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H. Buscail, C. Courty, J.-P. Larpin. Effects of Ceria Coatings on Pure Iron Oxidation. Comparison with Extra Low Carbon Steels. Journal de Physique IV Proceedings, 1995, 05 (C7), pp.C7-375-C7-380. 10.1051/jp4:1995745 . jpa-00254040

HAL Id: jpa-00254040

<https://hal.science/jpa-00254040>

Submitted on 1 Jan 1995

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Effects of Ceria Coatings on Pure Iron Oxidation. Comparison with Extra Low Carbon Steels

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Abstract. A comparison of results obtained on blank and coated specimens shows that ceria coatings strongly modify the microstructure and texture of the wüstite scale formed during low pressure oxidation of pure iron. On coated specimens, all the scale is composed of fast growing (200) oriented wüstite grains ; crystallographic orientations (different from (200)) are no longer present in the wüstite scale. The linear oxidation rates are always higher in the case of surface coated specimens due to the lack of epitaxial relationships with the metallic substrate. Cerium is located in the wüstite matrix as a CeFeO_3 phase which dissolves in FeO in time. Carbon and manganese, present as major impurities in an Extra Low Carbon Steel, have a strong influence on oxidation kinetics and on the rare-earth element location in oxide scales. Carbon, diffusing slowly from the matrix bulk to the metal-scale interface, promotes spallation of the wüstite scale, but carbon does not hinder CeFeO_3 formation. On the other hand, the manganese impurity prevents the formation of CeFeO_3 due to the lack of contact between the reducing FeO germs and the oxidant CeO_2 . This lack of contact is due to the high vapour pressure of manganese oxides, which evaporate at the beginning of the reaction, and promotes immediate CeO_2 coating spallation.

1. INTRODUCTION

The effect of very a small amount of reactive elements (La, Y, Ce, Hf, etc.) in improving the protection by chromia or alumina scales on binary or ternary alloys such as (Fe-32Ni-27Cr-0.07Ce) [1] (Fe-32Ni-20Cr) [2], (Fe-23Cr-5Al), (Fe-17Cr-12Ni) [3,4], (Fe-18Cr-9Ni), (Fe-17Cr) [5] has clearly been demonstrated using ion implantation, the sol-gel method, MOCVD, or cerium as an alloying element.

According to many authors the better scale adherence and the reduction of the scaling rate are the major important changes in the growth of the protective oxide scale [6-12]. However, Hou and Stringer [13] have shown that lanthanum implantation on a Fe-18Cr-5Al alloy accelerates the oxidation process and leads to more scale separation. They also suggested that the weakening of the interface may be caused by interfacial sulphur segregation but this last interpretation is in contradiction with the recent results of Grabke and co-workers [14] who proposed that sulphur starts to segregate to the free-metal surface as soon as the scale and metal separate. Even if they are controversial, all these results show that impurities such as silicon [15,16], carbon, or other metallic elements could play an important role and must be worth examination. Concerning the change of the diffusion mechanism in oxide scales, some authors have proposed that the reactive element is incorporated into the oxide scale and segregates along oxide grain boundaries. Some perovskite-type compounds are envisaged [8, 17,18]. Schumann [19] proposed the formation of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) particles segregated along $\alpha\text{-Al}_2\text{O}_3$ grain boundaries. A more complex oxide was also identified as $(\text{Ca,Ce})(\text{Ti,Fe,Cr,Mg})_{21}\text{O}_{38}$ in Cr_2O_3 or FeCr_2O_4 scales [20-22].

Nevertheless, even if the understanding of the role of reactive elements is making progress, many questions remain unanswered such as: (1) how to explain the location of the reactive element in an oxide scale? (2) in which mixed oxide can the reactive element be incorporated? (3) what is the influence of minor elements or impurities on the mode of reactive element introduction into an oxide scale? (4) on the subject of the mechanical properties and adherence of the oxide scales, is the reactive element able to modify the microstructure and texture of an oxide scale?

To answer these questions, we have chosen to study the oxidation of very high purity iron specimens. Pure iron was used as a reference metal to determine how a mixed iron-cerium-oxide can be formed and how the iron oxide scale texture can be modified by a ceria coating. The comparison of the pure iron oxidation with the Extra Low Carbon Steel oxidation will make it possible to determine the role of carbon and manganese impurities on the iron oxidation process and on the way cerium is incorporated into the iron oxide scale.

2. EXPERIMENTAL

Pure iron oxidation was studied in a vacuum containing oxygen with partial pressures in the flowing air ranging between $p(\text{O}_2)=2 \cdot 10^{-4}$ Pa and $p(\text{O}_2)=4 \cdot 10^{-2}$ Pa. These pressures were chosen to insure wüstite formation in the temperature range 700-1050°C. This paper will present detailed kinetic results concerning the oxidation of the pure iron and the steel under $p(\text{O}_2)=4 \cdot 10^{-2}$ Pa between 700 and 950°C. The morphology of the scales and the results of textural analysis will only be given for tests performed under $p(\text{O}_2)=2 \cdot 10^{-3}$ Pa at 800 and 950°C.

Electrolytic iron of 99,995 weight% purity is polycrystalline. At room temperature, its structure is composed of large α -iron grains, whose mean size is about two millimetres diameter. The chemical analysis of the substrate gives for the major impurities content : 0.002 weight% silicon, 0.0008 weight% carbon and less than 0.0001 weight% for all the other elements. The Extra Low Carbon steel contains as major impurities : 0.18 weight% manganese, 0.041 weight% carbon, 0.06 weight% aluminium, 0.023 weight% nickel and 0.015% chromium. The initial ingots were machined to prepare rectangular, 1mm thick plate specimens of around 3 cm² total area. The specimens were abraded to 400 grade. This polishing grade was chosen to facilitate the adherence of the cerium coating on the substrate and because no difference was detected between the rate constants of oxidation of a blank iron after cold-worked or diamond-paste finishing.

After polishing, specimens were washed in water and alcohol and dried, then subjected to a sol-gel treatment described elsewhere [23-24]. The sol-gel treatment is performed by dipping the specimen in a nitric cerium hydroxide solution before a quick drying in air at 50°C. The aim of this treatment is to cover the specimen surface with a 1-2 μm thickness of badly crystallized ceria scale. Then, blank and ceria-coated specimens were immediately tested in a micro-thermobalance.

Scale morphologies and partitioning of the different elements in the oxide scale were determined both by scanning electron microscopy (S.E.M.) and by energy-dispersive X-ray analysis (E.D.S.). Identification of the phases and preferential growth orientations of the scale were determined by X-ray diffraction (X.R.D.) using $\text{Cu K}\alpha_1=1.54 \text{ \AA}$ radiation.

The study of the preferential growth orientations was performed using a textural goniometry apparatus equipped with a computer for signal treatment and pole figure plotting as described elsewhere [26,27]. The pole figures of the (200), (111), (220) and (311) planes were realized on each specimen. Nevertheless, for simplicity we will only present the (200) pole figures which are the most representative of the texture of the wüstite scales. The oxide scales were examined while still attached to the metal substrate.

3. PURE IRON OXIDATION - FeO TEXTURE MODIFICATION BY A SURFACE APPLIED CERIA COATING

3.1 Pure Iron.

The scale is crystallographically related to the grains of pure iron. The pole figures of blank specimens oxidized in air with a partial oxygen pressure: $p(\text{O}_2)=2 \cdot 10^{-3}$ Pa at 800 and 950°C are presented on figure 1. At 950°C (γ -Fe), the (200) pole figure shows definite numbers of strong intensity spots corresponding to the different areas of wüstite grown on the large iron grains. Each iron grain imparts a particular orientation to the wüstite which is grown on its surface. At 800°C (α -Fe), there is a maximum diffraction intensity for the (200) planes in the middle of the pole figure. This indicates that a strong tendency to orientate the (200) wüstite planes parallel to the specimen surface occurs in the scale. This result also demonstrates that below 912°C, when iron is still in the α phase, the epitaxial relations between α -Fe and the FeO scale are not good enough to observe a texture induced in the scale by the substrate.

3.2 Coated iron.

The pole figures obtained for coated specimens oxidized with $p(\text{O}_2)=2 \cdot 10^{-3}$ Pa at 800 and 950°C are presented in figure 1. Under all conditions, analysis of the scales at each temperature exhibits a

maximum diffraction intensity in the middle of the pole figure for the (200) planes analysed. Thus, our results show that the (200) crystallographic planes present a strong tendency to be parallel to the specimen surface. Other pole figures - not presented here - also show that the (111) planes of the cubic structure are disposed with an angle of 53° with regard to the (200) planes. After coating, the wüstite texture was different from that obtained on blank specimens. It is the same on the whole specimen surface because no more epitaxial relationships are present between the scale and the substrate grains any more, due to the presence of cerium at the internal interface.

Cerium is found inside the FeO scale in a compound X-rayed as CeFeO_3 (JCPDS 22-166), located close to the internal interface. The cerium orthoferrite is formed through a solid state oxidation-reduction process between the Fe^{2+} ions of FeO in close contact with the Ce^{4+} ions of CeO_2 [28]. All our observations indicate that the CeFeO_3 phase tends to dissolve into wüstite with time due to the possible exchange of the Ce^{3+} ions of the CeFeO_3 phase with the O^{2-} ions of the FeO phase [28].

Fig. 1 : (200) pole figures of the wüstite scales formed on blank or ceria coated iron specimens.

4 . OXIDATION OF AN EXTRA LOW CARBON STEEL, COMPARISON WITH PURE IRON OXIDATION, ROLE OF IMPURITIES ON THE CeFeO_3 FORMATION.

Thermogravimetric measurements of high purity iron oxidation between 700 and 950°C and the thermogravimetric measurements of steel oxidation at 700°C are given in Fig.2, for uncoated and coated specimens ($p(\text{O}_2)=0.04$ Pa). We have not presented the kinetic curves of pure iron oxidation under $p(\text{O}_2)=0.002$ Pa because the coating and temperature influence on kinetics are very similar under $p(\text{O}_2)=0.04$ Pa or $p(\text{O}_2)=0.002$ Pa except that the linear rate constants are 20 times higher at $p(\text{O}_2)=0.04$ Pa.

4.1 Blank specimens.

During pure iron oxidation, only linear weight-gain curves are observed for experiments lasting for 24 hours or more. The linear behaviour is always maintained even in testing to complete oxidation of the specimen. The linear rate constants are proportional to the first power of the oxygen pressure. We

therefore consider that the oxidation rate implies oxygen adsorption as the limiting step : no diffusion processes can be considered as a limiting step in the conditions used.

During steel oxidation, the kinetic curve shows a weight loss during the first 30 minutes. This period is followed by a high-rate, linear weight gain for some hours. Finally, another linear weight gain curve is followed by a very slow rate until the end of the oxidation test. The initial weight loss of the specimen is attributed to the manganese oxide evaporation. This phenomenon is permitted by the rapid manganese impurity diffusion from the substrate bulk [29]. Manganese oxidize and the oxide formed evaporates due to the low pressure conditions of the test. The second part of the curve corresponds to the oxidation of the superficially purified specimen surface, oxidizing at a rate close to the rate of the pure iron oxidation. During this period the oxide FeO is formed. After 5 hours, a slowing down of the oxidation rate occurs : carbon present in the bulk, diffuses slowly to the FeO-steel interface [30-32] and accumulates at this interface because it does not diffuse through FeO due to the very low solubility of carbon in FeO [30,33-34]. Carbon is then oxidized by the oxygen dissociated from the FeO, carbon oxide is formed and the gaseous pressure increase induces scale spallation. Then iron diffusion from the substrate to the oxide scale becomes the slower process and the scale growth rate is greatly reduced [30-34].

a) Weight gain curves of pure iron oxidation under $p(O_2)=0.04$ Pa , effect of a ceria coating on the oxidation rate.

b) * Comparison of weight gain curves obtained with blank iron and steel specimens.
* Coating effect on steel oxidation kinetics.

c) Weight loss observed during the 30 first minutes oxidation of uncoated steel specimens.

Fig.2 Weight gain curves of pure iron and ELC steel oxidation. Effect of ceria coatings.

4.2 Ceria coated specimens

The presence of a ceria coating on pure iron specimens always induce a higher linear growth rate of the FeO scale. This is due to the presence of the fast growing (200) oriented FeO grains on the entire surface of the specimen (no epitaxial relationships between FeO and Fe force the scale to grow with another slow growing rate orientation. According to the crystalline growth laws, the crystallographic planes with the smaller Miller index have the fastest growth rate.

The presence of ceria on the initial surface of a steel specimen induces a much lower mass gain after 24 hours experiment : it has two major effects compared with blank specimens. Firstly, the weight loss of the specimen during the first 30 minutes is not observed. This is due to the presence of the coating, which hinders the quick evaporation of manganese oxide by covering the major part of the specimen surface. Secondly, due to the defect structure nature of CeO_{2-x} [35-37], the very high thermodynamic stability of manganese oxide and the presence of cracks in the coating, gaseous manganese oxide forms, and the pressure increase promotes decohesion of the ceria coating under our conditions, as illustrated in Fig. 3. At this stage no CeFeO_3 is formed, because no more CeO_2 remains in contact with FeO, so no oxido-reduction between the two oxides can occur. After CeO_2 spallation, FeO forms following a fast linear regime for a short time (1hr). Afterwards, carbon diffusing slowly from the substrate bulk to the FeO-steel interface, promotes FeO decohesion. The linear mass gain then registered is characterised by a slope close to zero. Confirmation of the effect of manganese on ceria spallation has been given by the oxidation of previously annealed steel specimens in a $p(\text{O}_2)=10^{-4}$ Pa vacuum, (this purifies the steel of superficial manganese impurities). The oxidation of such specimens permits formation of CeFeO_3 oxide at the initial stage of the reaction and leads to the homogeneous incorporation of cerium inside the FeO scale.

Fig.3 : Schematic drawing illustrating the effect of manganese impurities on CeFeO_3 formation.

5. CONCLUSIONS

The present work shows that cerium coatings applied by adequate dipping modify the microstructure and texture of a wüstite scale grown on highly pure iron. All the results indicate that the main effect of the coating is to prevent epitaxial relations between the iron and the wüstite. The whole surface is then covered with fast-growing scale and the pole figures show that the (200) planes of the wüstite structure are mainly oriented parallel to the specimen surface. Blank specimens always show a lower kinetic rate due to the presence of slow-growing-rate wüstite grains on the surface. In this case, the presence of wüstite grain orientations differing from (200) is imposed by epitaxial relationships with the metal, especially on γ -iron.

CeFeO_3 perovskite-type oxide appears to be a good atom arrangement for a homogeneous cerium introduction in oxide scales. The possibility of transformation of ceria into a cerium orthoferrite is attributed to the possible oxido-reduction solid-state reaction between FeO and CeO_2 if the oxides are in close contact.

Carbon has no detrimental effect on the CeFeO_3 formation due to the slow diffusion of this impurity in the steel bulk. Nevertheless, it promotes wüstite scale spallation due to the poor solubility of carbon in wüstite and the formation of gaseous carbon oxide at the scale-steel interface after some hours of testing.

Manganese hinders CeFeO_3 formation under low pressure oxidation conditions due to the high vapour pressure of manganese oxide at high temperatures. The immediate decohesion of CeO_2 from the steel surface does not permit the oxido-reduction process between FeO and CeO_2 oxides.

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