

Directions of the Development of the Metallization of Iron Alloy Products

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Abstract

The article discusses the future of the production of protective coatings based on the hot-dip galvanizing of iron-carbon alloys, such as steel or cast iron. Currently exploited zinc deposits will be exhausted in the next two decades and it will be necessary to start the exploitation of new deposits in order to maintain the supply or quantity of Zn on the global market. In both cases, it will be related to the increasing cost of zinc on world markets. Zinc-based protective coatings (one of the best corrosion protection methods) constitute almost 50% of the world's zinc consumption. Economic issues with the constant increase in the price of Zn will force the change or modification of hot-dip galvanizing technology. The article presents data on the production, consumption and development of zinc prices on the global market. Possible directions are presented which producers of zinc coatings will have to follow in order to maintain sales markets, such as the modification of chemical compositions of protective alloys which could be an alternative to pure zinc coatings and the possibility of limiting zinc consumption based on the influence of the surface of galvanized elements, i.e. its metal matrix, and surface roughness.

Keywords

hot-dip galvanizing, aluminizing, protective coatings, zinc

1. INTRODUCTION

Galvanizing is the most popular method to provide protection for Fe-C alloys against corrosion, especially of steel, but also cast iron or cast steel. Protective coatings consume 50% of global zinc production (Fig. 1).

Due to the very important role of zinc in the global corrosion protection industry, an analysis of the quantity, availability and price of this element was carried out, as well as the direction of potential development of the hot-dip galvanizing industry.

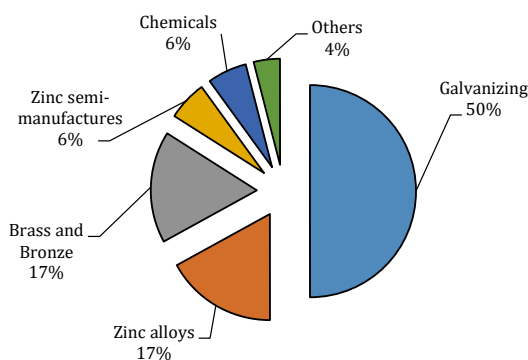


Fig. 1. End uses of zinc [1]

2. CASE STUDY

Zinc production shows an upward trend. In 1990 7.15 mln ton mine and 7.18 mln smelter production. In 2000 8.77 mln ton mine and 9.03 mln ton smelter production. In 2010 12.3 mln ton mine and 12.9 mln ton smelter production (Fig. 2).

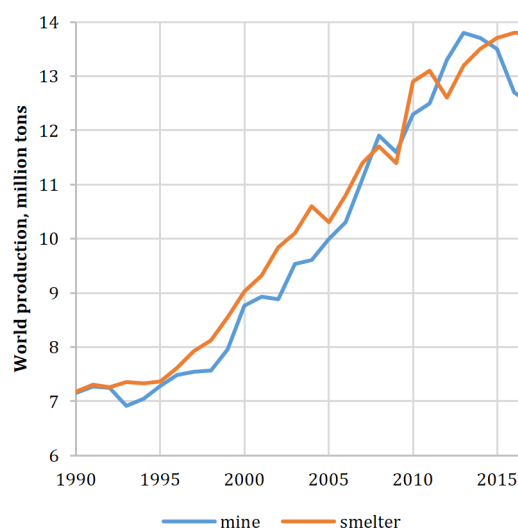


Fig. 2. Production of zinc (mine and smelter) since 1990 to 2017 [2]

The growing production of zinc is a symptom of the increasing demand for this element. Figure 3 shows the global consumption of zinc in the years 2004–2018.

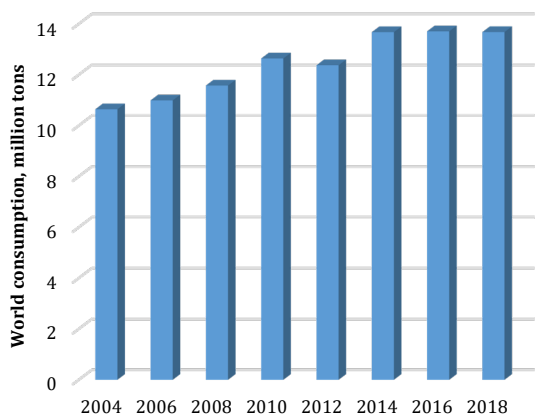


Fig. 3. Global consumption of zinc since 2004 to 2018 [3]

The constantly growing consumption of zinc also affects the price of this element. Figure 4 presents zinc prices from the last 14 years. The highest price was November 24, 2006 4,619 USD, the lowest in December 12, 2008 1,072.25 USD per ton.

In Table 1, production and reserves of zinc from 2004 to 2018 are compared for the seven world largest producers among the ten largest world zinc producers. Values of the reserves in this table means that these deposits are ready for mining at any time.

In order to understand the problem, it is necessary to present the unique nature of corrosion protection afforded by zinc coatings in relation to other protection methods. Zinc coatings provide active (cathodic) protection [4–6]. Over time, the zinc layer is lost and the protected surface does not corrode. This is a considerable advantage in relation to, for example, paint coatings that provide only passive (anodic) protection. The key to a flawless coating is to carry out proper chemical surface preparation.



Fig. 4. Zinc prices since December 1, 2005 to February 12, 2021 [7]

Table 1 Global production and reserves of zinc from 2004 to 2018 [3]

Country	Mine (ton/year)					
	2004		2011		2018	
	Production	Reserves	Production	Reserves	Production	Reserves
United States	739,000	30,000,000	769,000	11,000,000	790,000	11,000,000
Australia	1,300,000	33,000,000	1,520,000	70,000,000	940,000	64,000,000
Canada	790,000	11,000,000	612,000	7,800,000	340,000	3,000,000
China	2,300,000	33,000,000	4,310,000	43,000,000	4,300,000	44,000,000
Kazakhstan	360,000	30,000,000	495,000	10,000,000	390,000	13,000,000
Peru	1,200,000	16,000,000	1,260,000	18,000,000	1,600,000	21,000,000
Mexico	460,000	8,000,000	632,000	16,000,000	650,000	20,000,000
Other countries	2,400,000	59,000,000	3,207,000	74,300,000	3,840,000	49,200,000
World total	9,600,000	220,000,000	12,800,000	250,000,000	13,000,000	230,000,000

There are many ways to apply a zinc coating, such as hot zinc spray, electrogalvanizing or sherardizing. However, the immersion method (hot-dip) allows the most durable, resistant protective coating with the longest operating time to be obtained. Analyzing the data contained in the previous chapter, it can be concluded that global zinc consumption will stabilize at the level of 13.5-14 million tons (Fig. 3), although an upward trend and exceeding 14 million tons is more likely. World reserves of zinc from 2011 to 2018 decreased by 20,000,000 tons which means it still relies on existing mining areas. Assuming a continuous extraction of 13,000,000 tons per year, it can be concluded that the present world reserves of zinc in the form of fossil deposits will be exhausted within 18 years. The decrease in the amount of zinc on the global market and increased world consumption will cause an increase in zinc prices on the global market, which will lead to an increase in the production cost of zinc coatings. For this reason, opportunities should be sought to introduce savings in the production of dip coatings to compensate for the increase in the price of zinc.

One possibility is to introduce elements other than zinc into the immersion bath. Such an element might be aluminum (Al). The following protective baths alloy containing this element are known as:

- Galfan alloy containing the addition of 5% Al and 0.05% mischmetal [8-10];
- Galvalume alloy containing the addition of 55% Al and 1.6% Si [11, 12];
- pure aluminum.

The addition of Al increases corrosion resistance in marine and industrial environments, and at the same time has a lower cathodic protection in relation to pure zinc coatings. An additional problem is the higher temperature of the treatment than in the case of zinc alloy due to the melting point of Al and the increased viscosity of the metallizing alloy. At present, using an Al addition to zinc or a pure Al alloy is unpopular due to the technologically difficult process of obtaining a protective coating comparable with the standard hot-dip galvanizing process. However, with the increase the price of zinc, aluminum alloys (Galfan, Galvalume etc.) may find greater use and the development of new techniques for applying a dip coating containing a greater amount of Al. may prove to be more economically advantageous.

Another option is to obtain more knowledge and control over the process of the protective coating growth in the hot-dip galvanizing treatment. This would allow for the adjustment of the treatment technology – the preparation of the surface before galvanizing (etching and fluxing), as well as the time of the immersion of the iron component in molten zinc to obtain the appropriate level thickness of the zinc coating. This is meant to meet the requirements of the purchaser and applicable standards, and to ensure that the losses of zinc during production in the form of hard zinc and zinc dust were as low as possible. For this purpose, it is worth focusing on the often overlooked aspect, i.e. the roughness and metal matrix of Fe-C alloy.

3. OWN RESEARCH

The hot-dip galvanization of GJS-500-7 cast iron with ferritic and pearlitic matrix and roughness of 16.7 and 43 μm was conducted according to the scheme shown in Figure 5 [4]. The test results are presented in Figures 6 and 7.

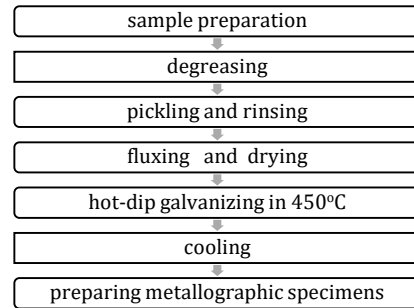


Fig. 5. Preparation of research samples

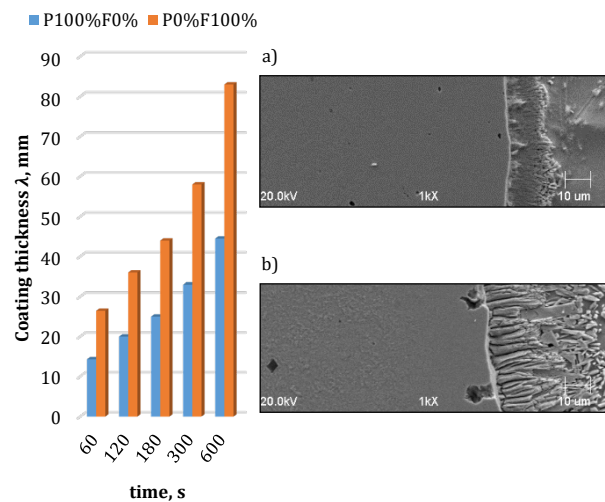


Fig. 6. Coating thickness of zinc phase alloy shaped on a ferritic and pearlitic metal matrix: a) matrix composition: P100%F0%; b) matrix composition: P0%F100% after 60-s hot-dip galvanizing

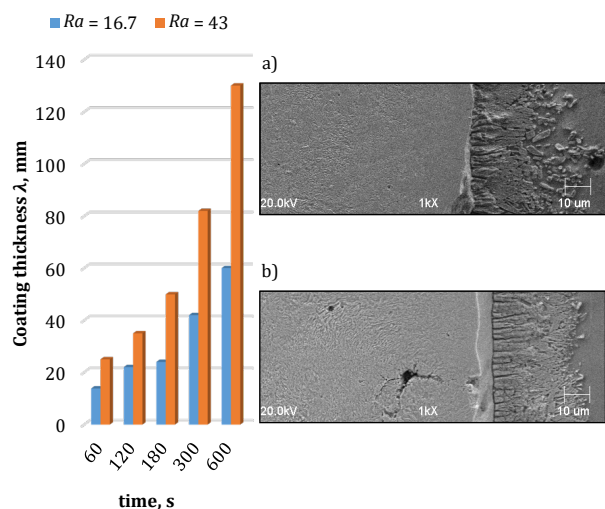


Fig. 7. Coating thickness of zinc phase alloy shaped on a surface roughness of 16.7 and 43 μm : a) 16.7 μm ; b) 43 μm after 60-s hot-dip galvanizing

It can be observed (after 60-s of hot-dip galvanizing) that the differences in the obtained thickness of the alloy layer on the ferritic matrix in relation to the pearlitic matrix was 1.84:1. In the case of the influence of different roughness (with the same metal matrix) it was 1.79:1.

The knowledge of the structure of the Fe-C alloy would allow the shortening or extension of the immersion time in molten zinc in order to obtain the appropriate thickness of the protective layer. At the same time, the simultaneous galvanization of similar elements but with a different metal matrix or roughness could be avoided.

Calculations of the diffusion coefficient

Another important aspect is the assessment of the diffusion coefficient *D*. It is certain that the zinc consumption in the hot-dip galvanizing process depends on the diffusion coefficient. If we learn to calculate in a simple way (measure this parameter), we can start looking for a new zinc-saving technology of hot dip metallization. Calculation of this coefficient, which combines the surface quality of the galvanized element (surface roughness and the type of metal matrix) as well as the influence of the fluxing treatment, allows for the most comprehensive designation of the thickness of the protective layer that can be obtained in a given time. To determine the diffusion coefficient, the microsegregation aspect can be considered. Microsegregation is an uneven distribution of

elements in crystallizing grains (crystals). Its cause is the difference in the solubility of the elements in the solid and liquid phases. The greater the distance between the liquidus and solidus lines in the equilibrium system, the greater the chemical heterogeneity of the crystallizing phase is to be expected. The influencing microsegregation factor is mass transport (diffusion) at the crystallization front (component separation). The analysis of the works [13, 14] shows that the description of segregation allows for theoretical consideration of the crystallization process for various conditions of the solid phase formation, using the Equation (1) describing the back diffusion parameter α .

$$\alpha = \frac{D \cdot t_L}{\lambda^2} \tag{1}$$

where:

- D* – diffusion coefficient of the component in the solid phase;
- t_L* – local crystallization time;
- λ – coating thickness.

Based on the assumed coefficient $\alpha = 0.87$ the solid-phase diffusion coefficient *D* was determined during galvanizing of cast iron with different (16.7 and 43 μm) roughness (Figs. 8, 9).

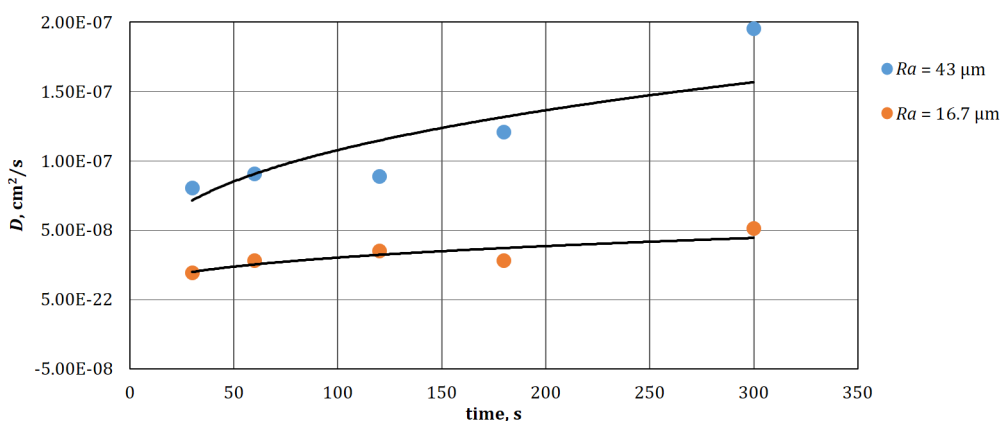


Fig. 8. Calculated diffusion during galvanizing from 30 to 300 s

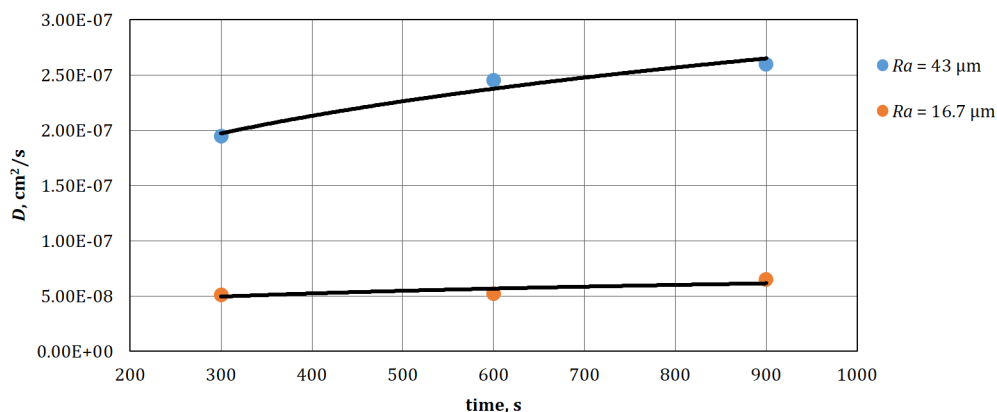


Fig. 9. Calculated diffusion during galvanizing μm from 300 to 900 s

4. SUMMARY

According to the above analysis, it can be concluded that:

- Zinc consumption and its price will increase.
- Without new zinc deposits, present reserves will be exhausted in less than 20 years with the current demand for zinc.
- Using a multi-component bath (addition of Al and other elements) will be more profitable with a rising price of zinc.
- The consumption of zinc during hot-dip galvanizing depends on the microstructure and surface roughness of the galvanized component.
- In the process of planning the galvanizing treatment, it is important to determine the rate of diffusion D , which allows us to know the rate of the growth of the zinc alloy layer.

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