Al-hot Dipping Followed by High-Temperature Corrosion of Carbon Steels in Air and Ar-0.2%SO_2 Gas

Muhammad Ali Abro*, Seung Boo Jung, Dong Bok Lee
School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, 440-746, South Korea
*E-mail: muhammad_aliabro@inbox.com

ABSTRACT: Al-rich coatings were prepared on hot rolled low carbon steel by hot dipping method in molten Al-bath to investigate the corrosion resistance with the possible outcomes and defects of aluminized coatings in air and Ar-0.2%SO_2 mixed gases. Coating microstructure was composed of an inner Al-Fe intermetallic layer and outer Al-rich layer. Aluminum oxidized preferentially to the thin, outer, protective α-Al_2O_3 layer, without forming the nonprotective iron/sulfur-oxide layer after heating at 800°C for 20 h, in both the gases and provided the resistance against corrosion.

1. INTRODUCTION

Hot rolled mild-steel is the most common and quite good steel for industrial applications due to lower cost than high alloy steels, but destructive at elevated temperature corrosion environments containing oxygen and/or sulfur. Steel sheets are exposed to high temperature oxidative environments during the process of hot-rolling, and also during operation industrially these steels are heavily oxidized by oxygen in open air and/or are sulfur corroded in the power plants, refineries and in the combustion gases. Generally, sulfidation rates are 10-100 times faster than oxidation rates because sulfides have much larger defect concentrations, and have lower melting points than the corresponding oxides [1,2]. Al hot-dipping is the greatest of various coating techniques to better the corrosion resistance of low-carbon-steels [3], where enriched Al surface is formed on the surface of the treated steel from an aluminum molten bath. Dense, continuous and protective Al_2O_3 layer covers the steel surface after exposure at elevated temperatures [4]. The interface between the matrix and the intermetallic layer appeared tongue-like morphology in most cases, and the intermetallic-layer mainly consisted of Fe_2Al_5 [5]. Due to high-aluminum content (49-59 wt%), the surface layer of the Fe-Al intermetallics has extremely good-resistance to wear and thermal erosion at temperatures between 450oC and 980oC [6], [7]. In this study, low carbon steel was aluminized by Al-hot dipping method, oxidized in air and sulfurized in Ar-0.2%SO_2 mixed gases at 800°C for 20 h. The effect of Al-hot dipping was discussed and results of the oxidation and Ar-0.2%SO_2 mixed gases were compared.

2. EXPERIMENTAL

For Al-hot dipping samples were machined (80×30×3mm^3) from the plates, cleaned and were immersed in 10 vol% HCl solution to remove surface oxides and washed with 20 vol.% KCl+AlF_3 (in 4:1 weight ratio) solution in water. After drying, they were put in pure Al-molten baths at 800°Cfor 10 min, on top of which a solid-flux (KCl+NaCl+AlF3 in 2:2:1 weight ratio) was spread to protect the molten baths from oxidation, cooled to ambient temperature in air and were further cleaned using 5 vol% HNO_3 solution to remove any flux adhered on the aluminized surface. Hot-dipped substrates were further cut into small rectangular shaped coupons with the dimensions of 5mm×10mm×5mm, followed by heat treatment for the microstructural analysis. The specimens were corroded in mixed Ar (99.9999% pure) and SO_2 gas (99.99% pure) inside a closed quartz reaction tube. Sulfur has major effect to corrode the specimens; oxygen also played a role for oxidizing the specimens as a result of O_2 from SO_2 gases. Morphology of the hot dipped and subsequently heat treated specimens was studied using SEM equipped with an energy-dispersive spectroscope (EDS).

3. RESULTS AND DISCUSSION

Fig. 1 shows the SEM/EDS results of low carbon steel after dipping in molen Al-bath. Cross-sectional microstructure (Fig. 1(a)) shows a uniform crack free surface with three well defined layers, the first one at outer side a thin Al top coat (around 38 µm thick), the second one in the mid thick hot-dipped intermetallic layer (around 240 µm thick) and Al free steel substrate in the bottom. Absence of any void and crack shows the good adhesion property of aluminum over base alloy. However, the intersection between the matrix and the alloy layer was highly variable showing tongue like peaks orientated towards the matrix. This tongue-like morphology originated from the preferential growth of Fe_2Al_5 along the diffusion direction [5]. Due to its orthorhombic crystal structure with 30% of voids along the c-axis, diffusion occurs rapidly in Fe_2Al_5. Reason for this tongue-like morphology formation was attributed towards the inward diffusion of Al through Fe_2Al_5 to the Fe_2Al_5/steel reaction front or the outward diffusion of Fe from the substrate through the Fe_2Al_5/steel reaction front into the Fe_2Al_5 phase, or the combination of these two

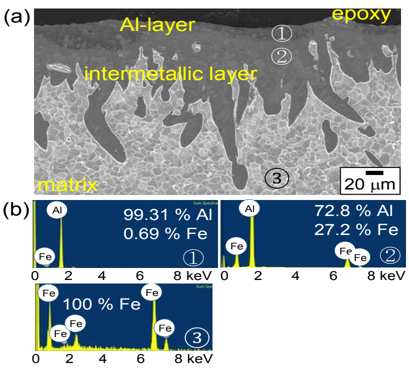

Fig. 1. Results of as-Al hot dipped low carbon steel, (a) Etched SEM cross sectional micrograph (b), EDS spectra of the spot ①, ② and ③.

reasons. Another possible reason may be the atomic size mismatch between Al (atomic radius; 0.143 nm) and Fe (atomic radius; 0.126 nm). The elemental composition (Fig. 1(b)) at spot ① suggests that top coat consist of similar composition like that of molten aluminum bath with minor iron dissolved in it, at spot ② it was suggested that Al5Fe2 [5] phase was formed and the spot ③was pure iron (i.,e the substrate).

Fig. 2 shows the SEM/EDS results of Al-hot dipped low carbon steel after heating in air. The Al-top coat Fig. 2(a) was disappeared, which was the main phase before heating. The results after heat treatment in comparison to as aluminized steel, indicates that thickness of intermediate alloy (~230 μm thick) layer has been slightly reduced due to the diffusion of aluminum into steel substrate after heat-treatment but tongue like morphology still exist. Fig. 2(b) indicates that tick alloy layer that consisted of Al-Fe intermetallics still exist but outer Al-layer was absent. More over EDS line profiles of Al, Fe and O (Fig. 2(b)) shows that composition of Fe and Al varies inversely; Al is higher at the outer layer and decreases along the surface, while Fe increases along the surface towards the steel substrate and becomes maximum, and oxygen was weakly distributed in the alloy layer.

Fig. 3 shows the SEM/EDS results of Al-hot dipped low carbon steel after heating in Ar-0.2%SO_2 mixed gases. Like air oxidation the main phase, Al-top coat Fig. 3(a) was absent, as a result of interdiffusion as explained earlier. The results after SO_2 corrosion in comparison to as aluminized steel and corrosion in air indicates that thickness of intermediate alloy (~130 μm thick) layer has been dramatically reduced due to the diffusion of aluminum into steel substrate, for this reason the tongue like morphology has also been converted to more evenly spaced intermetallic layer. Few Kirkendall voids were generated after SO_2 corrosion at the interface Fig. 3(a) and a very thin alumina scale α-Al_2O_3 can also be seen on the top exterior of the surface Fig. 3(b). However aluminum still dominating in the Al-Fe intermetallic layer and protecting the steel from excessive corrosion because the corrosion only occurred at the exterior of the coating. No sulfur products were detected by EDS analyzer after SO_2 corrosion. The primary phase aluminum, which was also the top coat after aluminizing, either oxidized to the α-Al_2O_3 layer after heating, or reacted with Fe to become Fe_2Al_5 [5].

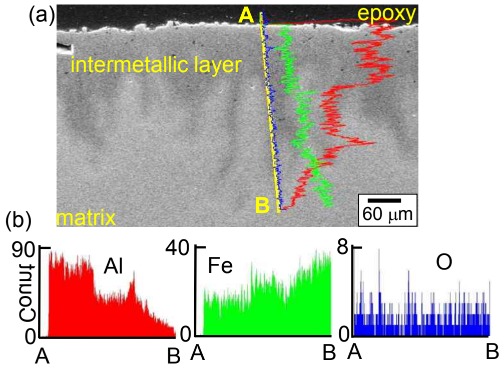

Fig. 2. Al-hot dipped low carbon steel after heating in air at 800°C for 20 h, (a) SEM cross sectional micrograph (b), EDS line profiles of Al, Fe and O along the surface from A-B.

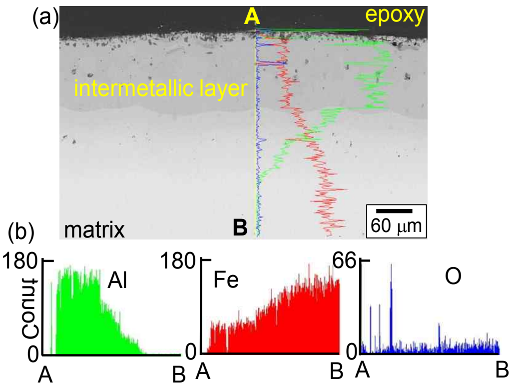

Fig. 3. Al-hot dipped low carbon steel after heating in Ar-0.2%SO2 mixed gases at 800°C for 20 h, (a) SEM cross sectional micrograph (b), EDS line profiles of Al, Fe and O along the surface from A-B.

4. CONCLUSION,

Results conclude that thick alloy layer rich in Fe_2Al_5 and thin top coat rich in Al has been formed as a result of Al-hot dipping. After heating aluminum present in the top coat melted and solidified during heating and cooling. Also some of aluminum oxidized to thin protective alumina scale α-Al_2O_3 and protected the steel from corrosion. The microstructural structure and phases formed were basically similar in both the conditions except few micro voids formed in the SO_2 corroded substrate. However aluminizing provided quite good oxidation resistance at both the corrosion conditions and protected the matrix without forming the bi layered iron oxide scales.

Acknowledgements

This work was supported by the Human Resource Development Program (No. 20134030200360) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy.

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