The effect of dual phase steel surface roughness on selective oxidation and surface wettability

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Abstract

Surface roughness effect on the morphological characteristics of the dual phase (DP) steel surfaces selectively oxidized during recrystallization annealing at 820 °C under 5vol.%H_2--95vol.%N_2 gas atmosphere was investigated in this study. Oxidation behaviour of DP steel was examined using X-ray photoelectron spectrometer (XPS) and scanning electron microscope (SEM) equipped with energy-dispersive spectrometer (EDS). It was found that on the unpolished steel sheets the thicker and more uniformly distributed surface layer of Mn, Al, Si and Cr oxides is formed. As a result, wettability of unpolished steel surface was considerably decreased. According to the results of this paper the presence of BN surface particles at the polished steel surface affects the full surface coverage by external oxides and in that way improves surface wettability.

Key words: dual phase steel, oxidation, surface analysis techniques, surface roughness, wetting

1. Introduction

High strength steels, such as dual phase (DP) steel, alloyed with Mn, Cr, Al, Si and Ti, possess a favourable combination of lower weight, high strength and good formability [1, 2]. This potential has led to the numerous structural applications. However, during protective hot-dip galvanizing these steels can exhibit problems, owing to the surface segregation and selective oxidation during recrystallization annealing governed by their complex chemical composition [3–5]. Selective oxidation mode and external/internal oxidation transition are influenced by the steel chemistry, surface roughness and annealing conditions [6]. External oxidation and appearance of non-wettable oxides on the surface have the main influence on the success of the corrosion-protective coating operation. Thermodynamical calculations show that it is impossible in practice to achieve annealing conditions which would insure pure elemental Fe steel surface and prevent presence of Al, Mn and Si oxides [7]. Therefore, it is necessary to gather information regarding different phenomena that take place during the annealing processes in order to determine the compositional and structural parameters of a steel surface suitable for hot-dip galvanizing.

The present work was undertaken in order to examine the effect of surface roughness of cold-rolled steel sheets on appearance of selective oxidation during recrystallization annealing in standard gas atmosphere at low dew point. Combining different complementary analytical techniques, oxidation mode and the nature of present external/internal particles were examined in order to improve surface wettability during corrosion protection processing.

2. Experimental

The investigated material was industrially produced dual phase steel (designated as DP500) with the chemical composition: Fe-0.07C-0.0059N-1.4Mn-0.1Si--0.037Al-0.0032B-0.45Cr-0.014P-0.025Ti (in wt.%). Steel was supplied by Thyssen Krupp Stahl AG in the form of 0.8 mm thick cold-rolled sheets. Samples, 15 × 15 mm in size, were metallographically prepared in dif-

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*Corresponding author: tel.: +381 11 2439454; fax: +381 11 2439454; e-mail address: ivanac@vin.bg.ac.yu ferent ways in order to achieve different surface roughness. One group of samples was only ultrasonically cleaned in acetone for 30 min prior to recrystallization annealing. Second group of samples was ground with SiC paper down to 1000 grit, and then polished using 3 μm diamond suspension before cleaning treatment.

The continuous annealing process was performed at 820 °C under the 5vol.%H_2-95vol.%N_2 protective atmosphere with traces of water (dew point of −40 °C). A flow rate of 1 l/min was established. The samples were heated from room temperature to 820 °C for about 130 s and hold at this temperature for 60 s.

The surface analysis of cold-rolled and annealed samples was carried out by field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS). A FE-SEM "LEO 1550 VP" equipped with energy dispersive spectrometer (EDS) at accelerating voltage of 15 kV was used to determine nature, size and lateral distribution of particles precipitated on the rough and polished sample surfaces during annealing.

The XPS analyses of the top surface concentrations and the bonding state of the elements were performed in a PHI Quantum 2000 XPS spectrometer. Oxide layer thickness was defined using the XPS depth profiles, which were recorded with a sputter rate of 2.67 nm/min.

The influence of the surface condition and its roughness on the surface wettability was determined by depositing a liquid droplet and measuring the contact angle, θ [8], when droplet shape was stabilized. Program package SCA20 was used for determination of θ value. For preliminary wettability investigations water with 0.9982 g/cm^3 density was used.

3. Results and discussion

Characterization of surface composition and microstructure of cold-rolled sheets, as a function of recrystallization annealing parameters, was conducted in order to better understand the conditions leading to a good surface wettability. Cold-rolled steel sheet was examined before annealing by means of FE-SEM and XPS. Using the same techniques after recrystallization annealing, sample surfaces with different roughness were investigated.

3.1. Cold-rolled steel sheet

XPS analysis of cold-rolled steel sheet surface showed presence of oxide layer, which mainly contains Fe oxides. Surface Fe oxide particles are confirmed with appearance of Fe and O peaks on XPS spectra shown in Fig. 1a.

A O1s peak is detected at 530 eV, which is consistent with that reported for transition metal oxides [9].

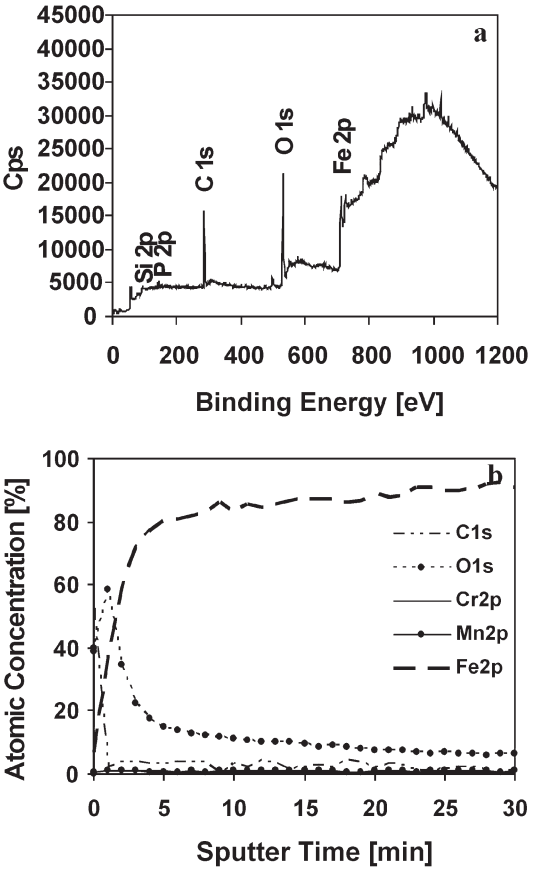

Fig. 1. XPS spectra of DP500 steel before recrystallization annealing: (a) surface survey and (b) concentration profile.

High oxygen concentration reveals the high amount of surface oxides. Relatively weak double Fe2p peak at 709.8 eV and 711.2 eV corresponds to Fe^{2+} and Fe^{3+}, respectively, implying that Fe_2O_3 and Fe_3O_4 cover the surface [10]. According to XPS concentration profile (Fig. 1b) oxide layer thickness is 29.4 nm. A very week Si2p peak at 98 eV confirms formation of SiO_2 at the surface because of great tendency of Si toward oxide formation. It should be noted that XPS spectra also show an appreciable amount of C at the sample surface, but surface C may only be present as a contaminant.

3.2. Annealed steel sheet

During recrystallization annealing Fe_2O_3 and Fe_3O_4 are completely reduced. Presence of Fe2p peak at 707 eV on XPS spectra of unpolished and polished samples shown in Fig. 2 confirmes reduction of air-formed Fe oxides and the complete steel surface coverage with metallic Fe.

Simultaneous surface enrichment with oxygen is the most important indication of advanced selective oxidation. Small Si2p peak at 102 eV confirms insig-

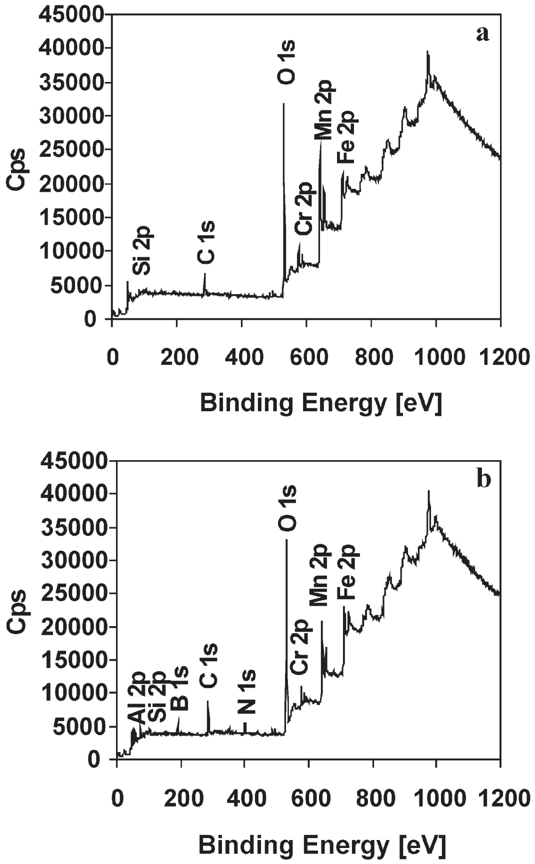

Fig. 2. Characteristic XPS spectra of: (a) unpolished and (b) polished surface of DP500 steel after recrystallization annealing in 5vol.%H_2-N_2 gas atmosphere for 60 s.

nificant Si surface segregation. However, a very pronounced double Mn2p peak at 641.6 eV and 654.8 eV and Cr2p peak at 576 eV demonstrate that Mn and Cr oxides are main products of selective oxidation of DP500 steel. XPS concentration profiles confirm external as well as internal presence of these oxides [7]. Surface roughness has no influence on the nature of external oxides, but preferred oxidation mode and segregation level of metallic and non-metallic elements like B and N are strongly influenced by metallographic sample preparation.

3.2.1. Unpolished steel sheet

Annealed unpolished steel surface is covered with densely distributed islands with different size and morphology (Fig. 3a). Larger lenticular or irregularly shaped islands, ~ 1 μm in size, are mainly distributed at the grain boundaries, while smaller globules, ~ 100 nm in diameter, are uniformly formed inside the grains at the steel surface. EDS analysis of oxide surface particles revealed the presence of Mn, Si and O (Fig. 3b) indicating formation of external Mn and Si oxides. These oxides may appear in the form of MnO and SiO_2 particles, but complex oxides can also be formed. However, double Mn2p peak at the XPS spectrum (see Fig. 2a) corresponds to Mn^{2+} showing that two types of Mn oxide particles may be distinguished. Position of Si2p peak does not reveal the presence of external SiO_2, implying that the formation of the mixed oxide of Mn-Si type is more probable. Actually, $MnSiO_3$ oxide islands, appearing as the first oxides at the steel surface, are identified at the grain boundaries, while the other oxide type is identified as MnO according to the Mn/Si ratio [11]. Cr2p peak at 576 eV shows that except MnO and $MnSiO_3$ particles small amounts of Cr_2O_3 are also detected at the steel surface. XPS concentration profile shows that the oxide layer is approximately 96.1 nm thick [7].

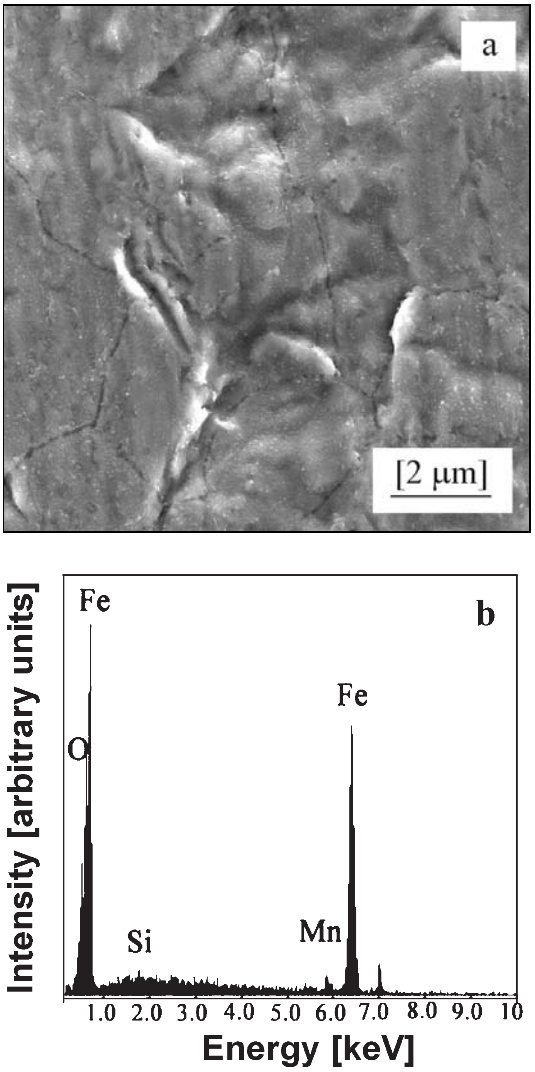

Fig. 3. Unpolished DP500 steel surface after recrystallization annealing: (a) FE-SEM micrograph and (b) EDS spectrum of surface oxides.

3.2.2. Polished steel sheet

Morphology of oxidized polished steel surface after annealing is shown in Fig. 4a. As can be seen, oxide islands, which cover the sample surface, have the same shape and distribution as those at the annealed unpolished surface. However, oxides islands are larger (0.3–1 μm) and the smaller surface coverage of metallic Fe with segregated particles is observed. Presence of a denser oxide layer at the unpolished samples is expected because of greater free steel surface for oxide formation.

EDS and XPS analysis confirmed the presence of Mn, Cr and Si oxide particles. Small amounts of Al are also detected at the surface. Position of Al2p peak at 66.4 eV corresponds to Al_2O_3. Grain boundaries are covered with complex Mn-Si oxide particles (Fig. 4b), while Mn oxide (Fig. 4c) in agglomeration with nodules of Cr oxide is detected inside the grains (Fig. 4b). The presence of $MnSiO_3$, MnO and Cr_2O_3 particles is confirmed by the appearance of Mn2p, Si2p and Cr2p peaks at XPS spectrum obtained from the polished surface (see Fig. 2b).

Double peak present at the binding energy for Mn^{2+} is less distinctive at polished surface suggesting less expressive external oxidation. An intensive Fe2p double peak at 707 eV and 720 eV binding energy indicates the presence of higher amount of metallic Fe and smaller oxide cover, but this does not totally explain the lesser external Mn oxides presence. The reduced appearance of Mn oxides can be fully explained by the following mechanism considering the fact that at the surface characterized with smaller roughness the segregation of B was detected. Namely, XPS surface analysis shows B1s peak at 191 eV (see Fig. 2b) indicating diffusion of B to the surface. The simultaneous appearance of a relatively strong N1s peak at 400 eV suggests that B is more likely present as nitride than as oxide or segregated atoms. Several mechanisms of BN formation were described in the literature [3, 12], but in this case B diffuses from the steel interior and reacts with N adsorbed from the nitrogen-rich atmosphere forming a thin layer of BN. According to the results obtained in this study, BN particles prevent full coverage of the steel surface by the external oxides causing in that way better surface wettability. However, it must be mentioned that some authors reported that these particles can provoke in some cases the poorer wettability of the surface [3].

During annealing of polished samples internally created oxide layer is thicker than in the case of unpolished samples. At unpolished surface larger coverage with external oxides limits the oxygen penetration to steel interior and consequently decreases the internal oxidation. Intensive internal oxidation of polished samples and detected MnO, Cr_2O_3 and Al_2O_3

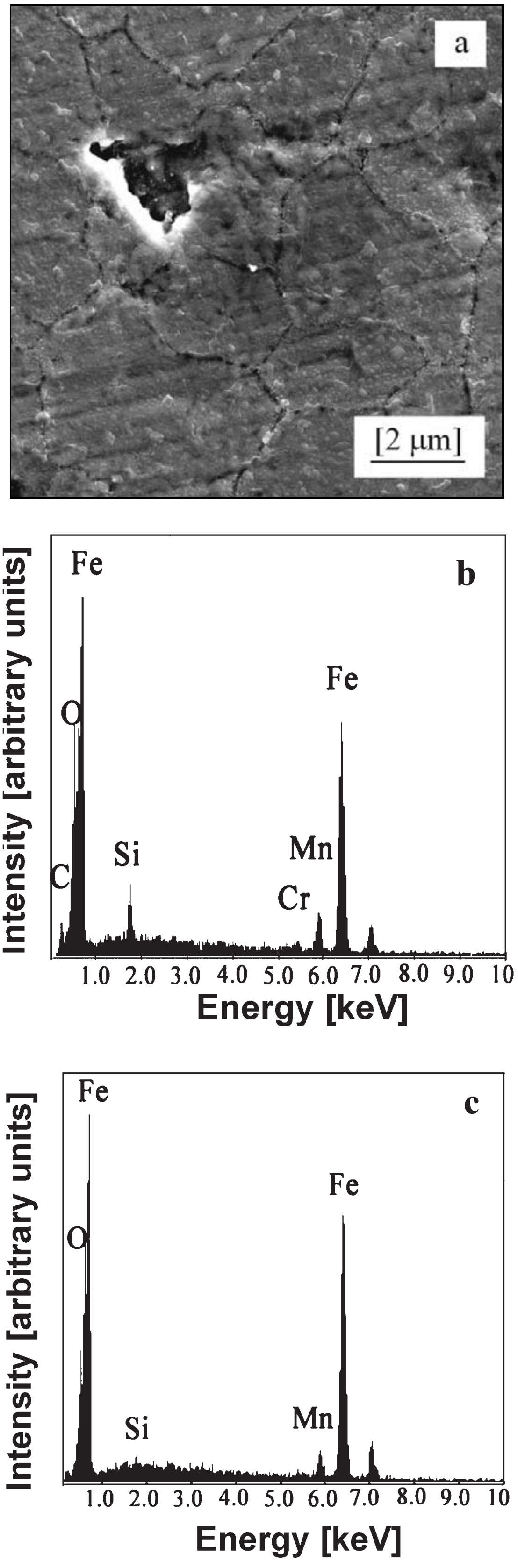

Fig. 4. Polished DP500 steel surface after recrystallization annealing: (a) FE-SEM micrograph, (b) and (c) EDS spectrum of surface oxides.

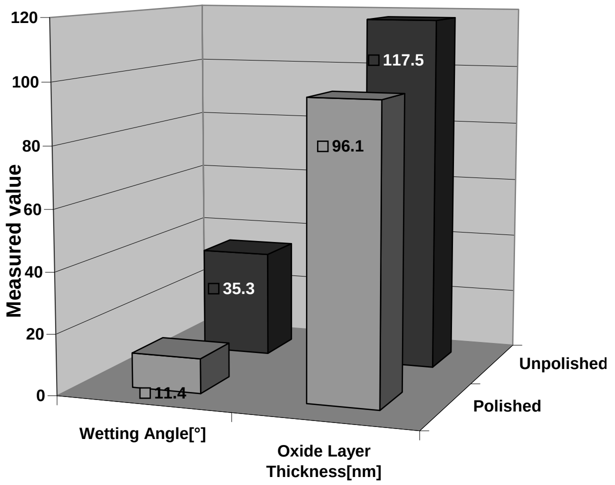

Fig. 5. Influence of oxide layer thickness on the surface wettability.

particles led to formation of 117.5 nm thick oxide layer.

3.3. Surface wettability

Wettability of oxidized steel surfaces after recrystallization annealing was determined and, as can be seen in Fig. 5, the interaction between droplet and steel surfaces was changed within a wetting regime, i.e. $\theta < 90^\circ$.

Optimizing the selective oxidation can improve the response of the investigated steel to wetting, by bringing undesired Mn, Cr, Si and Al oxides deeper below the surface. This may be accomplished during annealing by decreasing the level of the surface roughness, which will decrease the amount of external oxides. Wettability experiments showed that the decrease in the level of surface roughness stimulates the decrease of oxide layer thickness for 21.4 nm (Fig. 5) causing the increase of surface wetting capabilities.

4. Conclusions

The effect of dual phase (DP) steel surface roughness on the selective oxidation and surface wettability was the aim of the present paper. The following conclusions can be drawn from experimental results:

1. Recrystallization annealing of cold-rolled dual phase steel sheets at 820℃ in 5vol.%H_2-95vol.%N_2 gas atmosphere at −40℃ dew point leads to a complete reduction of Fe oxides, selective oxidation of Mn, Si, Cr and Al, as well as a slight segregation of non-metallic particles such as BN.

2. Selective oxidation may appear externally and internally. External formation of $MnSiO_3$ and MnO islands is predominant. Morphology of islands and surface coverage with these oxides are influenced by the surface roughness. Greater surface roughness leads to intensive external oxidation and appearance of greater non-wetted surface areas. The decrease in surface wettability is a consequence of the external appearance of Cr_2O_3 oxide.

3. Decrease in surface roughness favors internal oxidation and leads to increase of oxide layer thickness. Higher amount of MnO and Cr_2O_3 below the unpolished surface and appearance of internal Al_2O_3 particles influence increase of oxide layer thickness for approximately 20 nm.

4. Segregation of non-metallic elements and appearance of BN particles at polished surfaces reduce further oxidation and appearance of Mn oxide particles.

Acknowledgements

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