The Influence of Surface Roughness on the Selective Oxidation and Surface Wettability of Dual Phase Steel

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

Introduction

High strength steels, such as dual phase (DP) steel, alloyed with Mn, Cr, Al, Si and Ti find application in automotive industry where a combination of weight reduction, very high strength and a good formability is of the prime concern [1,2]. However, these steels can exhibit problems during protective hot-dip galvanizing, owing to the surface segregation and selective oxidation during recrystallization annealing governed by their chemical composition complexity [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 nonwettable 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 practise to achieve annealing conditions which would insure pure elemental Fe steel surface and prevent Al, Mn and Si oxidation [7]. Therefore, it is necessary to have information about 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 influence of surface roughness of cold-rolled steel sheets on appearance of selective oxidation during recrystallization annealing in standard gas atmosphere at low dew point. Oxidation mode and the nature of present external/internal particles were examined by combining different complementary analytical techniques in order to improve surface wettability during galvanizing.

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, 15x15 mm in size, were metallographicaly prepared in different ways in order to achieve different surface roughness. One group of samples was only ultrasonically cleaned with acetone for 30 minutes prior to annealing treatments. 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^{o}C under the 5vol.%H_2-95 vol.%N_2 protective atmosphere with traces of water (dew point of -40^{o}C). A flow rate of 1 l/min was established. The samples were heated from room temperature to 820^{o}C for about 130 seconds and maintained at this temperature for 60 seconds.

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 analysis 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.

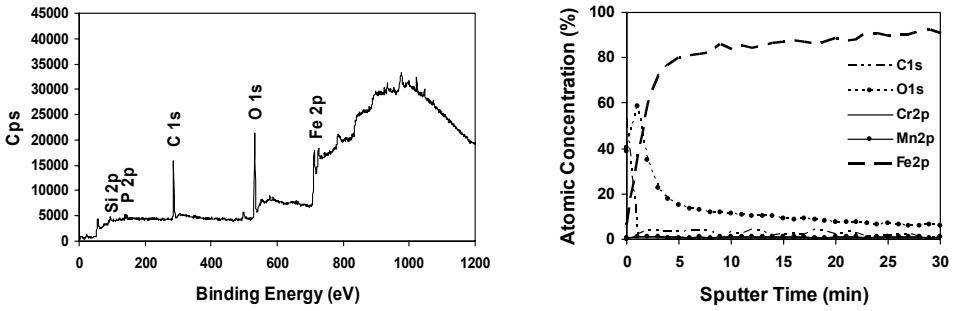
The influence of the surface state and its roughness on the surface wettability was determined by measurement of contact angle, θ [8]. Program package SCA20 was used for determination of θ value. For preliminary wettability investigations water with 0.9982g/cm^3 density was used.

Results and discussion

Characterization of surface composition and microstructure of cold-rolled sheets, as a function of 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 treatment, sample surfaces with different roughness were investigated.

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

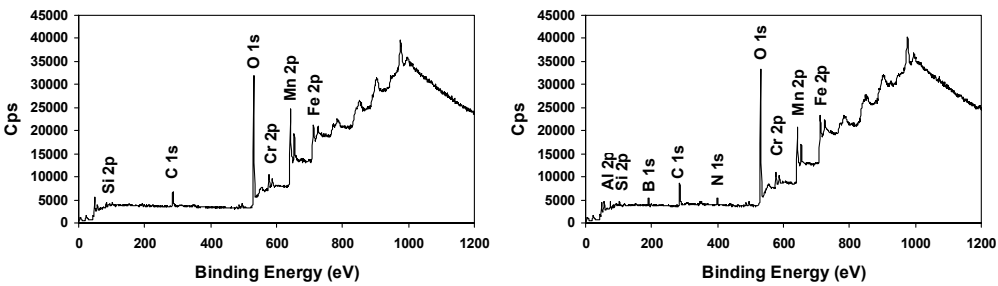
A *O1s* peak is detected at 530eV, which is consistent with that reported for transition metal oxides [9]. High oxygen concentration reveals the high amount of surface oxides. Relatively week double *Fe2p* peak at 709.8eV and 711.2eV corresponds to Fe^{2+} and Fe^{3+}, respectively, implying that Fe_2O_3 and Fe_3O_4 cover the surface [10]. According to XPS concentration profile (Fig. 1b) oxide layer thickness is 29.4nm. A very week *Si2p* peak at 98eV confirms formation of SiO_2 on 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.



(a) (b)

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

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



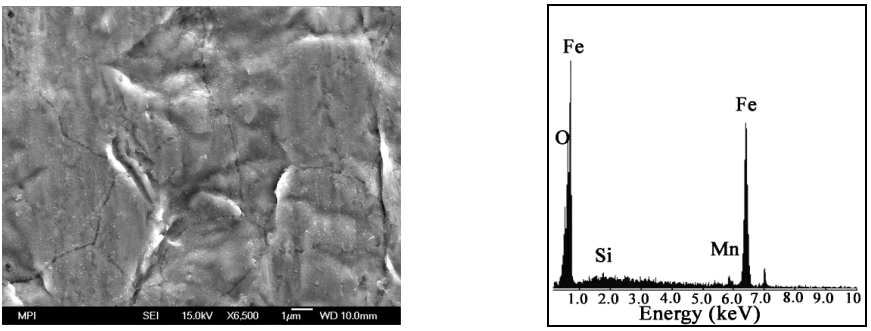
(a) (b)

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

Simultaneous surface enrichment with oxygen is most important sign of advanced selective oxidation. Small *Si2p* peak at 102eV confirms insignificant Si surface segregation. However, a very pronounced double *Mn2p* peak at 641.6eV and 654.8eV and *Cr2p* peak at 576eV indicate that Mn and Cr oxides are main product of selective oxidation in 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 nonmetallic elements like B and N is strongly influenced by metallographic sample preparation.

Unpolished steel sheet. Annealed unpolished steel surface is covered with densely distributed islands with different size and morphology (Fig. 3a). Larger lanticular or irregular shape islands, ~1μm in size, are mainly distributed at the grain boundaries, while smaller globules, ~100nm 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 (Fig. 2a) corresponds to Mn^{2+} showing that two types of Mn oxide particles can be distinguished. Position of *Si2p* peak does not indicate the presence of external SiO_2 but Mn-Si mixed oxide. $MnSiO_3$ oxides islands are identified at

the grain boundaries, which are the first oxide growing at the steel surface, the other oxide type is identified as MnO according to the Mn/Si ratio [11]. *Cr2p* peak at 576eV shows that except MnO and $MnSiO_3$ particles at the steel surface small amounts of Cr_2O_3 are also detected. XPS concentration profile revealed that the oxide layer is approximately 96.1nm thick [7].



(a) (b)

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

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

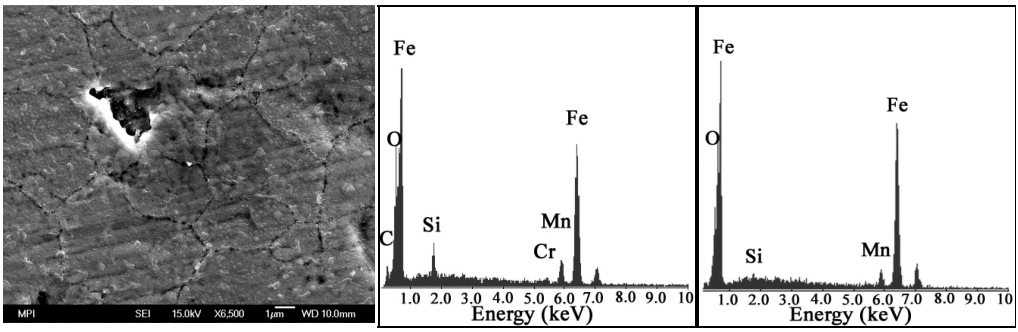
EDS and XPS analysis confirmed the presence of Mn, Cr and Si oxide particles. Grain boundaries are covered with complex Mn-Si oxide particles (Fig. 4b), while inside the grains Mn oxide (Fig. 4c) in agglomeration with nodules of Cr oxide is detected (Fig. 4b). The presence of $MnSiO_3$, MnO and Cr_2O_3 particles is confirmed by the appearance of *Mn2p*, *Si2p* and *Cr2p* peaks at XPS spectrum obtained from polished surface (Fig. 2b).

Double peak present at the binding energy for Mn^{2+} is less distinctive at polished surface indicating less expressive external oxidation. An intensive *Fe2p* double peak at 707eV and 720eV binding energy indicates greater metallic Fe presence and smaller oxide coverness, but this does not totally explain lesser external Mn oxide presence. With detected segregation of B at surface characterized with smaller roughness this can be fully explained by following mechanism. XPS surface analysis show *B1s* peak at 191eV (Fig. 2b) indicating diffusion of B to the surface. The simultaneous appearance of a relatively strong *N 1s* peak at 400eV suggests that B is more likely present as nitride than as oxide or segregated atoms. BN can be formed by several mechanisms [3,12], but in this case B diffuses from the steel interior and reacts with the nitrogen adsorbed from the nitrogen-rich atmosphere forming a thin layer of BN. BN particles prevents full coverage of surface by the external oxides, but on the other hand can cause the poorer wettability of the steel surface [3].

Small amounts of Al are also detected on the surface. Position of *Al 2p* peak at 66.4eV corresponds to Al_2O_3.

During annealing of polished samples internally created oxide layer is thicker than in the case of unpolished samples. At unpolished samples surface larger coverage with external oxides limits the oxygen penetration into the steel and consequently decreases the

internal oxidation. Intensive internal oxidation of polished samples and detected MnO, Cr_2O_3 and Al_2O_3 particles led to formation of 117.5nm thick oxide layer.



(a) (b) (c)

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

Surface wettability. Wettability of oxidized steel surfaces after annealing was determined by depositing a liquid droplet and measuring the contact angle, θ, when droplet shape was stabilized. As can be seen from Fig. 5 the interaction between droplet and steel surfaces was changed within a wetting ($\theta<90^o$) regime.

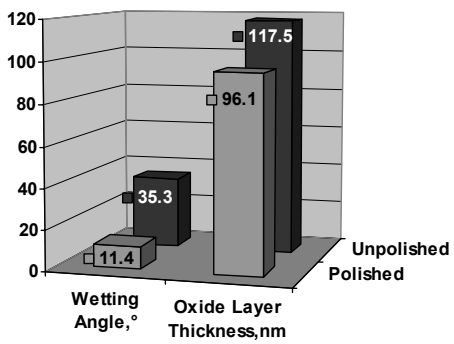


Fig. 5. *Influence of oxide layer thickness on the surface wettability.*

However, optimising the selective oxidation can help to improve the response of the investigated steel to wetting, by leading undesired Mn, Cr, Si and Al oxides to be buried deeper below the surface. This may be accomplished during annealing by decreasing the amount of external oxides by decreasing the level of surface roughness. Wettability experiments showed that increase in the level of surface roughness provokes the increase of oxide layer thickness causing the decrease of surface wetting capabilities.

Conclusions

The folowing conclusions can be drawn from the present study:

1. High temperature annealing of cold rolled dual phase steel sheets at 820°C in 5vol.%H_2-95vol.%N_2 gas atmosphere at -40°C dew point leads to a complete reduction of Fe oxides, selective oxidation of Mn, Si, Cr and Al, as well as slight segregation of nonmetallics.

2. Selective oxidation emerge externally and internally. External formation of $MnSiO_3$ and MnO islands is predominant. Morphology of islands and surface coverage with these oxides is influenced by the surface roughness. Greater surface roughness leads to intensive external oxidation and appearance of greater unwetting surface areas. Appearance of external Cr_2O_3 has effect on the decrease in surface wettability.
3. Decrese 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 appearence of internal Al_2O_3 particles inluence increase of oxide layer thickness for 21.4nm.
4. Segregation of nonmetallic elements and appearence of BN particles at polished surfaces reduce further oxidation and appearence of Mn oxide particles.

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