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Nanoscale analysis of the influence of pre-oxidation on oxide formation and wetting behavior of hot-dip galvanized high strength steel

M. Arndt [a,*], J. Duchoslav [a], R. Steinberger [a], G. Hesser [a], C. Commenda [b], L. Samek [a,b,c], E. Arenholz [b], D. Stifter [a]

[a] Zentrum für Oberflächen- und Nanoanalytik (ZONA) und Christian Doppler Labor für mikroskopische und spektroskopische Materialcharakterisierung (CDL-MS-MACH), Johannes Kepler Universität Linz, Altenbergerstraße 69, 4040 Linz, Austria
[b] voestalpine Stahl GmbH, voestalpine-Straße 3, 4031 Linz, Austria
[c] University of Applied Sciences Upper Austria, Metal Sciences (Metallkunde), Stelzhamerstraße 23, A-4600 Wels, Austria

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ABSTRACT

Hot-dip galvanized (HDG) 2nd generation advanced high strength steel (AHSS), nano-TWIP (twinning induced plasticity) with 15.8 wt.% Mn, 0.79 wt.% C, was analyzed at the interface between steel and zinc by scanning Auger electron microscopy (AES) in order to confirm and improve an existing model of additional pre-oxidation treatment before annealing and immersion into the hot zinc bath. Furthermore these steel samples were fractured in the analysis chamber of the AES and analyzed without breaking vacuum. In these measurements the results of an aluminothermic reduction of the manganese and iron surface oxides on the steel could be confirmed by AES.

1. Introduction

Improving passenger safety and minimizing fuel consumption due to weight reduction of the vehicles are the two contradicting requirements the modern automotive industry has to challenge. Therefore advanced high strength steels are used as material for structural body applications [1,2], because these steel grades exhibit excellent mechanical properties, depending on their composition and deformation mechanism with TRIP (transformation induced plasticity) and TWIP steels as examples [2–6].

The second generation of advanced high-strength steels have a microstructure which primarily constitutes of austenite stabilized by high amounts of Mn and C. They are typically designed with a Mn content ranging from 10 wt.% to 30 wt.%. High-Mn steels are classified according to their characteristic deformation mechanisms occurring during plastic deformation [6,7]. Depending on their composition and deformation mechanism, they are often referred to in literature as TRIP/TWIP, TWIP and nano-TWIP. High-Mn steels which exhibit both TRIP and TWIP effects during deformation at room temperature, are referred to as TRIP/TWIP steels. The so-called TWIP effect [7,8], in which twins are formed during tensile deformation, is responsible for the remarkable material characteristics of TWIP steel. The so-called nano-sized twinning induced plasticity steels have a reduced Mn content of about ~14–16 wt.%. Nano-TWIP steels offer the outstanding mechanical properties of 1000 MPa tensile strength by ~100% total elongation, due to the intense refinement of the microstructure during deformation [6,7]. Regarding automotive applications, the simple and cost effective formability achieved by cold rolling, as opposed to expensive and cumbersome hot forming operations, makes this steel even more attractive.

On the other hand, fully austenitic steels are known to be liable to aqueous corrosion [9–12], and thus a suitable corrosion protection is often necessary. In this context, hot-dip galvanizing of stated steels with standard Zn or some more advanced Zn alloyed coatings (e.g. Zn–Al, Zn–Mg–Al etc.) may provide sufficient and simultaneously cost efficient corrosion protection [13–20]. Nevertheless, the high Mn content of conventional TWIP-steels may lead to difficulties during the galvanizing process. These difficulties are linked to the formation of manganese oxides on the surface during the technologically necessary annealing step in production. These Mn based oxides were found to hinder the growth of a continuous Zn layer on the steel surface during galvanizing [21].

* Corresponding author. Tel.: +43 73224681468.
E-mail address: martin.arndt@jku.at (M. Arndt).

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However, there are some approaches to improve the wettability of high Mn steel with Zn: Blumenau et al. [22] suggest an additional pre-oxidation step in order to create a Mn/Fe mixed oxide on the steel surface. The Fe in the mixed oxide should then chemically be reduced during the annealing process by an extremely dry atmosphere and form an Fe_2Al_5 inhibition layer with the dissolved Al from the liquid Zn bath on top of the MnO, allowing the growth of the Zn layer. This approach has been successfully applied on simulator samples. They also report an improvement of the wettability by changing the Al concentration in the bath, the bath temperature and the temperature of the steel [23]. Cho and De Cooman [24] suggest two additional methods: one involving annealing at high dew points to provoke internal Mn oxidation, and the other involving flash coating of the surface with pure Fe. Furthermore, Kavitha and McDermid [25] have observed that longer dwell times in the Zn bath can reduce the thickness of a MnO layer due to an aluminothermic reduction of the MnO to metallic Mn, which is brought about by the oxidation of metallic Al to Al_2O_3.

The aim of our present work is the validation of the existing pre-oxidation approach [22] on a comparable high Mn steel and the verification and improvement of the existing model. We use Auger electron spectroscopy as the main analytical tool because it combines the excellent lateral resolution of scanning electron microscopy (SEM) with the superb determination of chemical compounds known from X-ray photoelectron spectroscopy (XPS). Our experience has shown that chemical analyses of surfaces using coarse methods such as XPS, X-ray diffraction (XRD), glow discharge optical emission spectroscopy (GDOES), energy dispersive X-ray spectroscopy (EDX) and even transmission electron microscopy (TEM) combined with electron energy loss spectroscopy (EELS) may yield misleading results, because these techniques have a high volume interaction [22–24,26,27]. If the analyzed surface or interface is not homogeneous, the data obtained from different areas mix and interfere. The measurement volume of AES is limited by the diameter of the primary electron beam (10 nm) and by influencing factors of the environment like vibrations and disturbing magnetic fields or backscattered electrons and the escape depth of the Auger electrons in the order of magnitude of 6 nm. This makes it safe to obtain the chemistry within a surface area of 100 nm via Auger. In order to avoid chemical changes during the preparation we used a fracture stage where the sample is cooled by liquid nitrogen and broken with a hammer inside the analysis chamber of the AES system at ultra high vacuum (UHV) conditions. Therefore we obtained a direct view of the chemistry at the interface.

Our work is not focused on the complete issue of galvanizability of a manganese reduced 2nd generation AHSS with Zn; rather, only the wetting behavior of the Zn layer is tested. For a complete analysis also the adherence of the Zn to the steel should be examined. Suitable for this task are, for instance, ball impact tests in accordance to SEP 1931 (Stahl–Eisen–Prüfblatt), in which the adherence properties of the Zn coating are classified by a school grade system.

2. Experimental

2.1. Sample material

The base material used in this study is a second generation advanced high strength steel taken from industrial production. In detail, the material is a nano-sized twinning induced plasticity steel. The chemical composition of the steel is 0.79 wt.% C, 15.8 wt.% Mn, 0.05 wt.% Si, <0.05 wt.% Al, 0.03 wt.% P, 0.002 wt.% Ti, 0.022 wt.% Nb, 0.036 wt.% N, and 0.03 wt.% Cr.

The sample material was cut out of the steel band into smaller sheets (see Fig. 1), which were hot-dip galvanized in a galvanizing simulator under controlled temperature and atmospheric conditions. The zinc bath contains small amounts of Al of about 0.2 wt.% to aid the formation of an inhibition layer of Fe_2Al_5 between the steel substrate and the Zn over-layer. Two kinds of treatments were applied to the sheets (see Fig. 2). In the first one

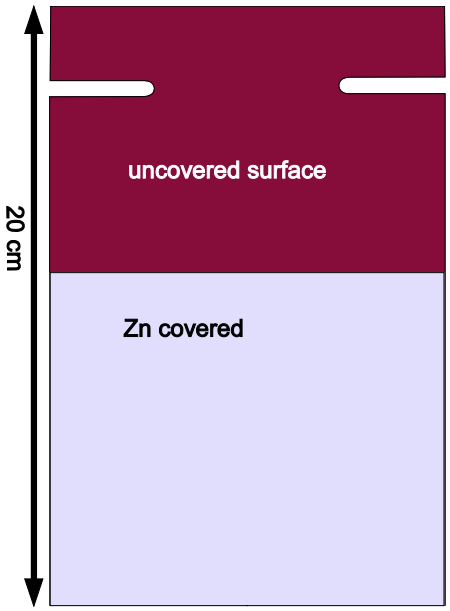

Fig. 1. The steel sheet is cut into pieces of 20 cm length suitable for the galvanizing simulator and heat treated under controlled atmospheric conditions. Subsequently the lower part of the piece is immersed into a liquid Zn bath and thus covered by a Zn layer, as illustrated in the figure.

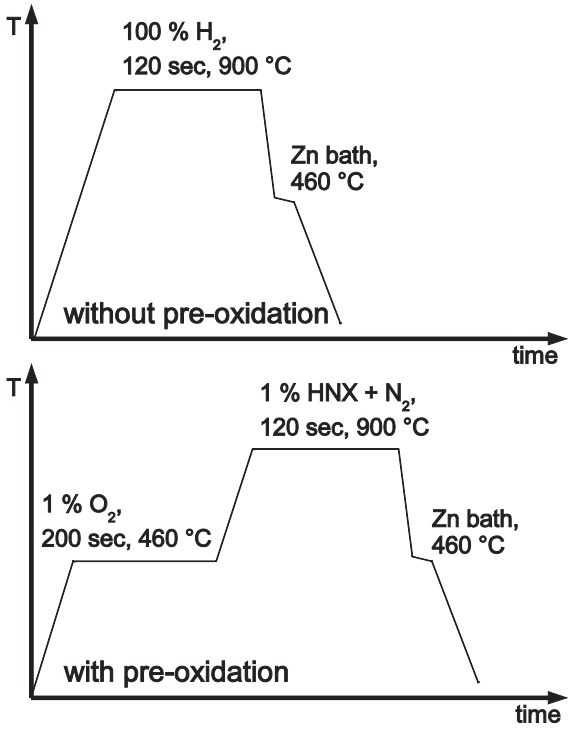

Fig. 2. The upper figure shows the standard heat treatment. The steel is first annealed at 900 °C and subsequently immersed into a liquid Zn bath. The annealing leads to the formation of MnO at the steel surface and a bad coatability with Zn. In the lower figure an additional pre-oxidation step is implemented before the annealing.