Back

Diffusion Zinc Plating of Structural Steels

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Abstract

The report deals with the research on diffusion zinc plating of structural steels when replacing their cyanide cadmium plating. The results of the experiments in the open air, in vacuum, in the inert atmosphere, under various temperatures (300 – 500ºC) for different steel brands are presented. It is shown that diffusion zinc plating in argon or nitrogen atmosphere ensures obtaining the qualitative anticorrosion coating with insignificant change of mechanical properties of steels. The process is simple , reliable, ecology pure and cost-effective.

Key words: diffusion zinc plating, replacing cyanide cadmium plating, structural steels, choice of environment, temperature, corrosion and mechanical tests.

INTRODUCTION.

Cyanide cadmium plating is widely implemented in different branches of industry for corrosion protection of the parts made of structural steel. The coating obtained is stable both in ordinary environment and in sea climate. But along with its evident advantages cyanide cadmium plating has a number of drawbacks. The main of them is high toxicity of cadmium and cyanide compounds and the related problems. Galvanic cadmium plating does not allow to obtain coatings in the holes, deep grooves, etc. The steel is hydrogenated in the process of cadmium plating, that causes high embrittlement of steel and loss of its strength as a result. To dehydrogenate the steel thermal vacuum treatment is necessary to be performed.

There were many attempts to find an equal replacement for cyanide cadmium plating. In our opinion, one of the perspective trends is diffusion zinc plating of steels. It is done by submersion of the part to be treated into the melt or into the powder of zinc at 350-400°C.

However, the first technique (submersion into the melt) cannot be applied for precision treatment of the parts to be coated, as there may be sags and runs of zinc, which don't give a uniform coating. There are no such drawbacks in case of the second way of zinc coating from the zinc powder.

It is worth noting that there are many variants of powder technique. However, they are too complicated from our point of view /1/. It would be reasonable to find some variant to replace cyanide cadmium plating with diffusion zinc plating in the zinc powder observing the following conditions:

- diffusion zinc coating or a variant of coating in combination of some uncomplicated additional treatment (e.g., phosphatic treatment) must not be worse than cyanide cadmium plating with regard to corrosion stability both in ordinary environment and in sea climate;
- diffusion zinc plating technology should be simple and reliable;

- diffusion zinc plating technology should be more cost-effective as compared with the cyanide cadmium plating;
- the technology must ensure the manufacturing of uniform coatings of various thickness;.
- powder mixtures must be simple and long-lived

The present report is devoted to decision of questions numbered above. The patent research and preliminary experiments have shown the possibility of their fulfillment.

EXPERIMENTAL RESULTS

Optimization of the Diffusion Zinc Plating Process.

In our experimental research it was necessary to select such a technique of diffusion zinc plating that would ensure application of uniform corrosion resistant coatings 3-30 microns thick with good adhesion to the surface. The coating should be obtained on the parts of a complex shape at maximum low temperatures. The process should preserve the parameters of the reacting mixture during a long period of time. That is why we varied such experimental parameters as the environment of zinc plating, the temperature and the time of the process, the zinc content in the blend etc.

Zinc Plating in the Open Air.

When the coatings were applied in the open air, there were studied:

- the dependency of the coating thickness on the temperature;
- the influence of the powder mixture composition on the coating quality;
- the influence on the coating thickness of a branch of steel used.

The dependency of the coating thickness on the temperature was studied when the process took place during 1 hour in the temperature range of 390-500°C. It was found out, that the temperature mode has a considerable influence on the speed the coating is formed at and on the quality of the coatings applied.

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The results of the study of the coating thickness as it depends on the temperature of the process are given in Table 1.

Table 1. The dependency of the diffusion coating thickness on the temperature (open air, the time is 1 h).

Coating thickness, μm	Temperature, °C
21	390
31	420
40	450
58	500

It is necessary to note that at 390-420°C there were stains of different shades on the coating, and the coating was not uniform in thickness.

At 450-460°C uniform good quality coatings were obtained. Further increase of the temperature up to 500°C also ensured the necessary quality of the coating. The optimum

Back

temperature of (450±15)°C was selected basing on the results of this research. It ensures application of high quality coatings of the necessary thickness.

There are the following drawbacks of this process. As it was already said, the high-quality coating was obtained at ≥450 °C. For many brands of steel, (especially for martensite steels), this temperature is too high, as their tempering takes place and their mechanical properties deteriorate. On the other hand, it is not possible to obtain the coatings of small thickness (3-6 µm) in the open environment. Besides, oxidation of the zinc powder in the open environment is a negative factor.

Zinc Plating in Vacuum.

It is well known /3 /, that it is possible to lower the zinc plating temperature in vacuum. Temperature influence on the coating thickness was controlled in the range of 300 - 400°C, when the content of zinc in the mixture was 80 and 50 % by weight. The results of the tests are adduced in Table 2 that makes it evident that at 300°C there is practically no process taking place. The low pressure of the zinc vapor at this temperature can explain it. At 350-400 °C, a good-quality zinc coating is obtained

Table 2.The dependency of the coating thickness on the temperature
(air pressure is $6 \cdot 10^{-2}$ Hg mm, the time is 1 hour).

Temperature, °C	Coating thickness, µm , when zinc content is		
	80%	50%	
	Preliminary treated surface	Preliminary treated surface	The surface is not preliminary treated
300	0,5	0,3	0,1
350	27,0	13,0	7,0
400	69,0	49,0	31,0

Besides, it was found out that when the coating was applied onto the samples not etched in the hydrochloric acid, the coating thickness was 1.5-2 times less, than in case the samples had preliminary treated surfaces.

The results obtained testify to the following. The temperature of 350°C is the most acceptable one to produce good-quality coatings in vacuum during 1 hour in the mixture that contains 50 and 80% of zinc, respectfully. Thickness of the coatings is from 13 up to 27 microns.

So, **it is possible to produce high quality coatings in vacuum at 350°C;** it is 100°C less than in case of application in the open environment. **However, the uniformity of the coatings is not good enough** because of the low thermal conductivity of the environment.

Zinc Plating in the Inert Environment (Argon, Nitrogen).

When zinc plating was done in vacuum, it was found out, that it is impossible to produce uniform coatings there because of the low thermal conductivity of the environment. At the same time, the increase of the air pressure results into the zinc powder oxidation. So, to improve the thermal conductivity of the mixture, on the one hand, and to prevent zinc powder oxidation, on the other hand/4/, it was decided to implement argon and nitrogen.

Back

Table 3 gives the data on the dependency of the coating thickness on argon pressure and the time of zinc plating at 350°C.

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Table 3. Dependency of the coating thickness on argon pressure
(zinc content - 80%)

Time, min	Coating thickness, µm, at the pressure of argon, Hg mm	
	200	650
20	2,9	5,1
40	6,0	9,7
60	9,9	14,6

As it is evident from Table 3, when the pressure of argon is reduced from 650 Hg mm to 200 Hg mm, the coating thickness decreases by 1.4 times on average. It is explained by degradation of the powder thermal conductivity under these conditions.

Thus, in an argon or nitrogen environment the obtaining of high- quality uniform coatings of any thickness is possible/4/.

Corrosion Tests .

The experiments were done using the samples made of different steel. The samples of analogous thickness were coated with diffusion zinc, galvanic zinc and cadmium (cyanide solutions) to compare them all. The experiments were made under conditions imitating tropical climate and salty mist. Corrosion resistance was evaluated visually until the first corrosion point appeared. The tests under tropical conditions showed that not a single sample showed any corrosion signs. Diffusion zinc coating became a little darker, the galvanic zinc coating was covered with colors of bluing, and the galvanic cadmium coating became dull instead of shiny. Table 4 gives the results of the tests of the coatings in the salt mist.

Table 4. Corrosion tests in a salt mist.

The material of the sample	**Type of the coating**	**Coating thickness, µm**	**Average time before the first corrosion sign appeared, h**
У8	Zn dif	3 - 6	449
		15 - 20	929
30 ХГСНА2ВД	Zn dif	15- 20	848
50 ХФА	Zn dif	15- 20	1087
Ст.45	Zn dif	3 - 6	984
		15- 20	1104
65Г	Zn dif	3 - 6	936
		15- 20	1203
30 ХГСА	Zn dif	3 - 6	473
		15- 20	821
У8	Cd galv	8-10	1150

Back

		15 - 20	1271
У8	Zn galv	8-10	209
		15 -20	264

So, protective capabilities of the 3-6 µm diffusion zinc coating makes up 450 - 900 hours, when it is 15-20 µm, it protects during 820 - 1200 hours, and the galvanic cadmium coating 8-10 µm thick and 15-20 µm thick protects during 1200 hours.
We may also draw a conclusion, that iron-and-zinc alloy produced during the diffusion zinc plating, is much more stable under salty mist conditions as compared to the galvanic zinc.

Mechanical Properties Study.

The experimental results are given in Table 5.

.Table 5. Dependence of the mechanical properties of steel 50
on the time of the diffusion process at 350°C.
(average value of 5 samples)

Time, min	**Thickness, µm**	**Parameters to be analyzed**		
		σ_B, H/mm^2	$\sigma_{0,2}$ H/mm^2	δ_5 %
0	0	1690	1570	9,5
8	4	1350	1270	10,0
22	13	1300	1230	12,0
40	20	1250	1170	12,5

It was found out, that when the zinc plating temperature is 350ºC, the structural limit and yield strength of steel 50 are reduced by 16%; the mechanical properties of 20XH3A steel stay the same. When the zinc plating temperature is increased up to 400ºC, the structural limit and yield strength of 20XH3A steel are decreased by 13%.

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CONCLUSION.

In summary it is possible to mark, that the developed diffusion zinc coating technology for structural steels satisfies to those requests, which were formulated before the beginning of work.

The technology ensures obtaining of uniform zinc (zinc- iron) coating, which anticorrosion properties do not concede galvanic cadmium coating and essentially exceeds galvanic zinc one. The technology is simple, ecology pure, and cheaper than cyanic cadmium plating. In an outcome of simple additional processing (for example, additional phosphate coating) corrosion stability of cover, especially of laminas (5-10 microns) essentially will increase.

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