

EFFECT OF ALUMINIUM AND MAGNESIUM ON THE CORROSION RESISTANCE OF ZINC COATINGS

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ABSTRACT

This article presents the research on corrosion resistance of Zn-Al-Mg coatings with varying aluminium and magnesium content. Aluminium and magnesium were added directly to the zinc bath at 10:1 rate. There was found more than sixfold increase in corrosion resistance of zinc coatings with aluminium content at the level of 4% of weight and magnesium content at the level of 0.4% of weight. In contrast to the amounts applied in the literature, such content of these alloy additives in the zinc bath limits to a significant extent the amount of intermetallic phases in zinc coatings obtained from such baths. This, in consequence, results in high resistance to corrosion with simultaneous retention of high plasticity of these coatings.

Keywords: hot-dip galvanizing, Zn-Al-Mg coating, corrosion resistance.

INTRODUCTION

Elements added to a zinc bath significantly influence the structure, appearance and submerging properties of zinc coatings. The main alloy additions must include aluminium, nickel, lead, tin, and magnesium. The most important of the additions is aluminium, which is typically added in the amount from 0.005 to 0.2%_{w/w}. Aluminium improves the plasticity of the coating, brightens, increases gloss, improves corrosion resistance by formation of a zinc coating Al₂O₃ on the surface. During zinc-coating on a solid/liquid interface, intermetallic Fe-Al phases are emitted, which constitute a barrier to the reactive diffusion of zinc, hindering growth of intermetallic Fe-Zn phases. The amount of aluminium in the bath determines the size of this barrier. Therefore, standard aluminium content in zinc-coating baths does not exceed 0.2%. However, tests prove that the obtained intermetallic Fe-Al phases are unstable and decompose during further zinc-coating [1, 7, 9,

18, 19], which means that the effect of restraining the coating thickness by aluminium is of the greatest importance for continuous zinc-coating. On steels with a high content of silicon, deliberate increasing aluminium content in the bath is proposed to limit the coating growth [9, 13, 15]. Zinc-aluminium coating with a higher aluminium content (5.0% and more) that has been developed primarily to increase the corrosion resistance of standard zinc coatings are also known [10, 20]. Another important element added recently to zinc baths is magnesium. It improves the wettability of a steel substrate, reducing the surface tension of the bath and also improves corrosion resistance [10, 14]. However, the most promising, and already used in various steel industries in the world, is hot-dip zinc-coating of steel in Zn-Mg-Al baths [3, 16, 17, 22]. In addition to the increased corrosion resistance [2], the coatings obtained from these baths have higher hardness and hence resistance to scratches [6]. Tests of zinc coatings with added magnesium and aluminium presented

in the literature focus, however, primarily on the coatings with a lower aluminium content in respect to magnesium [4, 5, 8, 12, 21]. There are very few papers that present the results of zinc-coating tests in baths containing more aluminium than magnesium, and these, in turn, present tests of baths containing substantial amounts of aluminium (over 15%_{w/w}) [11].

Based on previous experience, both in the use of zinc baths containing only aluminium or magnesium as well as baths containing both elements, it was found that the preferred solution, due to corrosion resistance while maintaining good plasticity of the coating, aluminium and magnesium may be added to the zinc bath, containing higher aluminium contents, in which the content of this element will not exceed a few percent. This paper presents research on the corrosion resistance of the Zn-Al-Mg coatings with different contents of Al and Mg maintaining a specified (10:1), fixed proportion of their dosing.

RESULTS

A steel sheet DD11 of the elemental composition given in Table 1 underwent (hot) dip zinc-coating in zinc baths with varying content of magnesium and aluminium added to the base bath (bath no. 2 according to Table 2) in proportions of 1:10. The elemental compositions of the tested baths are shown in Table 2.

The samples with dimensions of 20x25 mm were dip zinc-coated in the zinc baths prepared in ceramic crucibles, in a chamber furnace, in a reducing atmosphere formed from a mixture of

argon-hydrogen gases. The temperature of zinc-coating was 550°C in each case, immersion time was 30 sec. Prior to the zinc-coating, the samples were subjected to the standard surface preparation process that involved: sandblasting, degreasing in acetone, rinsing in water and etching in an HCl solution, re-washing in water and drying in a stream of compressed air.

As a result of these processes, in each case, a uniform zinc coat was formed, well adhering to the substrate, without “spangle” (Fig. 1). The structure of the obtained coatings is characteristic for zinc-coating at elevated temperature, constant and uniform, with a thickness of about 40 µm. An extensive diffusion layer with a fine-grained mixture of intermetallic phases Fe-Zn and Fe-Al (Fig. 2). On the basis of the conducted diffraction tests, there are single eruptions of zinc and iron Fe₄Zn₉, and iron as well as aluminium and Fe₂Al intermetallic phases were found in the coating (Fig. 3).

The conducted tests of concentration gradient of the elements in the zinc coatings showed an uneven aluminium and magnesium gradient in the coating. The highest aluminium concentration is in the area of the transition zone, the maximum aluminium concentration is achieved at about 0.7%_{w/w}. While the highest magnesium concentration is just below the coating surface, the maximum magnesium concentration reaches approximately 0.08%_{w/w} (Fig. 4). In addition, the diffusion speed of aluminium to the substrate is higher than that of magnesium. During the zinc-coating process, aluminium diffused into a depth of about 55 µm, whereas magnesium – only about 10 µm.

Table 1. Elemental composition of a steel sheet dip zinc-coated in the zinc baths tested

| Steel marking | C | Mn | Si | Cr | Ni | Cu | S | P | Ti | Al | Mg | Fe |
|---------------|-------|------|------|-------|------|------|-------|-------|-------|-------|------|-------|
| | % w/w | | | | | | | | | | | |
| DD11 | 0,10 | 0,60 | 0,14 | 0,005 | 0,01 | 0,02 | 0,003 | 0,009 | 0,005 | 0,035 | 0,00 | other |

Table 2. Elemental composition of zinc baths used for the tests

| Bath marking | Al | Mg | Tin | Mn | Fe | Cu | Cd | Pb | Ni | Zn | |
|--------------|-------|-----|-------|-------|--------|--------|--------|--------|-------|-------|-------------|
| | % w/w | | | | | | | | | | |
| 1 | 0.005 | | | | | | | | | | 99.995 (Z1) |
| 2 | 0.033 | - | 0.105 | 0.095 | 0.0013 | 0.0003 | 0.0004 | 0.0013 | 0.141 | other | |
| 3 | 4.0 | 0.4 | | | | | | | | | |
| 4 | 2.0 | 0.2 | | | | | | | | | |
| 5 | 6.0 | 0.6 | | | | | | | | | |



Fig. 1. Example of a zinc coating achieved on DD11 steel

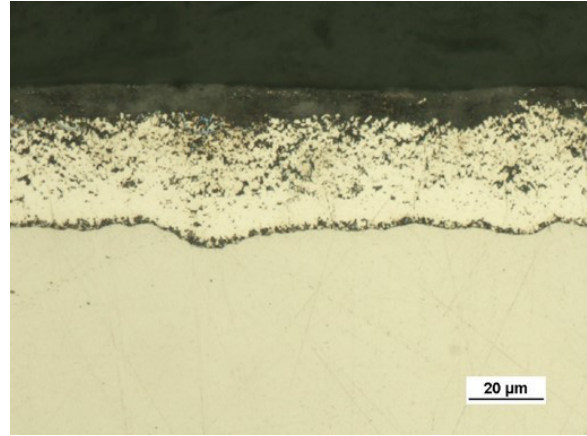


Fig. 2. Structure of a coating achieved in a zinc-coating process at 550°C

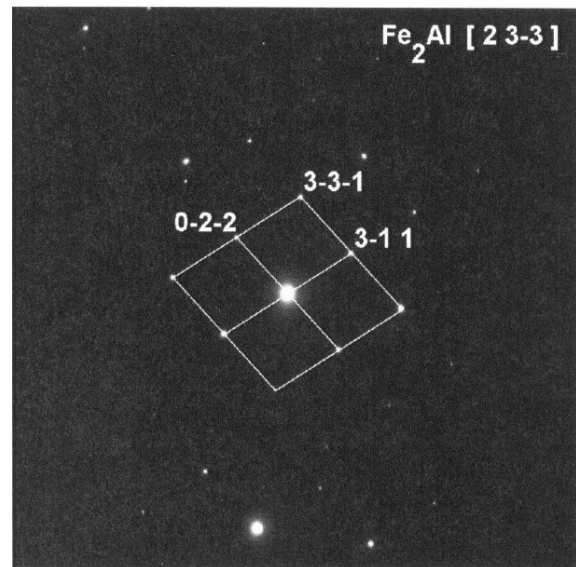


Fig. 3. Microstructure of the zinc and iron interlayer (a) and the stoichiometric analysis of the Fe_2Al phase (b) obtained on a zinc coating obtained from a zinc bath modified with aluminium and magnesium

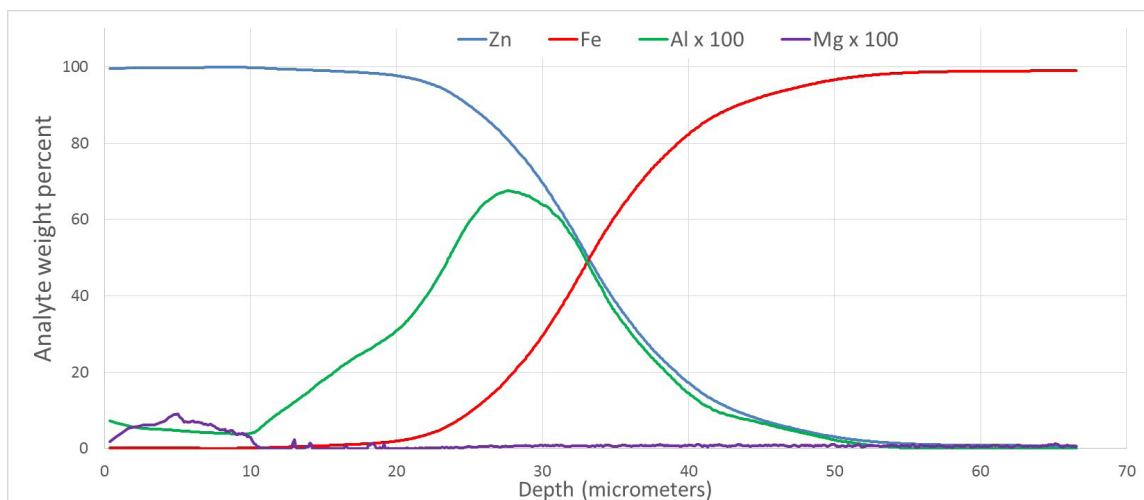


Fig. 4. Distribution of elements in zinc coating obtained from a zinc coating modified with aluminium and magnesium. Bath no. 4 according to Table 2

Table 3. Results of corrosion resistance of zinc coatings to the neutral salt spray effect tests – NSS Test

| Bath marking | Corrosive environment exposure time | | | | |
|--------------|-------------------------------------|-----------------|-----------------|-----------------|-----------------|
| | 240h | 480h | 840h | 1200h | 1500h |
| 1 | beginning of red corrosion | red corrosion | red corrosion | red corrosion | red corrosion |
| 2 | beginning of red corrosion | red corrosion | red corrosion | red corrosion | red corrosion |
| 3 | white corrosion | white corrosion | white corrosion | white corrosion | white corrosion |
| 4 | white corrosion | white corrosion | white corrosion | red corrosion | red corrosion |
| 5 | white corrosion | white corrosion | white corrosion | white corrosion | white corrosion |

Then, tests of corrosion resistance of the obtained coatings were executed. The tests were conducted for the resistance to neutral salt fog effect – NSS Test. They involved keeping the zinc-coated steel samples in a salt chamber, in which salt water with concentration of 50 ± 5 g/l NaCl, in the pH range from 6.5 to 7.2 (adjustment of reaction using the 0.1 N of the HCl or NaOH solution), at $35 \pm 2^\circ\text{C}$, was sprayed at a pressure of 70-170 kPa. The chamber corrosiveness was established on the basis of the reference steel sample mass loss (CR4) after 48 h of the test in the range of 70 ± 20 g/m², whereas the fallout of the salt spray was specified after a minimum of 16 h of the test as a pluviometric constant in the range of 1.5 ml/h \pm 0.5 ml/h. Accelerated corrosion tests were conducted in a total time of 1500 h, assessing the samples' resistance on the basis of macroscopic studies conducted after: 240, 480, 840, 1200 and 1500 h. The test results are presented in Table 3.

On the basis of the conducted tests, it can be stated that the presence of aluminium and magnesium in the zinc-coating bath has a positive impact on the increase of corrosion resistance of the obtained zinc coatings. Compared to the bath containing pure zinc and the standard zinc bath, the corrosion resistance of the coatings with aluminium and magnesium is significantly higher. The contents of aluminium at 4%_{w/w} and 0.4%_{w/w} causes over six times greater increase in the corrosion resistance in relation to the coatings obtained from pure zinc. Such a content of aluminium and magnesium in the zinc bath, in contrast to the amount used in the literature, greatly reduces the number of intermetallic phases in the zinc coatings obtained from these baths. Consequently, this results in a high corrosion resistance while maintaining the high plasticity of these coatings.

CONCLUSIONS

Based on the conducted tests, it can be concluded that:

- zinc coatings obtained from the baths containing the addition of aluminium and magnesium have higher corrosion resistance than the standard ones in use,
- corrosion resistance increases in proportion to the aluminium and magnesium content in the zinc bath,
- the use of larger contents of aluminium in relation to magnesium, while reducing this element to a content below 5%_{w/w}, reduces formations of intermetallic phases, which may translate into higher plasticity of these coatings.

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REFERENCES

1. Adachi Y. and Arai M. Transformation of Fe–Al phase to Fe–Zn phase on pure iron during galvanizing. *Materials Science and Engineering: A*, 254, 1998, 305-310.
2. Baoping L., Anping D., Guoliang Z., Shuangjie C., Hongwei Q., Chengjie H., Baode S. and Jun W. Investigation of the corrosion behaviors of continuously hot-dip galvanizing Zn–Mg coating. *Surface & Coatings Technology* 206, 2012, 3989-3999.
3. Bleeker R., Hannour F., Goos C., Maalman T.F.J., Smith S.M., Vlot M.J. and Vrenken J.W. Corus' new hot dip ZnAlMg coated steel for automobile applications. *Proc. of the 7th Int. Conf. on Zinc and Zinc Alloy Coated Steel Sheet, Galvatech'07, Osaka, Japan, 2007*, 510.

4. De Bruycker E., Cooman B.C. and De Meyer M. Experimental study and microstructure simulation of Zn-Al-Mg coatings. *Rev. Metal.*, 102, 2005, 543-550.
5. Diler E., Rouvellou B. and Rioual S. et al. Characterization of corrosion products of Zn and Zn-Mg-Al coated steel in a marine atmosphere. *Corros. Sci.*, 87, 2014, 111-117.
6. Dutta M., Halder A.K. and Singh S.B. Morphology and properties of hot dip Zn-Mg and Zn-Mg-Al alloy coatings on steel sheet. *Surf. Coat. Technol.*, 205, 2010, 2578-2584.
7. Guttman M., Leprêtre Y., Aubry A., Roch M.-J., Moreau T., Drillet P., Maigne J.M. and Baudin H. Mechanisms of the galvanizing reaction, Influence of Ti and P contents in steel and of its surface microstructure after annealing. Proc. of the International Conference on Zinc and Zinc Alloy Coated Steel, Galvatech '95, Iron and Steel Society, Warrendale, PA, USA, 1995, 295-307.
8. LeBozec N., Thierry D., and Rohwerder M. et al. Effect of carbon dioxide on the atmospheric corrosion of Zn-Mg-Al coated steel. *Corros. Sci.*, 74, 2013, 379-386.
9. Liberski P. Anticorrosion dip coating. WPS Gliwice, 2013.
10. Liberski P., Kania H., Podolski P. and Gierek A. The corrosion resistance of zinc-aluminium coatings obtained by of metallization immersion. *Corrosion Protection*, 10, 2004, 264-269, (in Polish).
11. Linjie G., Zhi L., Xiaowei K., Fucheng Y. and Hong J. Formation of periodic layered structure during hot-dip galvanizing in Al-Zn-Mg bath. *Surface & Coatings Technology*, 304, 2016, 306-315.
12. Kaczmarek Ł., Kula P., Sawicki J., Armand S., Castro T., Kruszyński P., Rochel A. New possibilities of applications aluminium alloys in transport. *Archives of Metallurgy and Materials*, 54 (4), 2009, 1199-1207.
13. Maffoni F. High aluminium alloying for general galvanizing. Proc. 15th Hot Dip Galvanizing Conference, Sliac, Slovak Republic, 2009, 116-119.
14. Marder A.R. The metallurgy of zinc-coated steel. *Progress in Materials Science*, 45, 2000, 191-271.
15. Memmi C., Bottanelli U. and Cecchini M. A new technology for batch hot dip galvanizing with a low-Al zinc alloy. Proc. 22th International Galvanizing Conference, EGGA, Madrid, Spain, 2009.
16. Nomura H., Kimata Y. and Kanai H. Corrosion resistance of prepainted Zn-11%Al-3%Mg-0.2%Si coated steel sheet [C]. Proc. of the International Conference on Zinc and Zinc Alloy Coated Steel, Galvatech'04, Warrendale, PA, USA, 2004, 763.
17. Schuerz S., Fleischanderl M., Luckeneder G.H., Preis K., Haunschmied T., Mori G. and Kneissl A.C. Corrosion behaviour of Zn-Al-Mg coated steel sheet in sodium chloride-containing environment. *Corrosion Science*, 51, 2009, 2355-2363.
18. Strutzenberger J. and Faderl J. Solidification and spangle formation of hot-dip-galvanized zinc coatings. *Metallurgical and Materials Transactions A*, 1998, 29A, 631-646.
19. Tatarek A., Liberski P., Kania H. and Podolski P. The mechanism of formation hot dip galvanizing on iron alloys containing silicon. *Materials Engineering*, 6, 2008, 788-791.
20. Tsujimura T., Komatsu A., Andoh A. Influence of Mg content in coating layer and coating structure on corrosion resistance of hot-dip Zn-Al-Mg alloy coated steel sheet. Proc. of the 5th International Conference on Zinc and Zinc Alloy Coated Steel, Galvatech'01, Belgium, Brussels, 2001, 145-152.
21. Unwin P.N.T. and Nicholson R.B. The nucleation and initial stages of growth of grain boundary precipitates in Al-Zn-Mg and Al-Mg alloys. *Acta Metall.*, 17, 1969, 1379-1393.
22. Yoshizaki F., Shimizu T., Miyoshi Y. and Andoh A. Atmospheric corrosion resistance of hot-dip Zn-6%Al-3%Mg alloy coated steel sheets, Proc. of the International Conference on Zinc and Zinc Alloy Coated Steel, Galvatech'04, Warrendale, PA, USA, 2004, 1025.