Investigation of surface structure and composition of \textit{in situ} annealed Fe–Mn binary alloy samples using RHEED and electron spectroscopy

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The formation of oxides at the surface of Fe–1.5%Mn and Fe–0.6%Mn binary alloys was investigated as a function of the conditions of the heat treatments. Both the influence of temperature and the atmosphere under which the experiments were performed were studied. The range of annealing temperatures was adjusted to 800°C. The atmosphere consisted of a mixture of N$_2$–5%H$_2$ and traces of water vapour, with different fixed dew points ranging from $-10$°C to $-30$°C. The state of the annealed surfaces was determined using \textit{in situ} analytical devices attached to the annealing reactor in order to avoid surface contamination or the formation of native oxides after the experiments due to contact with air. The structure and composition of the surfaces were determined by reflection high-energy electron diffraction (RHEED) and electron spectroscopy (XPS, AES). Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: selective oxidation; Fe–Mn alloys; \textit{in situ} annealing; XPS; RHEED

INTRODUCTION

In latter years, the quality requirements for steel sheets destined to panel parts on car bodies have been improved significantly. The oxidation, segregation and/or precipitation processes$^1$ that take place during the annealing treatments performed on steel sheets devoted to forming applications disturb the surface chemistry, affecting strongly the final quality of subsequent protective finishing treatments.$^2$ Because these protective coatings determine to a great extent the future corrosion behaviour and thus the lifetime of the steel parts, the importance of the study of the phenomena taking place on the sheets in the annealing furnaces is obvious. Unfortunately, the actual furnace designs do not allow direct sampling of material but if it was possible the surface state would be changed completely due to air contact. Thus, it is a necessity to simulate the habitual furnace conditions in the laboratory and, at the same time, avoid any air exposition of the samples after the experiments working with \textit{in situ} analytical devices.

In this work some of the results of the ECSC international project ‘New Methodological Approach to Selective Oxidation’ are presented. This project is dedicated to investigation of the oxidation phenomena on binary and ternary alloys, as well as industrial steel grades, combining complementary analytical techniques, simulations and theoretical models$^3$–$^5$ to obtain a knowledge of the mentioned phenomena. The paper is focused on the characterization of annealed Fe–Mn low-alloyed steels using x-ray photoelectron spectroscopy (XPS) and reflection high-energy electron diffraction (RHEED) to obtain qualitative information on the composition and crystal structure of the annealed surfaces.

EXPERIMENTAL

The annealing treatments were performed at standard furnace conditions: 800°C and N$_2$–H$_2$ (5% hydrogen content) atmosphere with traces of water (∼380 ppm, dew point = $-30$°C). The typical heating cycle is shown in Fig. 1. The gas mixture had a purity of 99.9999%. The steels used as specimens were Fe–Mn binary alloys (see compositions in Table 1) in order to simplify the study of the selective oxidation of Mn, avoiding competitive and more complex effects caused by the presence of additional alloying elements. The samples were ground and polished to 1 µm before being inserted into the annealing chamber.

The annealing and the analytical chambers are directly connected to avoid any further contact between the annealed samples and the laboratory ambient prior to analysis. After insertion, the annealing chamber was pumped down to a residual pressure of 10$^{-6}$ mbar and then the N$_2$–H$_2$ atmosphere was established. After annealing the gas flow was stopped, the chamber was pumped down and the sample was transferred to the analysis chamber.
Table 1. Composition of the investigated alloys (wt.% × 1000)

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>P</th>
<th>Si</th>
<th>Al</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Mo</th>
<th>V</th>
<th>Ti</th>
<th>C</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–0.6%Mn alloy</td>
<td>684</td>
<td>2</td>
<td>7</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>2.1</td>
<td>7.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe–1.5%Mn alloy</td>
<td>1580</td>
<td>2</td>
<td>8</td>
<td>9</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1.8</td>
<td>7</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 1. Temperature vs. time characteristics of a typical annealing cycle.

The ultrahigh vacuum (UHV) analysis chamber (base pressure = 10^{-10} mbar) is equipped with a double-pass cylindrical mirror analyser (Staib Instruments GmbH) suitable for use in XPS, Auger electron spectroscopy (AES) and reflection electron energy-loss spectroscopy (REELS). The analyser is calibrated with respect to the Ni 3p_{3/2} (66 eV) and Cu 2p_{3/2} (958.6 eV) peaks and the Fermi level of Ni. Non-monochromatic Al K \(\alpha\) radiation (1486.6 eV) was used to acquire the spectra. The RHEED system (Staib Instruments GmbH) installed in the UHV chamber is calibrated using a polycrystalline Cu film deposited in situ. A resolution of 0.01 Å can be achieved in the case of good crystalline samples. The energy of the electron beam was 35 keV \((\lambda = 0.06446 \text{ Å})\) for the measurements presented in this work.

RESULTS

After polishing, the samples presented an amorphous native oxide film at the surface. This film is eliminated after short annealing times at relatively low temperatures of 550 °C. Thus, no significant influence is to be expected concerning the results of the annealing treatments performed in this work. However, it could be of importance at the very beginning of the oxidation process, especially at low temperatures, and future work will be related to this problem by means of the use of plasma cleaning techniques to remove this oxide scale while conserving the underlying crystal structure of the steel.6

In Fig. 2, the 2p doublets of iron and manganese measured on an Fe–0.6% Mn steel sample after 600 s of soaking at 800 °C are shown. From the peak position it is possible to recognize the state of both elements. The 2p_{3/2} peak is centred at 708.5 eV, indicating that Fe was reduced almost completely (Fe^0 2p_{3/2} at 708 eV; Fe^{2+} 2p_{3/2} and Fe^{3+} 2p_{3/2} at 710 and 711.5 eV respectively). The Mn 2p_{3/2} peak is at 641 eV, indicating an oxidized state (Mn^2+ 2p_{3/2} at 639 eV). Taking into account the annealing conditions, the formation of MnO is to be expected. This point is confirmed by RHEED. As can be seen in Fig. 3, a sharp and strongly (200)-textured ring structure corresponding to MnO (Fm\bar{3}m space group, \(a = 4.4444 \text{ Å}\)) is observed on the pattern. Weak streaked rings corresponding to \(\alpha\)-Fe are also identified. The simultaneous observation of both structures indicates that MnO does not form a uniform scale over the iron matrix but is present as discontinuous scales or small crystallites grown within the grains. The latter morphology was confirmed by scanning electron microscopy observations showing faceting effects and differences in the MnO growth density, depending on the grain orientation. The discontinuous and streaked structure of the Fe diffraction rings is due to reconstruction of the iron surface during the annealing, mostly caused by thermal etching. The remaining stepped and, on a nanometre level, rough surface outermost layers are responsible for this effect. Similar but clearer structures have been observed on Fe and Ni surfaces annealed under high vacuum conditions and on r.f.-plasma-etched steel samples.6 Table 2 presents the result of the indexing of the pattern.

Table 2. Indexing results of the RHEED pattern presented in Fig. 3

<table>
<thead>
<tr>
<th>Phase</th>
<th>Plane</th>
<th>(d_{hkl}) theoretical (Å)</th>
<th>(d_{measured}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>(111)</td>
<td>2.56598</td>
<td>2.57</td>
</tr>
<tr>
<td>MnO</td>
<td>(200)</td>
<td>2.2222</td>
<td>2.20</td>
</tr>
<tr>
<td>MnO</td>
<td>(220)</td>
<td>1.57133</td>
<td>1.55</td>
</tr>
<tr>
<td>MnO</td>
<td>(311)</td>
<td>1.34004</td>
<td>1.32</td>
</tr>
<tr>
<td>MnO</td>
<td>(222)</td>
<td>1.28299</td>
<td>1.24</td>
</tr>
<tr>
<td>MnO</td>
<td>(400)</td>
<td>1.1111</td>
<td>1.09</td>
</tr>
<tr>
<td>MnO</td>
<td>(420)</td>
<td>0.9938</td>
<td>0.99</td>
</tr>
<tr>
<td>(\alpha)-Fe</td>
<td>(310)</td>
<td>0.90647</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Figure 3. The RHEED pattern obtained from an annealed low-alloy steel. The position of the identified rings, the major features of the pattern and the texture of the MnO rings (bold) and α-Fe streaks are indicated.

Complementary ex situ x-ray diffraction measurements show only sharp α-Fe and weak MnO peaks. According to the penetration depth of the x-ray radiation in iron, it can be pointed out that MnO is not only present at the surface but also in the first one or two micrometres under the surface. Both AES and secondary ion mass spectrometry (SIMS) depth profiles confirm the existence of internally oxidized manganese, expected from the theoretical models and simulations.4,5

CONCLUSIONS

The structural and compositional characteristics of in situ annealed low-alloyed Fe–Mn steels were studied. At the typical humidity fixed for the annealing atmosphere, iron is reduced from the native oxide film present after polishing to the metallic state, and manganese is selectively oxidized to MnO. The diffraction patterns show rings pertaining to MnO and α-Fe, indicating that the surface is not completely covered by MnO. This agrees with the growth of small crystallites at grain boundaries and within the grains, as observed by SEM.

Acknowledgements

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REFERENCES