THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^{0}. 2 – 2007, ISSN 1453 – 083X

IMPROVEMENT OF STEEL SHEET CORROSION RESISTANCE BY THERMIC COVERAGE METHOD WITH ZINC- ALUMINIUM ALLOYS

Maria VLAD, Olga MITOSERIU,
Stela CONSTATINESCU, Emil STRATULAT
“Dunarea de Jos” University of Galati
email: mvlad@ugal.ro

ABSTRACT

The paper presents the main physico-chemical characteristics (viscosity and superficial tension of zinc-aluminium liquid alloy in view of carry out protected layers on steel sheet with very good properties by thermal method. Tacking into account of experimental researches have been analysed alloy melted conditions and metallic covering according established technology

KEYWORDS: alloy, viscosity, superficial tension, corrosion

1. Introduction

Out of all protection coatings Zinc- coated plates are the most widely used.

Zinc coatings can be achieved by immersion into melt bath for film thickness of 20-50 μm or electrolitically for film thickness down to 10 μm .

The increased aggressiveness of the environment, the emergence of new fields of applications (automotive industry, chemistry, construction materials, etc) along with the world market price evolution and scarcity of some raw materials sources have all called for the development of Zn and alloys protection coats that basically form the Zn -Al binary system.

2. Experiments and results

The experimental researches are focused on determining physical-chemical properties of Zn-Al melts so as to establish a technological flow for the thermal plating/coating.

2.1.Zn - Al melt viscosity for different percentages of Al in Zn

The dynamic viscosity of Zn- Al alloys having 1 to 10 % Al, has been determined by Mayer Svidkovski method.

Viscosity variation vs. Al- content and temperature is illustrated in figure no.1

The experimentally determined values are consistent with those obtained by relation:

$$\eta = \eta_{Zn}\frac{\%Zn}{100} + \eta_{Al}\frac{\%Al}{100}$$

where: $\eta_{Al,Zn} = \eta_0$ exp (Ev/RT); η_0 - is pure metals viscosity, Ns/m^2; Ev – viscous flowing activating energy, J

Ev = 3,8 RTf
R = 8,3144 J/mol.K;
Tf – metal boiling temperature, K;
T – temperature at which measuring is performed, K.

The melt viscosity decreases with increased Al content and temperature (figure no.1); the decrease is severer within the concentration range 0-5% Al.

Decreased viscosity results in higher fluidity and further to the discharge of exceeding alloy thus improving coating quality

The viscosity of the Zn –Al alloy is also influenced by the presence of some small amount of alloying elements. This is better highlighted when such alloying elements are poured into the melt as pre-alloy, not in metal state.

The non- homogeneity of the alloy, due to the presence of metal inclusions in the metal bath, can be assessed through chemical or metallographic analyses.

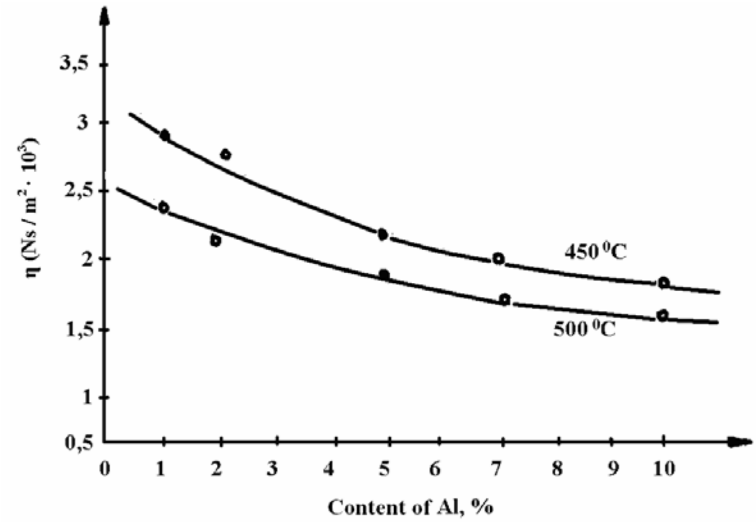

Fig 1. *Viscosity variation function of aluminum and temperature*

Fig.2 illustrates the microstructure of a sample from a homogenous bath while Fig. 3 shows the microstructure of a sample from a non homogenous bath.

The admissible Fe content in the melt alloy is max.0,2% because higher amounts form inter-metallic compounds of Fe with Zn (Fe Zn_3 , $FeZn_7$ etc).

The Fe and Zn compounds float away with the melt alloy and therefore the alloy viscosity increases.

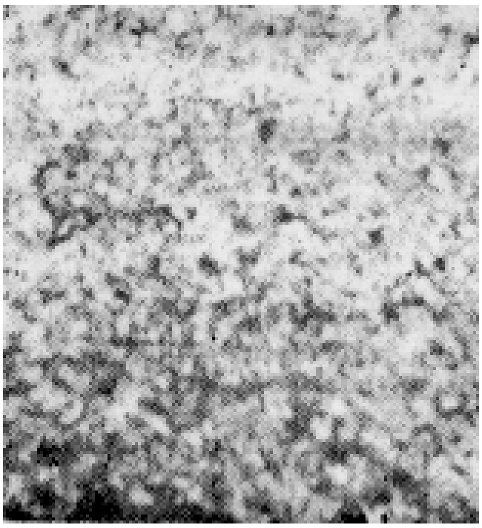

Fig 2. *Microstructure of the sample from the homogenous baths of ZnAl 7 with 0,08% Sb and 0,15% Si. Magnification 200X*

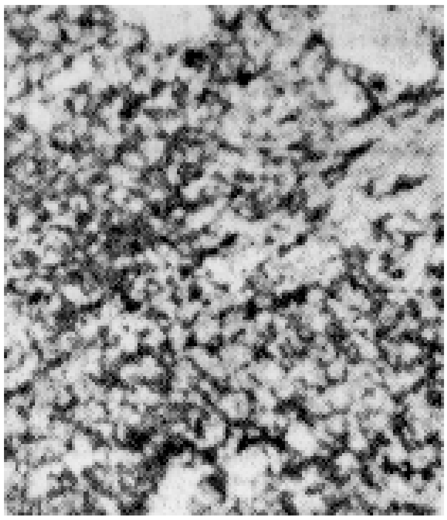

Fig 3. *Microstructure of the sample from the non homogenous baths of ZnAl 7 with 0,08% Sb and 0,15% Si. Magnification 200X.*

2.2. Superficial tension

With Zn-Al alloys the surface stress has been determined by the method of max air-bubble pressure. From a comparative study of the equilibrium diagram for the system Zn – Al, fig. 4, and the curve standing for the superficial tension vs. composition variation at a temperature higher by 50 ^oC than the melting temperature of composition alloy, fig. 5, it can be seen that between the remarkable points of the equilibrium diagram there is a certain correspondence (max is for eutectic, min for eutectoid).

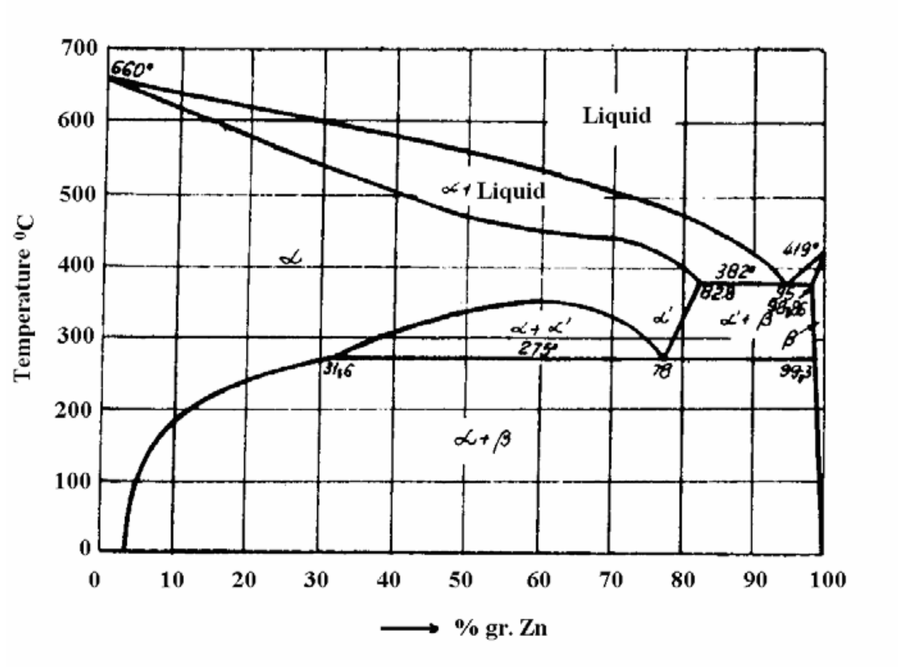

Fig 4. *Equilibrium diagram Al-Zn*

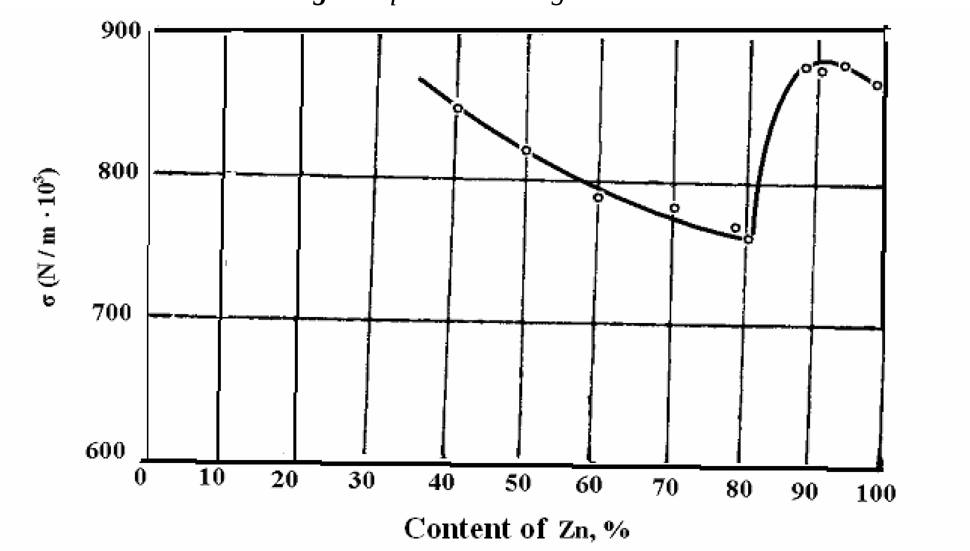

Fig 5. *Superficial tension function of composition variation and temperature*

In general, the alloying elements having a generalized moment higher than the generalized moment of the base metal (solvent) increase the alloy superficial tension.

For the generalized moment $\left(m = \dfrac{e \cdot z}{r}\right)$ of both Zn and Al the following values have been determined:

for Al; $m=9{,}61.10^9$;
Zn; $m=4{,}33.10^9$.

According to the diagrams in figs. 5,6, the alloy superficial tension decreases with increased temperature at certain concentrations of Al in Zn (up the eutectic composition of 5% Al in Zn) and at higher Al concentrations, the alloy superficial tension increases.

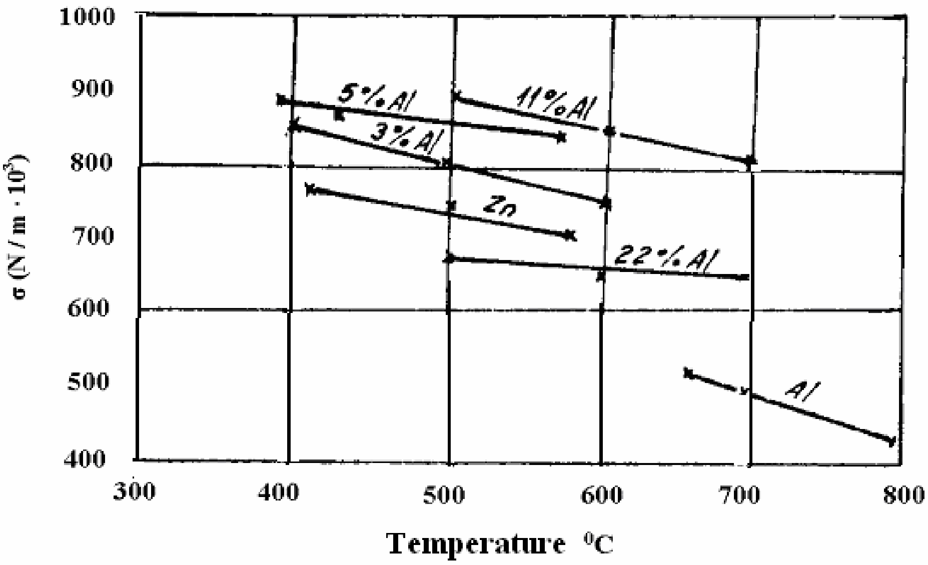

Fig 6. *Superficial tension vs. temperature variation at varied contents of aluminum*

With higher concentrations of the second alloy component, the basic molecular field is significantly modified which implies a modification of the number of free electrons assigned to one atom and the generalized moment of the metal dissolved is a function of the solvent metal concentration.

At high values of the superficial tension, the coating surface seems smooth.

Since for metallic coatings a certain temperature is imposed, the superficial tension can be increased by adding small amounts of Sb or max 0,2% Pb.

2.3 Influence of alloying elements in the metal bath on the coating quality

The Zn- Al alloys used for the coating achieved under the above mentioned conditions were prepared by re-melting the pre-alloys previously made in a (flame or electrical crucible) furnace. When pre-alloys are made, part of the Zn is melted (rectified Zn) and the melt thus obtained is overheated up to 500 °C Al is poured into it and everything is stirred and finally the remaining Zn is added acc. to the desired chemical composition.

The melt is kept at 475 ^{0}C for 10 min., the slag is removed, dezoxidation can be made, if applicable, with 0,03%-0, 8% Mg while keeping on stirring, slag is further removed, and finally the melt alloy is poured into ingots for further re-melting.

Taking into account the strong tendency of any Zn based alloy to inter-crystalline corrosion and grooves formation due to the presence of Cd, Sn, Pb and Fe, it is suggested to employ as pure as possible and rigorously controlled Zn and Al as raw materials. It is forbidden to overheat pre-alloys containing max 10% Al over 480 °C because otherwise a decreased oxidation of the alloy is found out along with lower physical – chemical properties of the coating.. In order to improve the coating technology and the qualities of the protection alloy film , the influence of different metals added in small amounts to the Zn-Al bath was studied. The presence of Pb amounts higher than 0 1% and Sn over 0.02% increase the coating tendency to exfoliations. Small amounts of sodium and berilium increase the melt surface stress and 01% Mg increase the coat corrosion resistance. The most efficient micro-alloying elements proved to be Si , Sb and Mg.

The max. 1% Si in Al added to the bath modifies the microstructure, improves the appearance, provides a smooth shiny texture, decreases the thickness of the inter-metallic layer.

Aluminum, an alloying element to be found in larger amounts than the others, favorably influence the coat quality as regards adherence, corrosion resistance, coating thickness, coating weight, while decreasing the inter-metallic film thickness.

2.4 Determining the technological flow to make Zn-Al alloy coatings

The laboratory and industry experimental researches on the different possible variants made it possible to establish the technological flow for the thermal achieving of Zn -Al alloy coated steel plates by immersion into melt while the main stages of the flow and the associated working parameters are given in table 1.

Table 1. *Determining the technological flow to make Zn- Al alloy coatings*

Substances used in composition	Temperature ^oC	Time, s
NaOH-80-100 g/l		
Na_2CO_3-40 g/l	80-90	1800
Na_2SiO_3-5 g/l		
NaOH-30-40 g/l		
Na_2CO_3-40-50 g/l	80-90	1800
Na_3PO_4-5 g/l		
	80-90	
H_2SO_4 15-20% sau HCl 15%	40-50 20	1800
$ZnCl_2$;NH_4Cl 6,6:1		40-60
$ZnCl_2$:NH_4Cl 12:1		40-60

Due to the high aluminum affinity to oxygen, slag is formed on top of the alloy; the slag grows and affects the coating quality with increased amount of Al.

Table 2. *Composition of fondants*

Composition, %									Temp. ^oC
Na_2SO_4	**$MgCl_2 . 6H_2O$**	**NaCl**	**$ZnCl_2$**	**KCl**	**$KHSO_4$**	**Na_3AlF_6**	**NaF**	**CaF_2**	
-	55	-	-	34	-	-	-	11	500
-	17	25	-	-	50	-	8	-	550
35	20	20	-	10	-	15	-	-	480
62	-	12,5	-	12,5	-	13	-	-	450
-	-	-	-	40	-	-	-	60	S
-	-	10	-	10	-	-	-	80	S
-	-	-	-	-	-	80	-	20	S
-	-	-	-	-	-	100	-	-	S
-	-	-	100	-	-	-	-	-	313

Table 3. Experimental results regarding deposition quality.

Technological flow	Temperature, ^oC	Al,%	Si,%	Sb,%	Deposition quality		
					Aspect	**Weight**	**Adherence**
$ZnCl_2$:NH_4Cl 87:13	450	1	-	-		Weight 260-430 g/m^2	C*
	450	3	-	-	shiry		C
$ZnCl_2$:NH_4Cl 10:1	430	6	-	-			C
	460	10	-	-			C
$ZnCl_2$:NH_4Cl 87:13	450	1	-	0,02			C
	450	3	-	0,02			C
$ZnCl_2$:NH_4Cl 10:1	430	6	-	0,02			C
	460	10	-	0,02			C
$ZnCl_2$:NH_4Cl 87:13	450	1	-	-			C
	450	3	-	-			C
$ZnCl_2$:NH_4Cl 10:1	420	6	0,2	-			C
	460	10	0,2	-			C
$ZnCl_2$:NH_4Cl 87:13	450	1	-	0,02			C
	450	3	-	0,02			C
$ZnCl_2$:NH_4Cl 10:1	430	6	0,2	0,02			C
	460	10	0,2	0,2			C

* C=good

3. Conclusions

1. Viscosity and superficial tension have been determined for different temperatures and aluminum contents in the alloys used to thermally prepare metallic coatings;
2. Experimental results regarding steel plate coatings from Zn-Al alloys have allowed for a suitable technological flow to be established;
3. Elements of Si and Sb micro-alloying at low concentrations decreases the alloy viscosity so that metallic melt fluidity is improved and thinner films can be obtained;
4. The quality of the protecting layers has been assessed in terms of aspect, weight and adherence to the base metal

References

[1]. Muizeh, K. s.a. In: Hutnik, Polonia, nr.2, pp. 34., 1981
[2]. Schulz, D.W. In: Neue Hűtte, R.D.G., nr.6, pp. 202., 1982
[3]. Junker, H.L. si Korner, W. In: Metallurgical Plant and Techn., S.U.A., nr.3, pp.59, 1983
[4]. Redsel, U. In: Metallurgical Plant and Techn., S.U.A., nr.4, pp. 72, 1984
[5]. Oprea F. s.a. Teoria proceselor metalurgice, Bucuresti, Ed., did. Si ped., 1978.
[6]. x x x Brevet de inventie nr. 77078811, S.U.A.< 4056366, India.
[**7]. Sivan, V.** In: Metal Finishing, Japonia, noe. pp. 21, 1980
[8]. Koyuhiro, T. s.a. In: Jap. Metal Finishing., Japonia, 33, nr.10, pp.516, 1982
[9]. Peisker P. In: Neue Hűtte, R.D.G., 6, pp. 205, 1982
[10]. Constantinescu,S., *Influence of manufacturing process on chemical and structural homogeneity of welded pipe sheets for tanks and vessels working under pressure.* “ Proceeding of the International Conference on Advances in Materials and Processing Technologies, 2001, Leganes, Madrid, Spain, p.57.