Flame Sprayed Zinc Coatings

Surface Structure and Anticorrosive Behaviour Studied by SEM

Zinc thermal spraying is widely used for steel coatings. In the present work, the morphology and the corrosion performance of the as-formed coatings is investigated. Initial observations took place with a low magnification stereoscope equipped with a CCD camera, while Scanning Electron Microscopy (SEM) was used for more detailed observation. Selected samples were also examined with High Resolution Electron Microscopy (HREM) in order to investigate the oxygen distribution which was detected by EDS analysis. Corrosion tests were accomplished in a Salt Spray Chamber (SSC) and the corroded samples were also examined with SEM. From this investigation it was deduced that the as-cast coatings are mainly composed by pure zinc. However, zinc oxide inclusions were also encountered in the form of nanoparticles. Regarding corrosion, the samples exposed in the SSC were uniformly attacked. Nevertheless the substrate was effectively protected.

Zinc Coating by Flame Spraying

Several methods of casting zinc coatings on steel are commercially available [1-2], since these coatings are widely applied to improve the corrosion resistance of ferrous substrates [1-4]. A promising method for this purpose is flame spraying, which apart from being simple, quick and effective, is also environmentally friendlier than the „traditional“ techniques (hot-dip galvanizing and electroplating [5-6]). In zinc flame spraying metallic zinc in the form of a wire is continuously fed to the tip of a fuel gas flame where it melts (fig. 1). The liquid metal droplets are accelerated by a stream of compressed air and propelled to the substrate where they form a laminar structure [5]. Unexpectedly ZnO nanoparticles were found inside the coating.

In the present work the morphology and microstructure of zinc coatings formed with the above-mentioned method are investigated. Moreover, their anticorrosive performance in connection with the presence of nanoparticles is also evaluated and useful data is gathered on this topic.
**Experimental Procedure**

The substrates used were sheets of commercial low carbon steel SAE 1010. The coupons were sandblasted prior to the coating process which took place with a Metco wire flame spray gun (fig.1).

The as-formed specimens were initially observed with a Zeiss M8 stereoscope. However, the main examination was accomplished with a 20 kV Jeol 840A SEM associated with an Oxford Isis 300 EDS analyzer. Selected samples were also examined with a 200 kV Jeol 2010 HREM after the necessary preparation. Corrosion tests were performed in a Salt Spray Chamber SC-450 Umwelttechnik GmbH (fig. 2), where the samples were exposed for 14 days in a fog of a 5 wt. % solution of NaCl in de-ionized water at 40 °C. The corroded samples were examined with SEM.

**Results**

The examination of the surface of the samples shows that it is very rough. In the images of figure 3a peaks, pores and channels are observed along with larger cavities. The observation of the same area with SEM (fig. 3c) revealed a more complicated relief. The macroscopically observed peaks are composed by several flat discs of different dimensions deposited one on top of the other (pancake form). Spherical particles are also likely to be attached on some of these forms. The shape of these particles implies that they refer to zinc droplets that were solidified during their flight, due to their small size which allows faster cooling. Furthermore, the SEM observation revealed that the pore density is much higher than initially assumed since most of the existing voids are invisible at low magnification. However the picture of figures 3a and 3c is not peculiar. By contrast, it is an inherent characteristic of the sprayed coatings and it is the result of the coating process [6]. As the droplets of the liquid metal strike the substrate, flatten and form thin lamellae that conform and adhere to the irregularities of the substrate and to each other. However, the droplets during their flight and consequently are partially or totally solidified the contact with the already formed surface is not perfect. As a result, the formed surface has low uniformity [5]. The above process is affected by several factors such as the zinc feedstock rate, the viscosity of the liquid metal, the droplet momentum at impact and the flame temperature [1, 5]. Hence the elimination of the roughness and the porosity of the surface is practically impossible.

Cross-sectional SEM examination of the same samples revealed that the coating
mass is more uniform (fig. 4a). In this micrograph, the boundaries of the above-mentioned lamellae are easily distinguished, along with many pores scattered throughout the whole thickness of the coating. The EDS analysis of the same area revealed that the coating is mainly composed by zinc, while oxygen is also present at low concentration. In order to determine the role of the oxygen with more accuracy, selected specimens were examined with HREM (fig. 5). In this case, nanoparticles of ZnO were observed along with nanoparticles of Zn. The formation of the Zn nanoparticles could be attributed to rapid cooling during the coating process. However ZnO is due to the superficial oxidation of the zinc droplets during their flight. Zinc is a very active material and its activity is enhanced in liquid form. As a result, the droplets react with atmospheric oxygen almost instantly, forming an oxide crust which is afterwards trapped in the coating. Nevertheless, the speed of the coating process does not allow the growth of the as-formed oxide and so only nano-sized particles are formed.

The corrosion effect is presented in figures 3b and 3d. From these micrographs, extended deterioration of the exposed samples could be assumed due to the formation of voluminous corrosion products (Zn oxides and chlorides) covering the coating surface almost totally. The actual attack is not so severe, however, as figure 4b and the inset stoichiometrical mappings show. The coating is uniformly corroded. Nevertheless the corrosive elements (oxygen and chloride) penetrate the coating but not enough to reach the ferrous substrate. Thus after 14 days of exposure the substrate is still protected from corrosion.

Conclusions

From the above investigation it turned out that:

- The outer surface of zinc thermal sprayed coatings is extremely rough due to the coating procedure, although the coating cross-section is more homogeneous.
- The coating is mainly composed by pure zinc while zinc oxide in the form of nanoparticles is also present.
- After 14 days of exposure in the SSC, the corrosive elements formed a large volume of corrosion products on top of the coating but the substrate was protected.

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Group of Metallic Coatings-AUTH

The group of metallic coatings of the Aristotle University of Thessaloniki began its
research activity during 1998. The research conducted is mainly focused on the growth and the structural characterization of hot-dip galvanized, thermal, plasma and diffusion (CVD) coatings. Furthermore, corrosion and mechanical behavior of the same materials is examined. In the last five years, the members of the group have published about 100 papers in international journals.

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