Metallurgical Factors Effecting External Corrosion of Tinplate Cans in Chloride Environments

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1. INTRODUCTION

Tinplate is produced either by hot dipping a clean sheet of steel into a molten bath of tin or by electro-depositing tin onto steel. The plate, in the latter case, is later subject to a short heating process known as "reflow". Therefore, the tin plate, regardless of its production route, will consist of at least 4 distinct layers, oxide film, the outer most, free tin, intermetallic $FeSn_2$, and lastly the steel substrate. Tin forms various types of alloys with iron according to Figure 1.

Subsequently, tin and steel are in perfect electrical contact. Each one can influence the corrosion of the other. There is also a layer of $FeSn_2$ intermetallic compound between the two layers and this fortunately plays a positive role in the performance of food cans. Tin will respond to exposure by growing an oxide film which normally does not affect its appearance significantly. On the other hand, steel will readily corrode in the presence of oxygen and moisture. This leads to the production of red rust at discontinuities in the coating. These may be inherent pores in the coating or sites of mechanical damage such as scratches, or scrape marks. Since tin is more noble than steel in normal environments, it cannot protect the exposed steel. The corrosion is more prorounced as the tin coating weight is reduced. Therefore, the most important factor is probably the quality and thickness of the tin coating and/ or lacquer where one is applied.

The number of pores for a unit area generally increases exponentially as tin coating thickness decreases, thus rendering thinner tin coating more prone to rusting than thicker coating weights. The most commonly used external coating weight for food cans is 5.6 gm/m^2, normally referred to as #50 plate. However some food packers also use #25 plate with a tin coating weight of 2.8 gm/m^2 in order to reduce the cost of the can.

Any operation which effects porosity and continuity of the coating, whether it be during handling, processing of tin plate or during can manufacturing and food packaging, can seriously affect corrosion resistance of the tinplate cans. The performance of stone finish tinplate (rough surface) shows a tendency to rust slightly more than does conventional bright finished plate having comparable tin coating. However the can life was proven not to be so affected. Beaded cans also tend to rust mainly on the peak where the tin coating is more subject to stress and damage, i.e. cracks on intermetallic layers.

Paper labels offer a certain amount of protection, but, so as not to promote corrosion, the paper used must be low in chloride and sulfate (<0.05% sodium chloride and <0.15% sodium sulfate) and the adhesive used should be non-hygroscopic.

Cooling water, used in processing, containing high chloride or sulfate concentration will encourage can corrosion. In general, the chloride level in cooling water is controlled not to exceed 10 ppm. However some cannerries allow the level to be 20-50 ppm. total chlorine, but these levels are not recommended. Corrosion is also increased by long

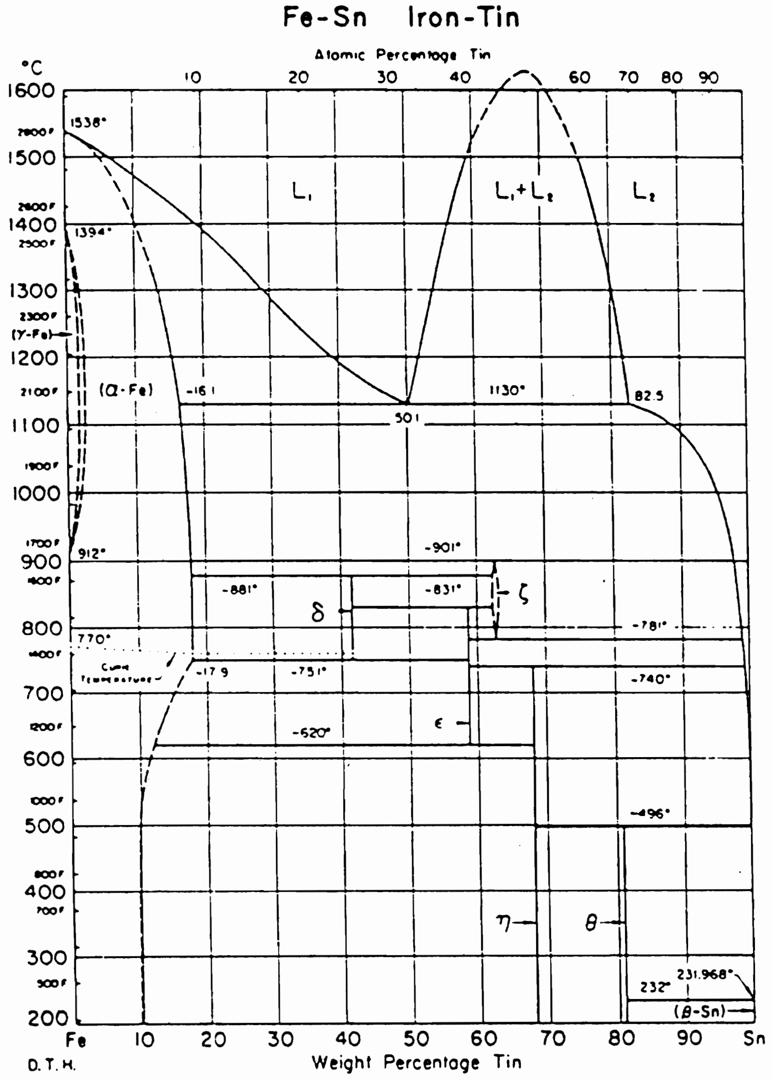

Figure 1. Phase diegram of Fe-Sn (Ref. 7)

contact time with cooling water. It is also recommended to dry cans as fast as possible prior to casing to avoid corrosion during storage. External corrosion of tinplate cans us frequently caused by unsuitable conditions for transport and storage. "Sweat- damage" for example, occurs during journeys from a temperate to a tropical zone. The corrosion process is further enhanced by presence of chloride in the atmosphere.

2. STANDARD TEST FOR TIN PLATES

Even though there are various methods of testing for corrosion resistance of tinplate, there is no single test which is universally accepted to predict the corrosion behaviour of the tinplate cans. The more common tests which were selected to characterise the tin plate in this study are outlined below.

2.1 Iron Solution Value

The iron solution value of tinplate can be determined on more heavily coating material by exposure to a solution containing sulphuric acid, hydrogen peroxide and ammonium thiocyanate. After 2 hours, the solution is analysed and the quantity of dissolved iron determined. The iron solution value (I.S.V.) is a porosity index for the tin coating but it is not suitable for todayûs thin tin coatings. Alternative methods have been developed for these coatings.

2.2 Tin Crystal Size

The tin crystal size of tinplate (TCS) refers simply to the size of the tin crystals that are revealed when the surface of the tinplate is lightly etched. The solution used contains hydrochloric acid, iron (III) chloride and sodium sulphide. After etching, the tinplate is compared visually to standard micrographs and given a grading. Smaller tin crystal size automatically means a greater density of grain boundaries per unit area. It is at grain boundaries that detinning occurs most rapidly and, therefore, tinplate with small tin crystals, tends to detin faster.

2.3 Coating Continuity Tests

Generally porosity of plated coating is inversely related to the coating thickness. As the tin coating on tinplate is very thin, it is not surprising that steel is exposed through this coating. Where this occurs, the unprotected steel is more susceptible to corrosion. A numerical or visual rating of the porosity is useful for comparing the coating quality of different tinplates and for assessing the susceptibility to corrosion, especially atmospheric corrosion. There have been many methods for assessing porosity of tinplate. Some of the more common routine tests are outlined below.

2.3.1 Ferricyanide

This consists of applying to the test sample a paper that has been soaked in a salt solution containing potassium ferricyanide so that the exposed steel is corroded. The iron dissolved forms blue spots on the paper and the result of a simple count of the blue spots may be related to a specified maximum or a grading system, such as that provided in ISO 1462.

2.3.2 Sulphur Dioxide Test

The principle of the test is that, in an atmoshere of nearly constant temperature, with relative humidity in the range of 70-90% and containing a small amount of sulphur dioxide, easily visible and fairly stable rust forms on the steel substrate at discontinuities in the tin coating. In the laboratory, the required conditions may be realised within a closed vessel maintained at constant temperature by the addition of a measured quantity of sulfuric acid to an excess of sodium thiosulphate solution.

This test may also serve as a rust-resistance test, in which case the test samples are not given a cleaning before the test is carried out.

2.3.3 Electrochemical Thiocyanate Porosity Test

In this test, two complementary measurements of porosity are made. These are the corrosion potential and the polarisation conductance. The measurements give values which correspond to an area of the exposed steel.

The corrosion potential of tin relative to a saturated calomel electrode in an ammonium thiocyanate solution is about -400 mV whilst the potential of steel is about -730 mV. The corrosion potential of tinplate will therefore depend upon the relative proportion of tin and steel at the surface.

3. EXPERIMENTAL PROCEDURE

3.1 Tinplate

The coating weight of tinplates used in this experiment were #100/#50. The #100 weight side is used for the internal surface of the can as it will be in contact with a more corrosive environment than will be the exterior. Attempts were made during its manufacturing to vary the tin crystal size and the thickness of the alloyed layer.

3.2 Cleaning

Prior to the corrosion test, the samples which had been taken from the central location of the supplied plates had to be cleaned and degreased. Its passivation layer was also removed. The following is a brief description of the cleaning and preperation of the test pieces.

i) The samples (5 x 5 cm) were degreased by immersing them in alcohol. They were later blow dried.

ii) The samples were then cathodically cleaned, at 4.0 Volts, for 3 minutes to remove the passivation layer.

The electrolyte was 1% Na_2CO_3. The samples were subseqently blow dried.

iii) To prevent the edge from corroding preferentially to the flat surface, transparent tape was applied to cover the exposed area of the steel.

iv) the cleaned samples were then ready for further testing.

3.3 Tests

The samples were first characterised by their tin crystal size and the weight of the alloyed tin layer. They were later subject to exposure tests (chloride, SO_2). Exposed steel areas and porosity were checked by I.S.V., and thiocyanate tests. Structure of the alloyed layer, taken by a SEM, is shown in photo 1.

For the chloride exposure test, the samples were hung in a glass jar containing brine solution. The salt content was 32 g/l, simulating sea water. The sample was left in the jar for 6 days before being removed for inspection.

Contrary to the chloride test, the SO_2 exposure test required less time. It was found that 19 hours was an optimum duration. Longer than this yielded such heavy corrosion product on the surface that valid comparisons were not possible.

4. RESULT AND DISCUSSION

Results of the tinplate characteristics are shown in Table 1.

Results for the I.S.V. and thiocyanate Test are shown in Table 2 and Table 3 respectively.

Results of the chloride and SO_2 exposure test are shown by photo 2, 3, 4 and 5. It was observed that

a) For chloride exposure of the #50 thickness, order of the corrosion severity was (sample number) 4, 2, 1, 5 and 3, with 3 being the most severe. For this group, as the free tin layer was relatively thin, the alloyed layer seemed to offer a major resistance to the chloride attack. This is supported by a decrease in corrosion rate as the alloyed layer thickness is increased.

On the other hand, the alloyed layer seemed to have played a lesser role in protecting the steel substrate for the #100 plate as its thickness was not indicative of the corrosion severity (most severe 3, 4, 1, 5, 2 least severe).

b) As far as the grain sizes are concerned, no conclusion can be drawn as yet. This could be attributed to the insignificant change in the tin crystal size of samples tested in the experiment.

c) Simulation of lacquer curing (heating at 190^{O} C for 10 minutes) showed a significant increase in the corrosion severity (Photo 5) of the tinplate.

d) The I.S.V. test as shown in Table 2 show inconsistency within itself. The bottom side (#100) of samples number 1, 3 and 5 exhibit higher I.S.V. which is contrary to the coating weight. Within a transverse axis, the I.S.V. vary unsystematically from the operator side to the drive side.

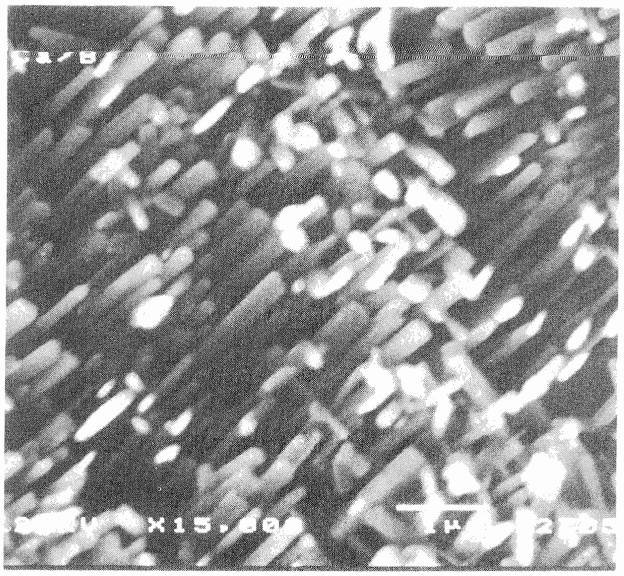

Photo 1 Electron-micrograph showing typical alloye layer structure (20 kv, 15000 X)

e) The thiocyanate value test showed more consistent and predictive results. All bottom values (#100 thickness) were lower than those of the top layer (#50 thickness). Variations within a sheet were much superior to results obtained from the I.S.V. test. Hence the thiocyanate seems to be a more promising test for evaluating the tinplate quality.

f) As far as correlating the I.S.V. and the thiocyanate tests to the SO_2 and the chloride exposure tests are concerned, no conclusion can be discerned at the present time.

5. CONCLUSION

Studies of corrosion behaviours of tinplate in a chloride environment, in relation to metallurgical properties, were conducted. It was found that, for

Table 1 Tin crystal size and allayed tin weight of the tinplate use in the experiment. (DR. stands for driver side, C for center and OP. for operator side.)

Sample Number	TCS	Side	Alloyed Tin (g/m ^{2})			
			DR	C	OP	Ave
1	7-8	#50 #100	0.88 0.77	0.87 0.81	0.95 0.88	0.90 0.82
2	7	#50 #100	1.19 1.17	1.12 1.10	1.17 1.16	1.16 1.14
3	7-8	#50 #100	0.60 0.39	0.58 0.35	0.56 0.39	0.58 0.38
4	9	#50 #100	1.16 1.10	1.05 1.02	1.11 1.02	1.11 1.05
5	8	#50 #100	0.65 0.53	0.61 0.42	0.63 0.45	0.63 0.43

tinplate with tin coating weight #50, the free tin offers less significant resistance to the chloride corrosion than does the intermetallic layer. The reverse is true for the #100 coating weight. The chloride test, though requising more time to conduct, is a more pertinent test to a real situation. The standard industrial tests, conducted in this experiment, show no viable consistency with the chloride test. Tests are being conducted to revaluate the test results. Further work is planned for site exposure tests in a marine atmosphere. Internal corrosion behaviours of the tinplate and its activity with various fruit acids are to be conducted. Alloy-tin couple test, electrochemical polarization measurment, and ITRI porosity tests will also be included.

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Table 2 Results of the I.S.V. test (T = Top side #50 thickness, B = Bottom side #100 thickness, OP = operation side, C = Center and DR = Driver side)

Condition	Coating Weight	I.S.V. ($\mu g/m^2$)			
		OP	C	DR	Av.
1	#50	0.06	0.04	0.12	0.07
	#100	0.08	0.16	0.12	0.12
2	#50	0.18	0.16	0.14	0.16
	#100	0.08	0.12	0.10	0.10
3	#50	0.08	0.10	0.12	0.10
	#100	0.12	0.10	0.10	0.11
4	#50	0.08	0.12	0.10	0.10
	#100	0.10	0.08	0.06	0.08
5	#50	0.08	0.06	0.08	0.09
	#100	0.08	0.10	0.08	0.09

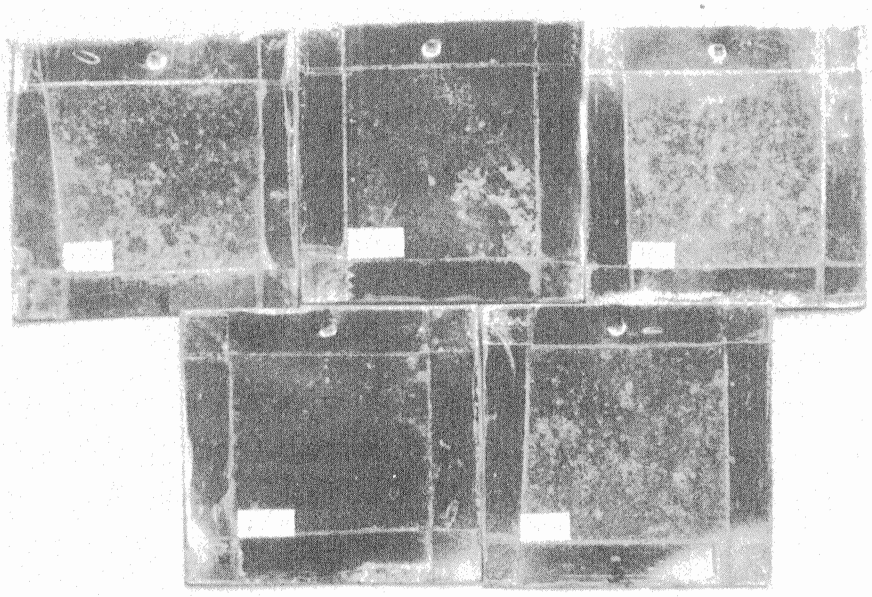

Photo 2 Chloride exposure test sample pieces. Coating thickness #50 Exposure time 6 days.

Table 3 Results of the Thiocyanate test.

Condition	Coating Weight	Thiocyanate Value (mg/dm ^{2})			
		OP	C	DR	Av.
1	#50	1.481	0.365	0.333	0.816
	#100	0.091	0.091	0.079	0.087
2	#50	0.683	0.804	0.512	0.666
	#100	0.091	0.091	0.091	0.091
3	#50	0.139	0.182	0.212	0.178
	#100	0.018	0.018	0.018	0.018
4	#50	0.242	0.363	0.163	0.256
	#100	0.030	0.043	0.030	0.034
5	#50	0.151	0.169	0.375	0.232
	#100	0.030	0.024	0.018	0.024

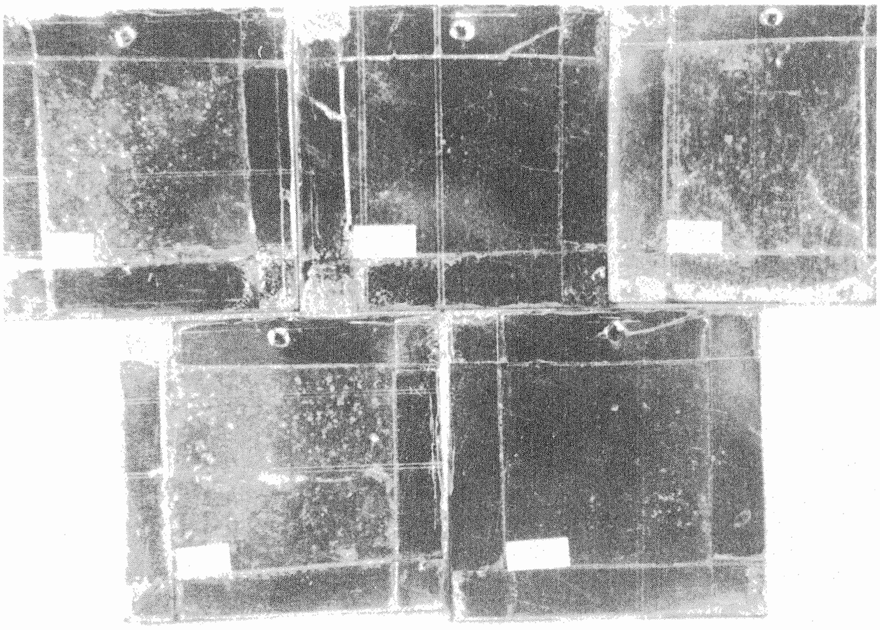

Photo 3 Chloride exposure test sample pieces. Coating thickness #100. Exposure time 6 days.

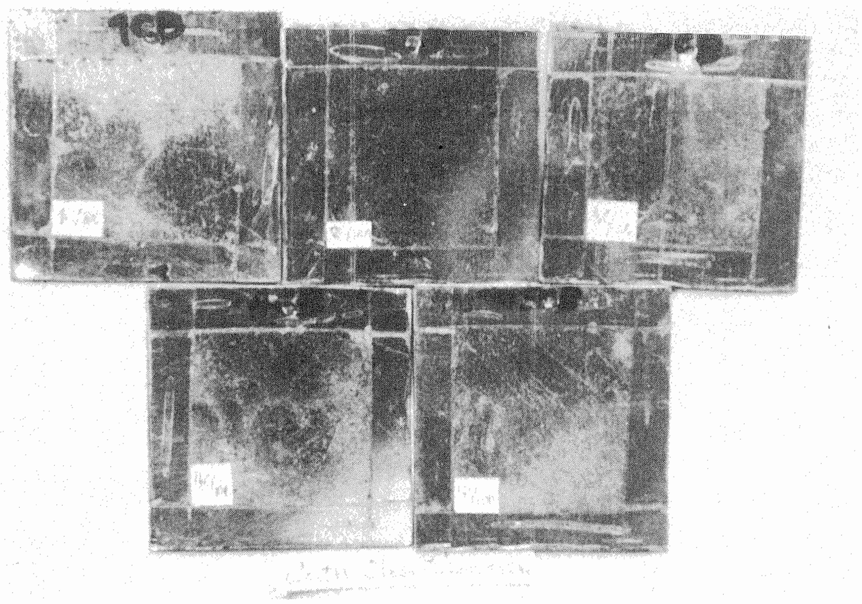

Photo 4 Sulfur dioxide test sample pieces. Coating thickness #50. Exposure time 19 hrs.

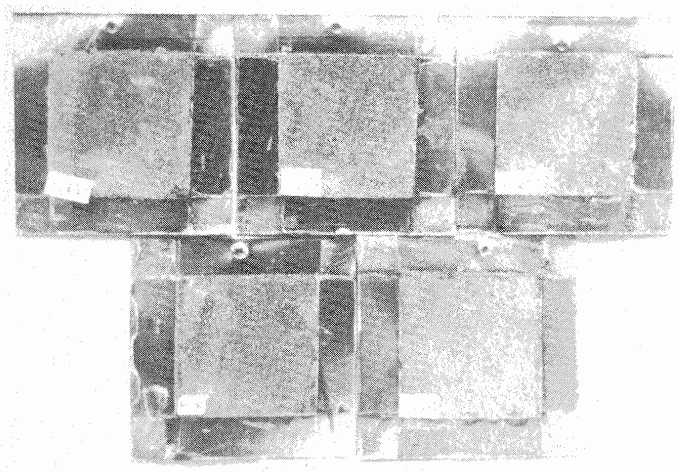

Photo 5 Sulfer dioxide test sample pieces baked at 190°C. 10 min. Coating thickness #50. Exposure time 19 hrs.

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