) pretreated in air at 850°C.

spectrum under dipole selection rules and seven or eight peaks are usually resolved. The eight found here are the same as in γ-Ce and many of its intermetallic compounds with one f-electron in the ground state.

The contrast between the above spectrum and that for a sample treated only in air at 850°C is great. Essentially none of the Ce^{III} peaks are found, although weak intensity at about 881–882 and 898 eV may be due to residual Ce^{III} in the surface layer. The assignment of these peaks is difficult and must take into account hybridization between the Ce 4f and O 2p states in the $3d^94f^1$ and $3d^94f^2$ configurations as discussed by Fujimori [13]. The spectrum is not as simple as that found, for instance, in La [12] which also has local $3d^94f^1$ final state configurations. Nevertheless, whilst these complications are related to the electronic structure of the Ce^{IV}, there can be no question that this spectrum is derived from Ce atoms which are chemically 4-valent.

The spectrum of the sample treated at 850°C in argon can be reproduced by superimposing the spectra of the sample treated only in air and of the sulphidized sample in approximately the ratio 1 : 1. This means that both Ce^{III} and Ce^{IV} are present in the surface layer analysed. Although we cannot say anything definitive about the distribution of Ce^{III} and Ce^{IV} or the composition through the whole cerium containing oxide layer, it is probable that it is mostly Ce^{III} with a little Ce^{IV} in the surface layer.

3.3. ESCA measurements

Preliminary ESCA measurements of the air-pretreated coated specimen after sulphidation showed that the protective layer was Cr-rich even at the gas–solid interface. Using Scofield's XPS cross-sections and peak intensities we estimated that the oxygen content exceeded that of sulphur even after the initial 30 s sputtering to remove superficial contamination. The sulphur content dropped off slowly as the layer was sputtered away. Some Ce appeared from all depths in the protective layer but the XPS cerium peaks were too weak for detailed XPS studies of the chemical state of Ce.

In the specimen pretreated in air but not sulphidized, the Ce peaks were stronger, indicating a higher Ce concentration.
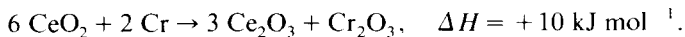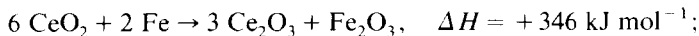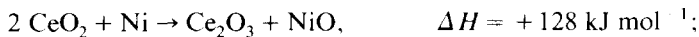
4. Discussion

As shown by the thermogravimetric results reproduced in fig. 1 coating with cerium oxide is very promising for protecting stainless steel against sulphidizing environments. However, there are significant differences depending on whether the sintering heat treatment was performed in air or in argon. This is similar to earlier results of Bennett et al. [3], who found a favourable influence of pre-oxidation on the behaviour of cerium oxide coatings on a 20/25/Nb

chromium–nickel steel. By contrast Ecer et al. [2] found a beneficial effect on the oxidation rate of Ni- and Fe-base alloys when no preoxidation had been applied. Our results show that preoxidation, or at least pretreating in air after application of the coating, is essential for protection under sulphidizing conditions.

We now consider the mechanism of passivation of the Incoloy by the cerium oxide. As shown clearly by the ESCA (XPS) results the layer present on the surface is not a pure cerium oxide but a mixed oxide containing cerium in a distributed form. But XAS clearly shows that more Ce^{IV} is present in the air-treated layer and it is attractive to link the protection to its presence. As indicated in the introduction the possible mechanisms of passivation include formation of a diffusion barrier or better adherence between the oxide containing Ce and the metal surface. Also deactivation of "active" corrosion areas on the metal may occur. The surface layer of both air and Ar pretreated cerium oxide layers are clearly reduced by the H_2/H_2S containing gas. This must result in a major reorganization of the atoms of the overlayer. It seems improbable that the air-formed overlayer would remain impervious under these conditions, while the argon-treated layer does not. We thus discard the mechanism of passivation by diffusion barriers made impervious by the presence of cerium. This is supported by the ESCA measurements which indicate that by sulphidation the cerium content of the protective layer is decreased.

Because of the limited penetration depth of the X-ray absorption measurements it has probably not been possible to determine the state of the Ce throughout the whole layer.

Ce^{IV} is unlikely to oxidize the steel surface. The heats of formation in kJ mol^{-1} at 300 K for some relevant oxides are: $CeO_2 = 1090$, $Ce_2O_3 = 1790$, $FeO = 272$, $Fe_2O_3 = 824$, $Cr_2O_3 = 1160$, $NiO = 128$. Thus reduction of CeO_2 by the alloy constituents is energetically unfavourable at room temperature, e.g.:

$$2\ CeO_2 + Ni \rightarrow Ce_2O_3 + NiO, \qquad \Delta H = +128\ kJ\ mol^{-1};$$

$$2\ CeO_2 + Fe \rightarrow Ce_2O_3 + FeO, \qquad \Delta H = +118\ kJ\ mol^{-1};$$

$$6\ CeO_2 + 2\ Fe \rightarrow 3\ Ce_2O_3 + Fe_2O_3, \qquad \Delta H = +346\ kJ\ mol^{-1};$$

$$6\ CeO_2 + 2\ Cr \rightarrow 3\ Ce_2O_3 + Cr_2O_3, \qquad \Delta H = +10\ kJ\ mol^{-1}.$$

Such reactions are thus unlikely to be a strong factor, even at 550°C.

5. Concluding remarks

In this study we have illustrated the potential of XAS at the 3d edges to investigate protective layers of cerium oxides and the presence of Ce^{III} or Ce^{IV}

therein. The extremely high sensitivity of XAS allows the discrimination between the chemical state of the atoms in the protective layer more easily than XPS. We feel that X-ray absorption studies in the soft X-ray region have further potential for this sort of investigation. In this particular case we were able to show that effective passivation of the metal investigated, Incoloy 800H, could be correlated with the presence of an increased Ce^{IV} concentration in the overlayer after pretreatment.

Our results lead to further questions such as the nature of the interface between the metal and the Ce containing oxide layer and the variation of the composition of this layer with depth. Also the distribution of oxygen and sulphur in the sulphidized layers must be known before it is possible to reach a full understanding of the mechanism of the protection. Studies concerning these factors could be attempted by combination of XPS (ESCA), X-ray absorption and sputter-profile methods.

Clearly the presence of cerium has a very positive effect on the behaviour of stainless steel under sulphidizing conditions. This opens several new channels for investigation. For instance one is not restricted to the use of coatings, small additions of cerium as an alloying constituent of the steel may provide a similar effect if heating in air causes surface segregation and oxidation to Ce^{IV}.

Acknowledgements

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