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Damage of Ti-stabilized interstitial free steel by gas corrosion

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Abstract

Degradation of Ti-stabilized interstitial free steel and damage of this steel caused by selective oxidation during 60 s of recrystallization annealing at 820 ℃ under the different compositions of protective H_2-N_2 atmosphere at low dew point (−40 ℃) was investigated using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). During the high-temperature annealing the reduction of the native Fe-oxide layer occurred. Results of the analyses also showed that Mn, Al and Si oxide particles are the main products of selective external and internal oxidation. Moreover, appearance of greater nonwetted surface areas was caused by the increase of the H_2 content in gas atmosphere, which favours external oxidation.

Key words: Ti-IF steel, selective oxidation, material damage, XPS, SEM, EDS

1. Introduction

Hot-dip galvanizing is one of the most commonly used techniques for corrosion-protective coatings deposition in automotive industry [1–3]. Selective oxidation and surface segregation of low-carbon and high strength steels during recrystallization annealing prior to hot-dip coating may cause the poor wettability of the steel surface by molten baths and in that way can reduce the quality of protective coatings [4, 5]. The main influence on the steel surface coverage with coatings has external presence of nonwettable Mn-oxides. However, it is impossible to prevent external oxidation completely and to achieve a pure elemental Fe surface [6]. In addition, in Ti-bearing steels and at sufficiently low dew points, surface segregated Ti can react with nitrogen from the atmosphere forming nitrides, which affects the wettability of hot-dip coating melts [1, 7]. Considering these facts, it is of a great importance to determine the annealing conditions and surface morphology, which would improve the steel surface wetting with coating melts.

Effects of protective H_2-N_2 atmosphere composition on the selective oxidation mode of Ti-stabilized interstitial free steel (Ti-IF) and external/internal particle characteristics were investigated in this paper.

2. Experimental

The investigated Ti-IF low-carbon steel was industrially produced. Chemical composition of steel, supplied by Voest-Alpine Materials Handling GmbH in the form of 0.8 mm thick cold-rolled sheets, was (in wt.%) as follows: Fe-0.0028C-0.0033N-0.085Mn-0.006Si-0.044Al-0.0001B-0.016Cr-0.006P-0.006S-0.073 Ti.

Samples, 15 × 15 mm^2 in size, were cut from the steel sheets and prior to annealing treatment ground with SiC paper, polished using 3 μm diamond suspension and cleaned for 30 min in an ultrasonic bath with acetone. Metallographically prepared samples were then annealed for 60 s at 820 ℃ under the 5 vol.% H_2-N_2 and 15 vol.% H_2-N_2 protective atmosphere. Gas atmosphere also contained traces of water, which corresponds to the dew point of −40 ℃.

Steel sheet surface composition and morphology, before and after annealing, were determined using a LEO 1550 VP field emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectrometer (EDS) operating at an accelerating voltage of 15 kV and PHI Quantum 2000 X-ray photoelectron spectrometer (XPS) characterized by a monochromatic Al Kα primary X-ray beam and a photoelectron take-off angle of $\pi/4$ against the sample nor-

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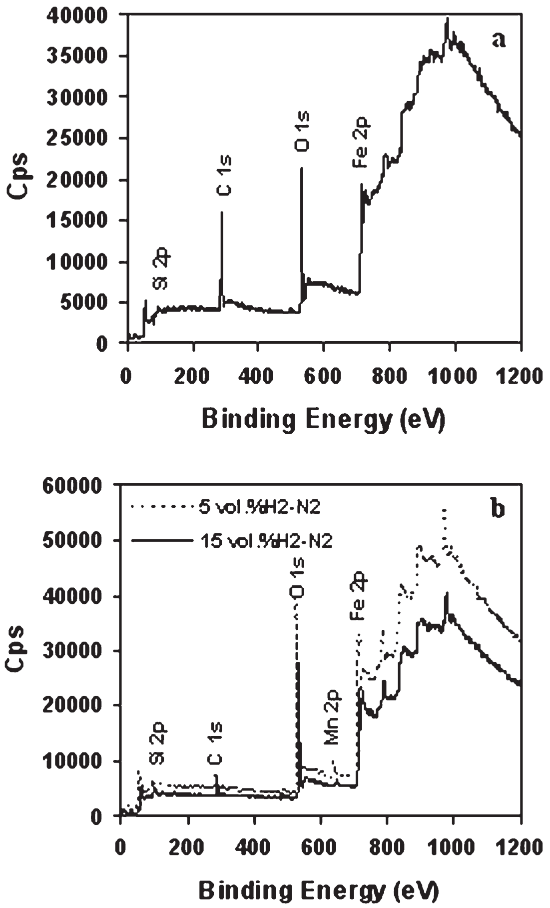

Fig. 1. XPS spectra recorded on as-cold rolled sheet surface of Ti-IF steel (a) before and (b) after annealing under H_2-N_2 protective gas atmosphere for 60 s.

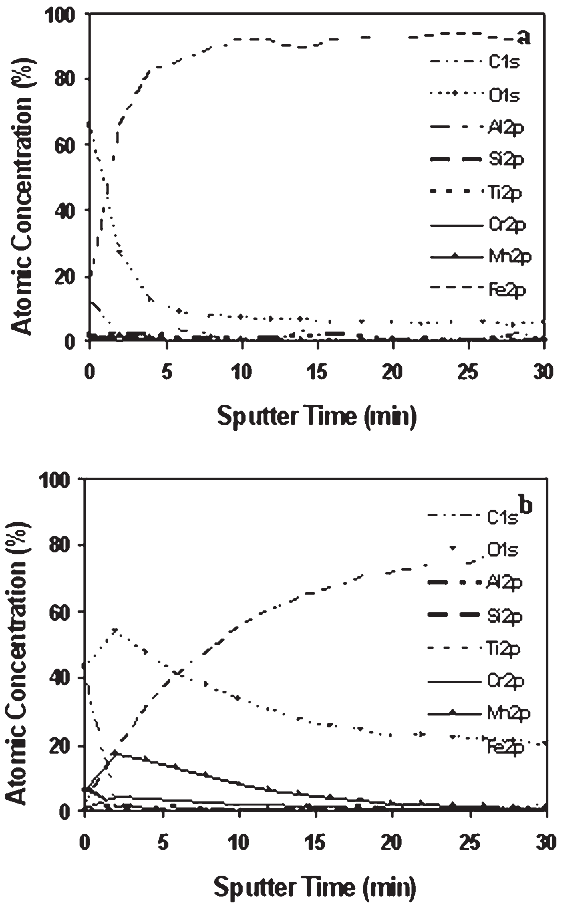

Fig. 2. XPS in-depth profiles on Ti-IF steel after annealing under (a) 5 vol.% H_2-N_2 and (b) 15 vol.% H_2-N_2 atmosphere for 60 s.

mal direction. The XPS depth profiles were recorded with a sputter rate of 2.67 nm min^{-1} in order to define oxide layer thickness. Namely, oxide layer thickness was calculated by multiplying the sputter rate with the sputter time in which atomic concentrations of oxygen and other detected elements were drastically changed.

3. Results and discussion

The XPS analysis of cold rolled sheet surface showed that it is covered with 38.9 nm thick oxide layer, mainly containing Fe_2O_3 and Fe_3O_4. The presence of these oxides is confirmed with appearance of O1s and two Fe2p peaks on XPS spectrum shown in Fig. 1a at 530 eV, 709.8 eV and 711.2 eV, respectively [8]. A weak Si2p peak at 98 eV binding energy indicates that SiO_2 is also present, while an appreciable amount of C may only be present as a contaminant [9].

During annealing at 820 °C the native Fe-oxides are reduced which is confirmed with the shift of the Fe2p peak towards lower binding energy with the value of 707 eV corresponding to the metallic Fe (Fig. 1). Simultaneously, the external and internal oxidation of alloying elements is progressive (Fig. 2).

Main products of selective oxidation are the Mn oxides growing at the sheet surface. Namely, presence of double Mn2p peak at 642 eV and 654.8 eV and Si2p peak at the 92 eV energy position, which does not correspond to the formation of SiO_2 (Fig. 1b), indicate that different types of external Mn oxides are present (Figs. 3 and 4). Particles of MnO and mixed Mn-Si oxide are identified. However, nodular MnO islands, formed inside the grain, are found only after annealing under 15 vol.% H_2-N_2 atmosphere (Figs. 4a,b). Another Mn oxide, detected as a complex $MnSiO_3$ oxide, is precipitated at the grain boundaries during annealing under both conditions (Figs. 3a,c and 4a,c).

Since the partial pressure of oxygen is decreased with increased H_2 content in the gas atmosphere, segregating elements have enough time to diffuse to the surface. As a result, the outer oxide layer is thicker

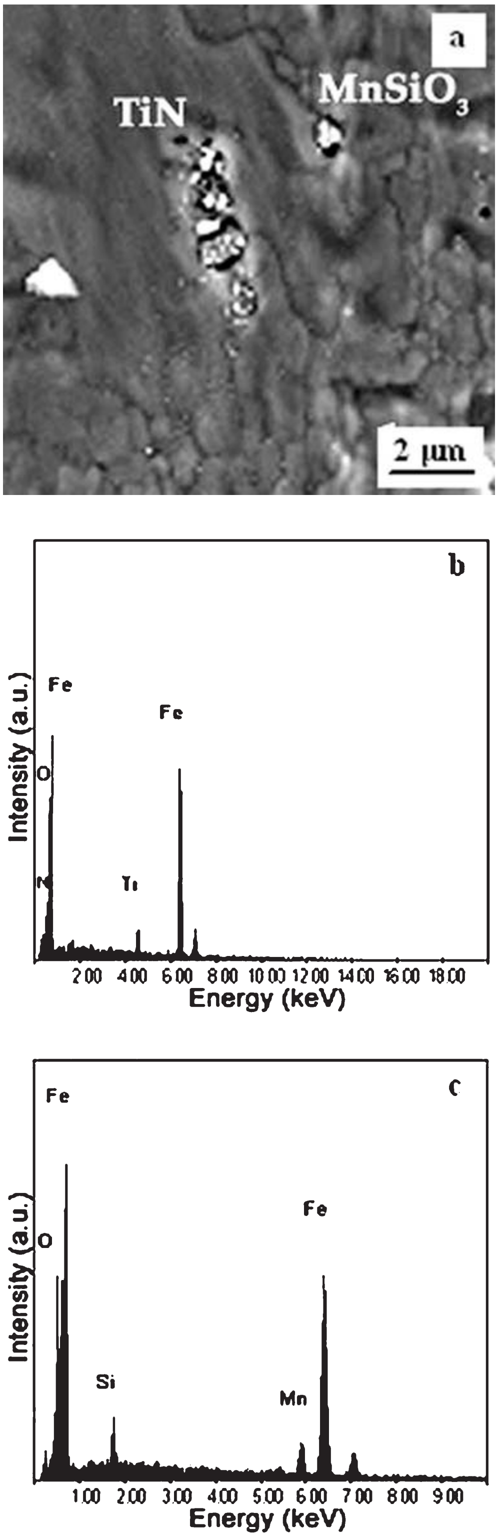

Fig. 3. Ti-IF steel surface after annealing under 5 vol.% H_2-N_2 atmosphere: (a) FE-SEM micrograph and EDS spectrum of (b) TiN and (c) $MnSiO_3$ particle.

than on the sheet surface annealed under 5 vol.% H_2-N_2 atmosphere. The formation of 39.2 nm thick

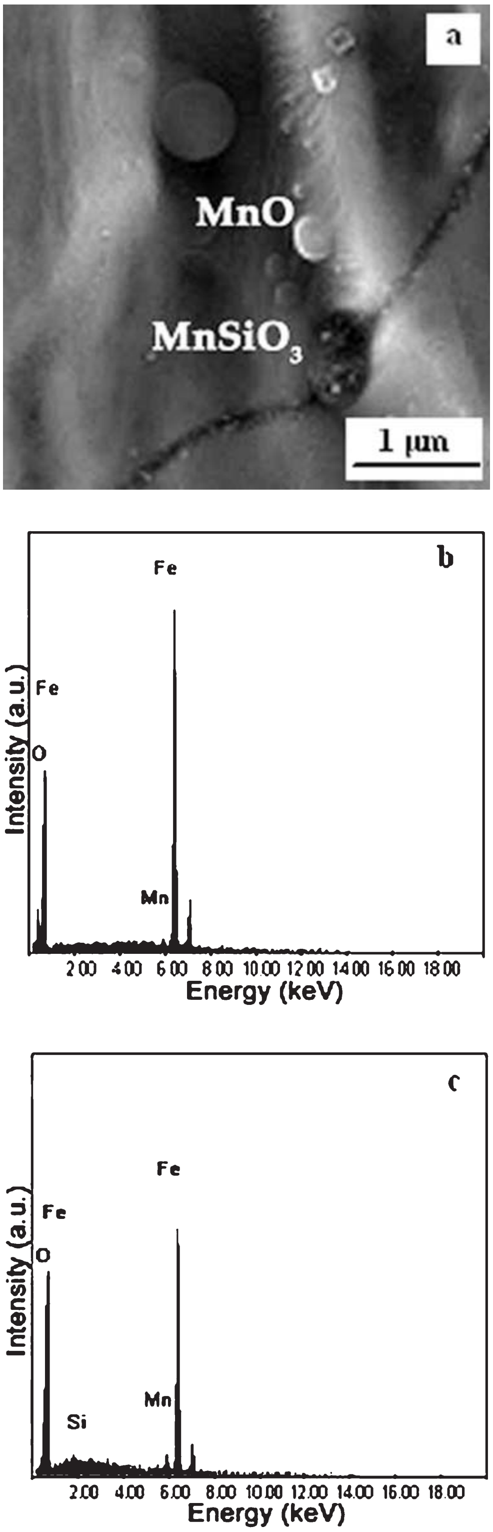

Fig. 4. Ti-IF steel surface after annealing under 15 vol.% H_2-N_2 atmosphere: (a) FE-SEM micrograph and EDS spectrum of (b) MnO and (c) $MnSiO_3$ particle.

oxide layer is primarily consequence of the intensive external oxidation. Large surface coverage with external oxides limits the oxygen penetration into the steel and decreases the internal oxidation as shown in Fig. 2b. As can be seen from XPS in-depth profiles, only the concentrations of Al and Cr increase slightly with depth indicating the presence of a small amount of internal Al_2O_3 and Cr_2O_3 oxides.

The behaviour of Ti-IF steel during annealing under 5 vol.% H_2-N_2 atmosphere is quite different. The smaller surface coverage with externally formed particles is observed. Except separate $MnSiO_3$ islands (Fig. 3a) the particles of other oxides are not present at the surface. Namely, although the grains interior is not covered with the oxides, the grain boundaries, as short circuits for diffusion, are affected by oxidation. Full surface coverage by the external oxides after annealing under 5 vol.% H_2-N_2 atmosphere is also prevented with the presence of beneficial TiN particles (Figs. 3a,b). The coarse TiN particles of regular shape are observed sporadically at the annealed steel surface. Surface segregation of Ti nitrides can occur when Ti diffused from the steel reacts with the nitrogen adsorbed from the nitrogen-rich atmosphere.

On the other hand, intensive internal oxidation and deeper presence of Al_2O_3 oxide led to formation of 50.4 nm thick oxide layer, i.e. 11.2 nm thicker than the layer formed during annealing under gas atmosphere with higher hydrogen concentration.

It should be pointed out that in both cases no continuous oxide film is observed on the external sheets surface. The grain boundaries are always affected by oxidation, while oxide density above the grains interior is not uniform and clearly depends on the annealing atmosphere.

4. Conclusions

Results of present investigation showed that during short-time annealing at 820 ℃ selective oxidation of Ti-stabilized interstitial free steel (Ti-IF) occurred externally and internally.

Selective oxidation is strongly dependent on the H_2-N_2 protective atmosphere composition. Namely, as the H_2 content decreases from 15 to 5 vol.% the surface coverage with nonwettable oxides, such as Mn oxides, decreases. On the other hand, decrease in the H_2 content favours internal oxidation and leads to increase of oxide layer thickness for 11.2 nm, as can be seen from the XPS results.

SEM and EDS analysis revealed that external formation of $MnSiO_3$ particles at the grain boundaries is predominant, while MnO is present inside the grains only after annealing under atmosphere with lower H_2 content. Even though external presence of TiN particles is detected after annealing in atmosphere with lower H_2 content, formation of complex Mn-Si oxide could not be avoided.

Internal appearance of Al_2O_3 oxide contributes to the overall thickness of oxide layer.

According to the information gained in this study, an effective way to increase the surface wettability and galvannealing reactivity of the Ti-IF steel is to suppress the formation of the nonwettable oxides at and inside the grain boundaries by short-term annealing the steel sheets at 820 ℃ in H_2-N_2 gas atmosphere with lower H_2 content, i.e. 5 vol.% H_2-N_2 atmosphere.

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