Galvanizing reactive steels

a guide for galvanizers and specifiers

International Lead Zinc Research Organisation

Contents

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Introduction

A hot dip galvanized coating on steel, produced under typical commercial conditions, is expected to be smooth, shiny and frequently with a crystalline 'spangle' pattern on the surface (Fig. 1). The cross section of such a coating (Fig. 2) shows that it is made up of a series of largely coherent iron-zinc alloy layers, topped by a layer of unalloyed zinc. This structure provides the hot dip galvanized coating with its unique combination of toughness and corrosion resistance. However, from time to time all or part of the steel being galvanized reacts very rapidly with the zinc producing a coating which is dull grey in appearance, excessively thick, brittle and poorly adherent. Such coatings have two broad types of structure shown in cross section in Figs. 3a and 3b.

1.
Surface appearance of a normal galvanized coating.

(Photo courtesy of the American Galvanizers Association, 1997.)

2.
Cross section of normal galvanized coating.

3a.
Cross section of a Sandelin coating.

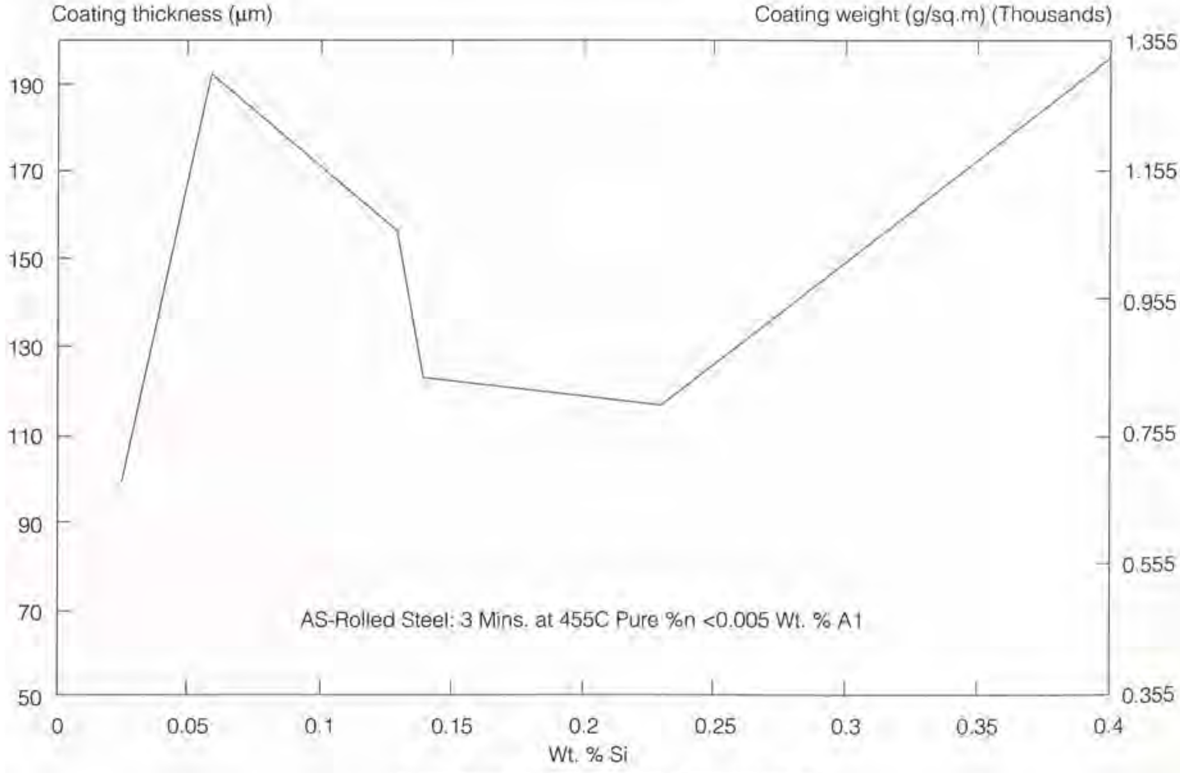
3b.
Cross section of a Hyper- Sandelin coating

High reactivity galvanizing - although recognised for well over 50 years - now occurs more frequently. This has been associated with changes in steelmaking practice, and particularly with the more widespread use of continuous casting. Continuous cast steels are generally treated with silicon. Whilst silicon has been implicated in high reactivity for many years, it is also recognised that it is not the only factor involved.

Researches aimed at explaining steel reactivity in galvanizing have suggested the influence of a wide range of factors including steel composition, surface preparation, and bath composition. However, no satisfactory explanation of the phenomenon was possible up to 1990: although the need for a comprehensive investigation had become more urgent. In that year a major research was started, with the support of the International Lead Zinc Research Organisation, at the University of Wales (Cardiff, UK). The results of 4 years intensive work have established a definitive reactivity classification for a broad range of steels, including all those normally requiring to be galvanized. The results do not enable the galvanizing of a reactive steel to be controlled.

However they indicate comprehensively those ranges of steel composition which can be expected to give problems in galvanizing, those where inconsistencies may occur and - of course - the much broader range of compositions where a tough durable coating will be produced and which will give many years of satisfactory service.

This document provides a short review of the background to the project, describes the techniques used in the research and summarises the results. Most importantly it also sets out the significance of those results in a form which will help the engineer/designer and the galvanizer to appreciate the circumstances in which problems of steel reactivity may arise and the much more frequent situations where hot dip galvanizing will be completely trouble-free.



4. The Sandelin curve

Taken from: D. Horstmann in Proceedings of Galvanizing of Si-Containing Steels, Liege, Belgium, 1975 (ILZRO&CRM)

Background

A literature survey on the reasons for this behaviour undertaken in 1990[1] cited more than 100 references - an indication of the many efforts over at least the last 55 years which have aimed to find the reasons for this behaviour. Of these investigations that of Sandelin[2] has to date been the most influential.

Sandelin's work was interpreted by later authors as indicating that the phenomenon arises as a result of the silicon content of the steel. The 'Sandelin reactivity curve' (Fig. 4 at foot of facing page) shown by Horstmann in 1976 has perpetuated that view, indicating a reactivity peak in the region 0.05-0.125 Si lower reactivity in the range 0.15-0.25 Si with reactivity increasing rapidly with Si above 0.25%.

In fact a re-interpretation of the Sandelin results[3] showed that the original experiments had in fact taken other factors into account, particularly the role of phosphorus, which had earlier been reported by Bablik in his book[4] first published in English in 1950.

Subsequent work by Pelerin et al[5] formed the basis of a French standard for galvanizing steel (Fig. 5) which was issued in 1986; work by Hansel[6] and Horstmann[7] formed the basis of a galvanizability standard (Fig. 6) produced by Beratung Feuerverzinken (the German Galvanizers Association). Both these standards express galvanizability in terms of silicon and phosphorus content of the steel, although the ranges and ratios differ somewhat.

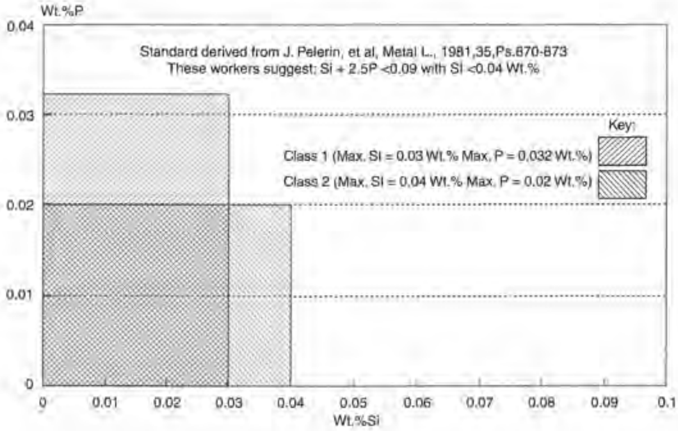
Other studies over the years have also implicated carbon, nitrogen and several other elements. It has also been suggested that the surface composition - rather than the bulk composition - controlled reactivity.

Whilst steel composition undoubtedly seems to be most important, some researchers suggested that process factors are involved - pickling conditions, dipping temperature and time - as well as the degree of cold working, prior annealing and steel geometry.

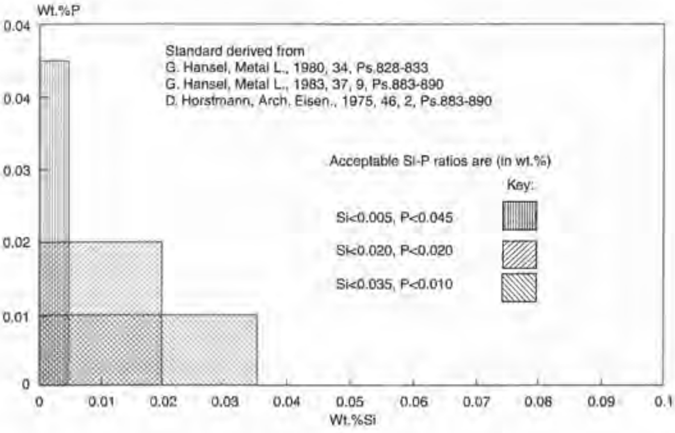
The situation is further complicated by the fact that supposedly 'safe' steel compositions, galvanized under 'correct' conditions occasionally produce the coatings characteristic of 'reactive' steels.

By 1990 it was therefore clear that although voluminous, the information available was incomplete, sometimes inconsistent and occasionally contradictory. A comprehensive, methodical study of all the potential factors involved in reactivity was needed to set the record straight and to reassure both designers and galvanizers about the extent of the problem.

5. French standard for galvanizability of steels NF. A 35-50



6. German industry document on galvanizability



Scope of research

To ensure that the work really covered all the possibilities raised by earlier studies, a very wide range of factors were examined for their effect on the galvanized coating. These included:

- *steel bulk compositions* - covering silicon, phosphorus and the other elements frequently encountered in steel as well as the 'tramp' or impurity elements.
- *surface compositions* - where these might have an effect on galvanizing behaviour.
- *annealing before dipping*
- *changing pickling acid*
- *extended pickling times*
- *stripping the coating and re-galvanizing*
- *surface roughness and surface stress*
- *hydrogen absorption*
- *'spalling' of coatings in the galvanizing bath.*

Galvanizing tests were carried out on a total of 172 different commercial steels. These steels covered those known to be 'high reactivity' producing unsatisfactory coatings; those known to be perfectly satisfactory; and those giving intermittent trouble.

The intention throughout the researches was to produce coatings using conditions comparable to those encountered in industrial galvanizing, but with very close control to avoid the variability which is inherent in industrial practice.

Meticulous examinations were made of the coatings produced and where appropriate of the steel itself, using both conventional metallographic techniques - sectioning the samples, polishing and examining them under a microscope - and a series of sophisticated analytical techniques.

Because of this very wide range of factors which had been claimed to have an effect on the coating, a great deal of effort was involved in finding out just which factors really did influence the coating formed and, *importantly, which did not!*

Test pieces

Quantities of each steel sufficient for the preparation of the required test samples were provided by steel companies, galvanizers and by members of the International Lead Zinc Research Organisation (ILZRO).

To ensure maximum consistency and comparability of the results, specimens were made 20mm by 100mm and between 2 and 5mm thick - generally the thickness at which the steel was supplied to the researchers.

All samples were degreased using a commercial alkaline degreasing agent, pickled in 20% HCl (except where other acids were used for comparison), fluxed with a standard zinc ammonium chloride solution and dried.

Galvanizing conditions

The test pieces were all dipped in a laboratory test rig designed to reproduce consistently conditions considered 'typical' in the galvanizing industry.

The zinc used was 'GOB' / Prime Western grade (EN 1179 Grade Z5; ASTM B6-87), saturated with iron and with aluminium controlled to below 0.002%. Dipping times were generally 2 mins, 6 mins and 10 mins at temperatures of 440, 455 and 470°C. After dipping the samples were withdrawn at a uniform rate and quenched within 4 seconds.

In industry, the galvanizing bath surface is skimmed periodically to minimise pickup of zinc oxides and flux residues on the surface of the coating. In a laboratory rig, access is much more difficult, and so nitrogen shrouding was used in many of the experiments, to reduce formation of oxides on the zinc bath surface. This technique had an important secondary benefit. The nature and thickness of the zinc iron alloy layers reflect the reaction which has taken place between the steel and the zinc, while the thickness of the top most layer is largely dependent on the rate of withdrawal of the steel from the bath, and not on the reactivity of the steel. By arranging the nitrogen shrouding in the form of a 'gas knife' which straddled the specimen as it emerged from the bath, a degree of control on the thickness of the free zinc layer was achieved. In turn this meant that one further cause of inconsistency could be removed, particularly in the gravimetric tests described below.

Measurements made

Bulk steel analyses - the starting point

Comprehensive analyses of all the steels were made using conventional spectrographic methods. The results are given in Appendix 1 on page 18.

Metallography - alloy layer development

The thickness and nature of the alloy layers produced were measured, using conventional metallographic techniques, on sections cut through the specimens.

Gravimetric tests - corroboration

Most investigations on galvanizing have been based on measurements of total coating thickness. However, because the reactivity of the steel controls only the alloy layers, the majority of the measurements in this research were made on the alloy layers.

Nevertheless it was thought advisable to corroborate the results of the alloy thickness measurements with those for the entire coating. This was possible because of the gas shrouding technique described above.

Standard stripping tests were carried out on a portion of the samples, using an inhibited hydrochloric acid. The results were consistent with those from the alloy thickness measurements.

Galvannealing - reaction rate determination

A novel method was used to obtain information on the rates of reaction involved in the development of the alloy layers. Specimens were prepared in the usual way, galvanized for 30 seconds at 455°C and withdrawn through the gas knife to produce a consistent free zinc layer of 10µm. After quenching the specimens were 'galvannealed' - heated in vacuum at 455°C - and the reflectivity of the surface measured.

Reflectivity decreases sharply as the reaction is completed, and all the free zinc is consumed by the growing alloy layers, enabling the rate of reaction to be calculated.

Steel surface analysis

Several different methods were used as appropriate to measure the surface compositions of a selection of the steels.

These comprised:

- Scanning electron microscopy - EDAX measurements on tapered sections of the steel, enabling the composition to be established to ±1% accuracy to a depth of 160µm .
- Secondary Ion Mass Spectroscopy (SIMS) gave a rapid semi-quantitative measure of surface composition.
- X-Ray Photoelectron Spectroscopy - the main tool - detects elements down to 0.1% and quantifies them above 0.5%.

A total of more than 6,000 test pieces were examined. Details of the analytical methods used, together with detailed results are given in the research reports[8]

Experimental work and results

The 6000 or so tests were carried out in several phases. Phase 1 examined the galvanizing behaviour of 59 different commercial steels available to the researchers at the time. In this phase the effects of silicon and phosphorus were determined, together with the supposed influence of surface, as opposed to bulk, steel composition. Phase 2 used a smaller but representative number of steels from the total number available. The effect of other elements in the steel composition was examined along with the several other factors said to influence galvanizing behaviour. Phase 3 extended the investigation of silicon and phosphorus to a large number of further steel compositions. Taken together the results enabled a new reactivity classification for steels to be established.

Phase 1

Galvanizing tests - alloy layer measurements

Samples were galvanized at the specified three dipping times and three bath temperatures. Average alloy layer thicknesses were then measured for each steel for each set of galvanizing conditions.

From these results, several general results emerged:

- *All the steels produced thinner coatings than would have been expected from earlier work on steels of comparable silicon and phosphorus content - possibly due to the lower levels of tramp elements in modern steels.*
- *Increased dipping time and temperature within the range studied always produced thicker coatings, although variability increases with temperature and dipping time. The overall increase is consistent with, but does not follow exactly, normal reaction kinetics (Arrhenius' Law). This is contrary to earlier observations where a higher temperature sometimes produced a thinner coating.*
- *A statistical analysis of the results showed that there is greater variability with thicker alloy layers than with thinner ones. These results suggested that this is due to the less compact structure of the coating and the tendency to produce outbursts on one of the alloy layers.*
- *The reactivity of steels in terms of Si and P content was broadly but by no means completely consistent with the earlier work of Sandelin and others* [2,4,5,6,7]*. These results could not be refined as the compositions of steels then available did not cover adequately the necessary ranges: further steels were subsequently obtained and tested in Phase 3.*

Corroboration through galvannealing tests

The galvannealing tests described earlier were carried out on all 59 steels.

Times to complete reaction of the 10µm of free zinc were substantially shorter on reactive steels than normal ones, corroborating the results of the galvanizing tests.

Surface analysis of steels

To test the reported influence of segregation of some elements to the surface of the steel, an exhaustive series of surface analyses were carried out on representative steels from the range of 59 compositions.

Preliminary scanning electron microscope/EDAX tests of 33 of the steels

These tests were carried out on samples pickled in the standard way.

The results showed that there were no concentrations greater than 0.5% of the elements Si, P, Mn and Al in the top 160µm of any of the steels.

Secondary ion mass spectroscopy

This method gives very accurate quantitative results. By using a special etching technique it can be used to make analyses at different depths below the surface, in steps of 20 Nm (= 0.02μm).

The results on the selection of steels tested showed no surface enrichment of any of the elements in question: they reflected accurately the bulk composition of the steel.

Phase 2

Galvanizing tests: Effects of C, N, Al, Mn & Ti

To study these effects, additional steel compositions were required, in addition to those tested in Phase 1. Twenty-six were made available and 15 representative compositions were chosen for study from steels additional to those tested in Phase 1. Thirteen were notionally 'safe' compositions in terms of Si and P, but with a matrix of variation in the levels of other elements. Two steels were nominally reactive. Overall the choice was designed to enable the effects of each of the elements to be deduced.

The results of microsection examination following the galvanizing tests showed that none of the listed elements had a major effect on reactivity

There is some evidence that Ti-killed steels appear slightly more reactive than comparable compositions without Ti.

These results are in contradiction to claims made in earlier work. It was however noted that when tests were carried out at the much shorter dipping time of 12 seconds the results showed that nitrogen could retard the reactivity and Ti enhance it. Interestingly these results also showed that a steel with 'unsafe' Si and P behaved normally at very short dipping times. Such results are of course not directly applicable to industrial practice.

Effects of pickling/surface chemistry

Four steels were chosen from the original 59 used in Phase 1. The experiments were designed to see whether any elements segregated into the residual scale left after pickling and whether this affected reactivity; to see whether the pickling acid used had an effect; to determine whether any other surface enrichment could be involved; and to see whether greater depths within the steel needed to be studied.

Pickling and surface analysis

As received specimens of the steels, which were largely free of millscale, were pickled either

- in HCl as usual or
- in 19% w/v sulphuric acid at 60°C,
  the same length of time (7 mins); or
- using an electrochemical pickle (details withheld by ILZRO).

After pickling, the specimens were washed, brushed lightly to remove any remaining 'smut', rinsed, dried and the surface analysis determined by XPS.

To determine whether the depth from the surface was important, argon etching of one steel composition was continued until 2 and subsequently 5μm of steel had been removed.

The results of all these tests (which are given in detail in the research reports) showed clearly that, whatever the pickling treatment, Fe, C, O and Ar (from the analytical equipment) were present along with traces of Na, K, Ca, Cl and S, (mainly from pickling). There was however no sign of enrichment in any of the other elements either in the residual pickling scale, or at the metal surface, with strong indications that the same was true down to a depth of 2 and 5μm.

Confirmatory galvanizing tests on these steels showed no change with the pickling regimes.

Pre-dip annealing of steels

Earlier work had suggested that annealing the steel before galvanizing could produce changes in reactivity. To test this, seven steels were chosen - six of them classed as reactive, and one as normal. Pairs of specimens were annealed in a partial vacuum at 580°C ± 10°C for 1 and 2 hours. One of each pair was then pickled, fluxed and galvanized (6 mins at 455°C) in the usual way. The other sample was pickled and the surface analysed. A third specimen was pickled, fluxed and galvanized in the same way without annealing, to provide a control.

Alloy layer thicknesses showed no change as a result of the annealing treatments.

Prolonged pickling/stripping and re-dipping

It has been reported from time to time that both steels expected to be normal and those expected to be reactive formed thicker coatings after prolonged pickling or when they were stripped and re-galvanized. It had also been suggested that stripping and re-dipping could solve the problems of excess brittle coatings. Three steels (two normal, one reactive) were chosen for a series of tests in which pickling times were extended to 72 hours before fluxing and galvanizing. Further samples were given up to 8 cycles of strip and re-dip.

Overall results showed that excess pickling or stripping and re-dipping increased coating thickness but there was no change from 'normal' structure to that characteristic of a reactive steel.

Results showed considerable scatter and inconsistency however, which could provide the basis for earlier observation of thinner coatings after strip/re-dip.

It was suggested that the inconsistent results observed meant that a combination of factors was important - possibly including increased surface roughness, variations in sub-surface composition and possibly hydrogen absorption.

Subsequent tests indicated that surface roughness could be discounted, and - given the depth of steel removed by alloying at each galvanizing dip - so could sub surface composition changes.

Surface roughness and residual stress

A series of tests were carried out on specimens which had been roughened by sand, grit and shot blasting. All these processes give rise to cold work on the surface and hence to residual stresses in the surface area. The extent of cold working was measured by x-ray diffraction. To separate the effects of roughness from those of cold work, some samples were annealed after blasting and before dipping to remove residual stresses.

The results showed that it was the surface roughness and not the residual stresses which affected the thickness of the coating. The greatest coating thickness was produced from the roughest surface (from shot blasting) irrespective of annealing, while sand blasting which gave the largest residual stress produced the least increase in coating thickness. The increases with surface roughness were more pronounced on higher reactivity steels.

Phase 3

In this phase, galvanizing tests were carried out on a further 93 commercial steels, using the same conditions as in the earlier tests. The matrix of compositions (Appendix 1) shows the wide range of silicon and phosphorus contents (0>0.55% Si and 0-0.12% P) and the wide ranges of impurity/tramp and other minor elements.

The rates of reaction were determined by metallography on cross sections of the samples, and the total coating thicknesses were determined by the gravimetric tests described earlier. A selection of the results is given in Appendix 2 on page 22.

Following these measurements, the types of coating produced in all the tests were grouped into three broad groups:

- **Normal reactivity or hypo-Sandelin:** (lower Si/P contents)
- **Sandelin steels:** (as has generally been defined)
- **Hyper-Sandelin:** (those with the highest Si/P contents)

These types of coating are illustrated in Figs. 2 and 3. on page 3.

The relationship between the silicon and phosphorus contents and the coating produced is illustrated in Figure 7a (a basic chart) and 7b (a 3-dimensional contour diagram). This relationship forms the basis of the new classification of steels, which is considered and explained in more detail in the following sections.

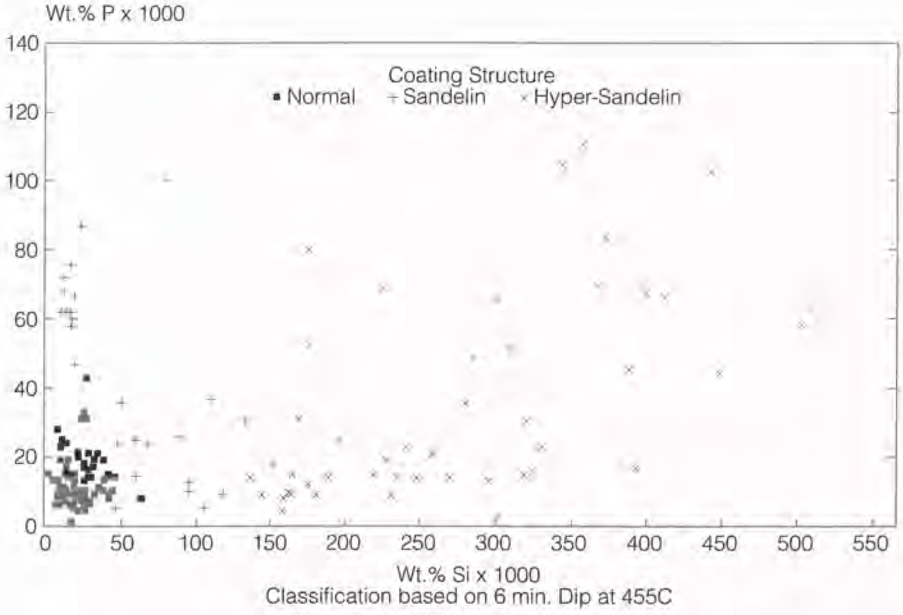
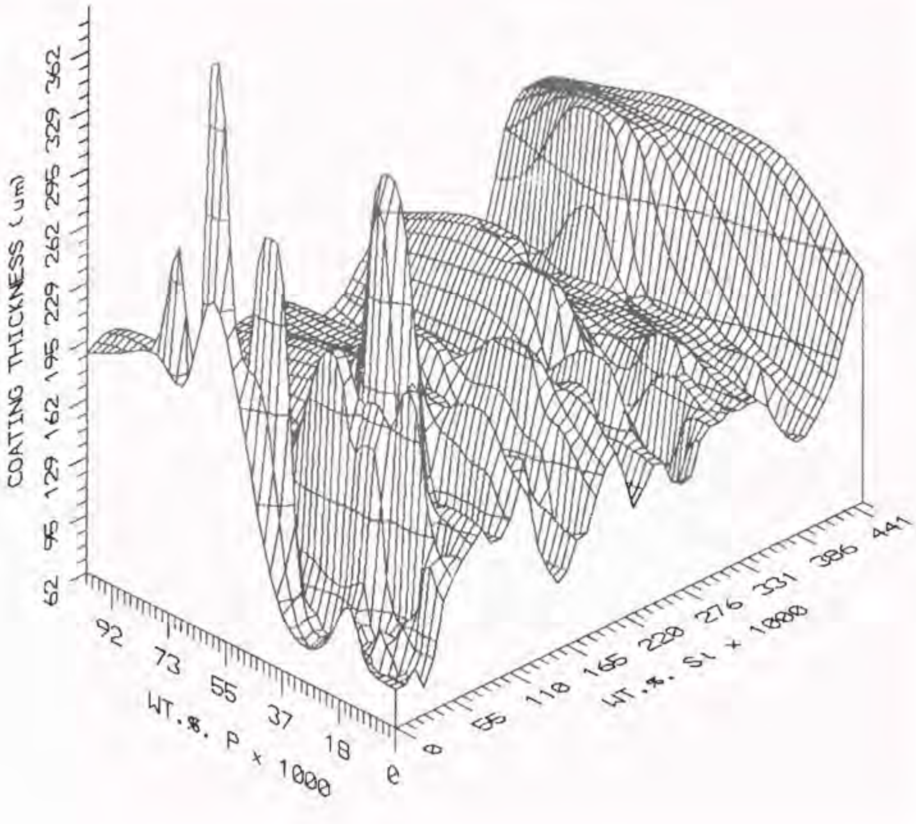


Fig 7a:
A simple plot of coating type versus silicon and phosphorus content

Figs 7a and b: Relationship between silicon and phosphorus content of steel and type of coating.

Fig 7b:
A three-dimensional plot of coating thickness related to silicon and phosphorus content



Mechanism of coating formation and effects of Si and P

The mechanism by which a galvanized coating forms - whether normal or high reactivity - is of less concern to the structural steel designers and galvanizers than is the effect, of whatever coating is formed, on the serviceability of the steelwork concerned. However the researchers have proposed a mechanism which is outlined below.

As reaction between steel and zinc proceeds and the Fe-Zn alloy layers form, there is a considerable volume change - the volume of the Fe-Zn intermetallics is 13-15 times greater than that of Fe. This would suggest that the compressive stress introduced during alloy formation would be such that an adherent layer could not form - but clearly it does in many cases, so there must be a mechanism for relieving the compressive stresses.

It can be argued that the compressive stresses in the alloy layer are relieved by plastic flow in the steel near the interface, through creep or other mechanisms. The role of Si and P would then be to interfere with the ability of the substrate to deform. Si and P are much less soluble in Fe-Zn intermetallic than in the steel substrate. This infers that their concentrations would build up in the steel ahead of the advancing alloy layer, preventing plastic flow and hence causing the delta and zeta phases to spall away from the surface. A similar mechanism is proposed for the effect of Ni bath additions, since the solubility of Ni in Fe-Zn is negligibly small.

These factors were examined in detail[8]. An electro-chemical method was developed to allow each layer of the coating to be removed successively, and XPS analysis carried out on the surface, so exposed. Using this rather sophisticated approach there appeared to be some evidence for the accrual of Si, P and tramp elements at the steel intermetallic interface. This in turn could lead to reduction of the ability of the substrate to accommodate the stresses within the alloy layer and hence the most vulnerable alloy layer (the zeta layer) would crack, allowing zinc access to the lower Fe-rich layers. Formation of zeta is normally rate-controlling: cracking of zeta would short circuit that and increase reaction.

A new reactivity classification for steels to be galvanized

Previous attempts to classify the galvanizability of steels began with the work of Sandelin[2] and continued with the French[5] and German[6,7] efforts which led to galvanizability standards.

A re-examination of Sandelin's work undertaken as a part of this study showed that it had been subsequently over-simplified and misinterpreted.

The work summarised here has established that when interpreted correctly, Sandelin's results provide a valid outline classification of reactive steel behaviour. However, a much more comprehensive classification is needed to take account of all the variations in behaviour encountered in commercial galvanizing.

This new classification is summarised in Table 1, and described and illustrated in the following paragraphs. The classification also seeks to address the behaviour of steels whose composition borders regions of different reactivity

Table 1: Summary of a new reactivity classification for steels

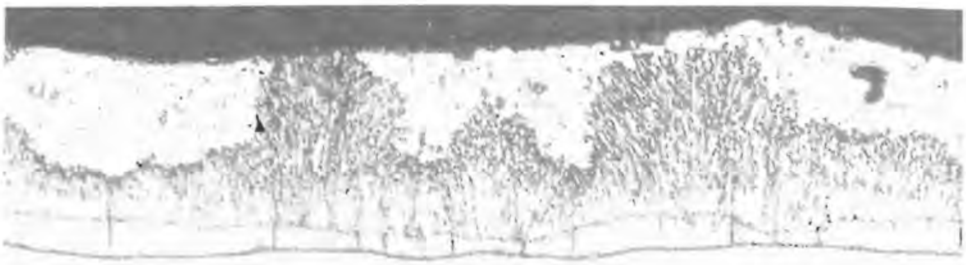
Class	Silicon content (wt%)	Phosphorus content (wt%)	Steel reactivity	Coating appearance
1 Normal/hypo Sandelin	0-0.35	0-0.025	Generally normal but occasionally low	Few defects
2 Semi-Sandelin	0-0.04	0.025-0.035	Normal	Localised defects due to outbursts of zeta alloy
3 Non-classical Sandelin	0-0.04	>0.035	High, especially with high phosphorus content	Pronounced surface defects (eg 'tree bark): high tendency to flake
4a Sandelin (low phosphorus)	0.04-0.135	<0.01	Moderate, increasing with silicon content	May appear normal with few defects
4b Sandelin (high phosphorus)	0.04-0.135	>0.01	High	Generally few defects
5a Hyper-Sandelin (low phosphorus)	0.135-0.35	<0.03	High, but generally thinner coatings than on Class 5b	May appear normal with few defects
5b Hyper-Sandelin (high phosphorus)	0.135-0.35	>0.03	High	Tendency to flake, especially with high phosphorus content
6 Extreme hyper-Sandelin	>0.35	>0	High, and increasing with silicon content	Tendency to flake, increasing with phosphorus content

Class 1: Normal reactivity or hypo-Sandelin steels

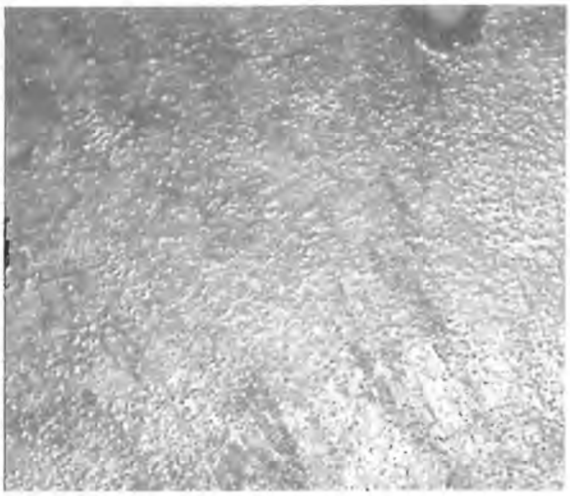
8.
Normal reactivity coating (also called 'hypo-Sandelin')

Silicon: 0-0.035%
Phosphorus: 0-0.025%
Normal coating structure
Alloy layer thicknesses: 50-85µm
Total coating thickness: 65-120µm
Occasional problems with 'thin' coatings compared with the usual 'standard' thickness of 85µm

Class 2: Semi-Sandelin steels



9.
Coating on a semi-Sandelin steel.



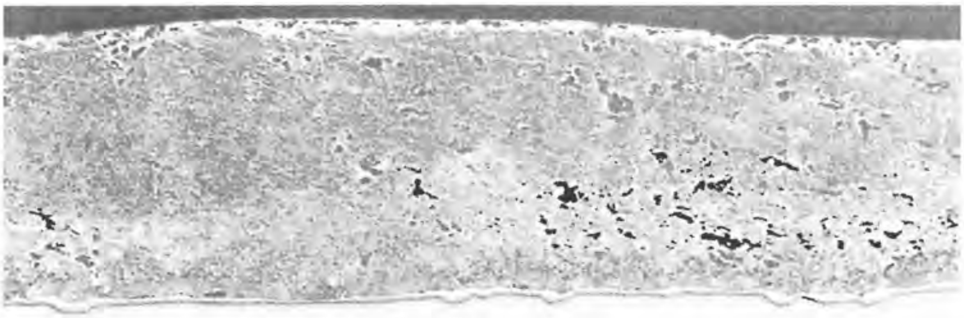
10.
Surface appearance of a steel showing the 'outbursts' illustrated in Figure 9.

Silicon: 0-0.040%

Phosphorus: 0.025-0.035%

Generally normal reactivity and coating thickness but may show frequent local outbursts of reactive coating - either 'pimples' (Fig.10), striation, or a 'tree-bark' effect, giving localised thicknesses up to 500µm. Can show a completely Sandelin structure when near the composition limits. Tubular or curved sections show these effects at lower Si and P contents.

Class 3: 'Non-classical' Sandelin steels



11.
Coating on 'non-classical' Sandelin steel.

Silicon: 0-0.04%

Phosphorus: >0.035%

Coating thicknesses: 150-330µm
with areas up to 500-1000µm especially with P content >0.05%.

Show typical 'Sandelin' high-reactivity coatings but outside the expected high-reactivity range.

Coatings are very thick with little or no outer layer of unalloyed zinc; frequent surface defects: poor appearance - easily damaged.

Class 4: 'Classical' Sandelin steels

Silicon: 0.04-0.135%

Phosphorus: all ranges

All show Sandelin coatings with little or no unalloyed zinc, and are not particularly susceptible to defects or delamination.

Class 4a: Low Phosphorus

12.
Coating on a 'classical' Sandelin steel with low phosphorus.

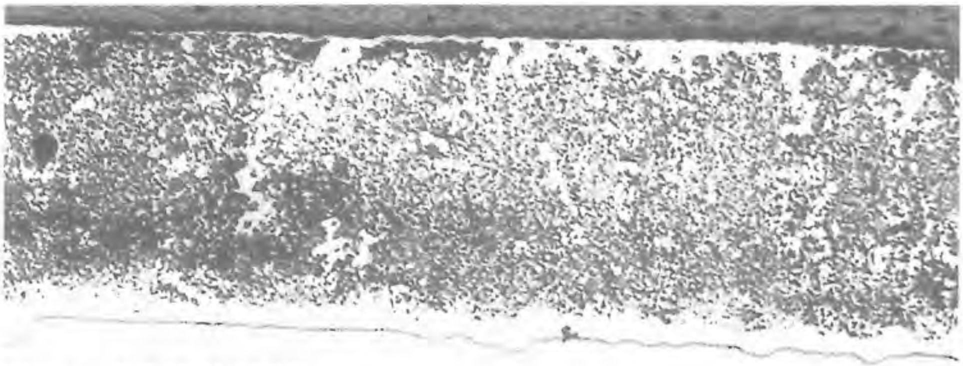
Silicon: 0.04-0.135%

Phosphorus: 0-0.010%

Coating thicknesses: 100-180µm

Usual 'Sandelin' structure but thinner than Class 3 or Class 4b. Not generally subject to coating defects. Presence of unalloyed zinc may disguise the structure

Class 4b: Higher Phosphorus



13.
Coating on a 'classical' Sandelin steel with higher phosphorus.

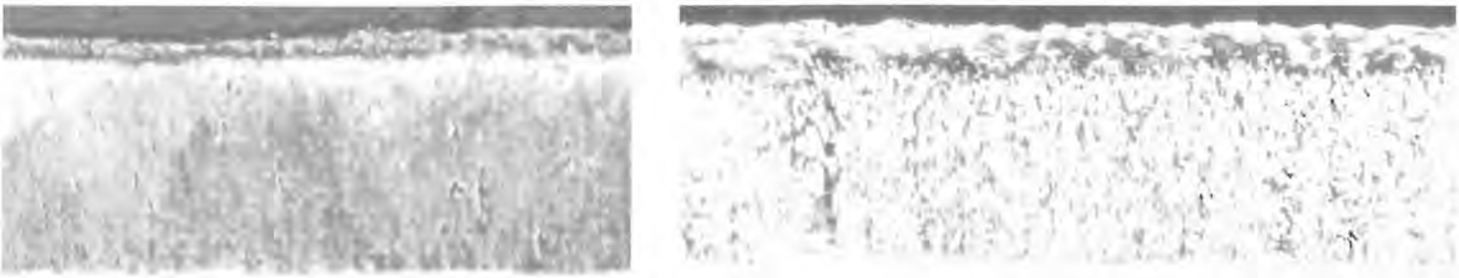
Silicon: 0.040-0.135%

Phosphorus: >0.010%

Coating thicknesses: variable 180-500µm

Shows usual Sandelin structure.

Borderline steels



14a and14b: Variations of coating structure on a steel bordering the Sandelin/hyper-Sandelin range

Where compositions are at - or near - the borderline between Class 4 and hyper-Sandelin (Class 5) surfaces may have larger or smaller areas which show Class 5 behaviour, due to local inhomogeneity especially regarding P.

Class 5: Hyper-Sandelin steels

Silicon: 0.135-0.350%

Phosphorus: all ranges

Class 5a: Low phosphorus

15a & b.
Coating structure on two steels in the Hyper-Sandelin range:

15a.
Illustrates the coating on a steel near the borderline.

15b.
Is a steel which is definitely Hyper-Sandelin.

Silicon: 0.135-0.350%

Phosphorus: 0-0.030%

Coating thicknesses: 120-200µm
Average coating thicknesses: 165µm

Generally with unalloyed zinc layer present.
Not particularly susceptible to surface defects or delamination.

Class 5b: Higher phosphorus

16.
Coating structure on an unequivocally Sandelin composition steel.

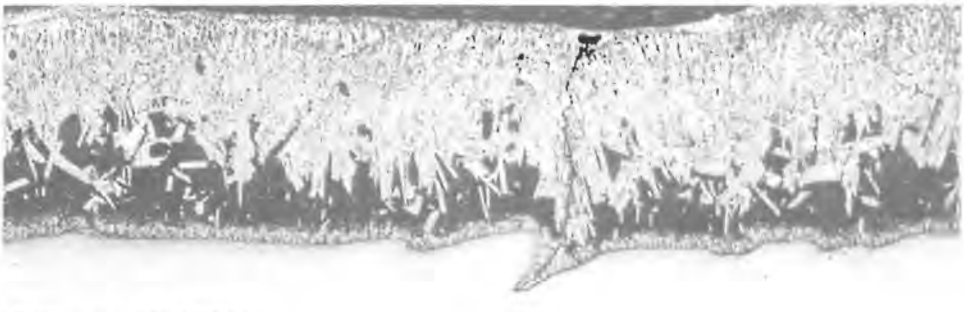
Silicon: 0.135-0.350%

Phosphorus: >0.030%

Coating thicknesses at upper end of range for class 5a.

Hyper-Sandelin structure, nearly always with outer layer of zinc.
More easily damaged and delaminated than for class 5a.

Class 6: Extreme Hyper-Sandelin



17.
Extreme Hyper-Sandelin steel

Silicon: >0.450%

Phosphorus: All ranges

Hyper-Sandelin structure. Higher phosphorus increases tendency to delaminate and reduces likelihood of an unalloyed zinc coating being present.

Conclusions

This project has greatly increased knowledge of the phenomenon of high reactivity galvanizing, and in particular has shown that:

- Silicon and phosphorus contents are jointly the most important factors in determining whether steels give rise to high reactivity in hot dip galvanizing.
- Other elements found in commercial steels have little or no effect on galvanizing behaviour.
- There is no evidence that the effect is caused by segregation of any elements at the surface of the steel.
- Prolonged pickling, stripping and re-dipping, or blast cleaning may increase the thickness of the coating produced, but will not change its structure.

A new reactivity classification has been established which enables the type and thickness of a galvanized coating to be predicted from the bulk analysis of the steel substrate.

References

(1) ILZRO Project ZM-375: Progress Report No. 1. August 1990

(2) R W Sandelin: Wire and Wire products 1940, *15*, 11 and 12, pp657-676; ibid1941, *16*, 1, pp28-35.

(3) R W Richards and H Clarke: ILZRO Project ZM-375: Special Report on Original Work of R W Sandelin

(4) H Bablik: Galvanizing (Hot Dip), published by Spon Ltd., London 1950.

(5) J Pelerin *et al.*; Metall 1981, *35*, 9, p870.

(6) G Hansel: Metall 1980 *34*. 9, p828; ibid 1983 *37*, 9, p883.

(7) D Horstman: Arch. Eisen. 1975, *46*, 2, p137.

(8) A total of 10 detailed reports on ILZRO project ZM-375 were issued between1990 and 1994. Copies are available on request from (ILZRO), International Lead Zinc Research Organisation, at the address shown at the foot of this page:

Appendices 1 & 2 appear overleaf on pages 18 to 22.

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Appendix 1:

Analyses for silicon and phosphorus of all the steels used in this study

STEEL	1000x WT%Si	1000x WT%P	TOTAL COATING THICKNESS (μm) 2 6 & 10 mins @ 455˚C			COATING STRUCTURE	PROJECT ZM-375 CLASS
LST1	1	15	85	117	159	HYPO-SANDELIN	1
HA	4	15	49	83	121	HYPO-	1
AU1	6	6	60	83	112	HYPO-	1
X3753	6	13	55	86	111	HYPO-	1
AU3	7	8	59	81	101	HYPO-	1
AU2	7	9	63	81	102	HYPO-	1
C1384	7	28	56	74	109	HYPO-	1
AF7	8	6	63	84	109	HYPO-	1
AF3	8	13	62	79	96	HYPO-	1
BSC C	9	9	70	98	112	HYPO-	1
AG14	9	9	65	79	99	HYPO-	1
M101	9	9	59	78	109	HYPO-	1
PDC33	9	9	66	85	103	HYPO-	1
PDC34	9	11	60	85	100	HYPO-	1
PDC35	9	19	62	85	100	HYPO-	1
PDC25	9	23	57	78	96	HYPO-	1
S32-1	9	68	82	120	169	SANDELIN	3
D329	10	8	62	81	106	HYPO-	
M7254	10	25	51	88	152	HYPO-	
HER1	10	62	115	388	403	SANDELIN	3
X3809	12	9	55	77	101	HYPO-	1
X2850	12	11	67	90	119	HYPO-	1
M103	12	9	56	83	106	HYPO-	1
M102	12	15	62	84	106	HYPO-	1
HER2	12	72	101	289	358	SANDELIN	3
LST2	13	10	71	136	178	HYPO-	1
N104	13	17	66	87	112	HYPO-	1
HB	13	24	77	99	116	HYPO-	1
I9	14	9	42	61	110	HYPO-	1
N105	14	14	63	81	100	HYPO-	1
D311	14	19	57	97	113	HYPO-	1
PASB	14	62	115	235	298	SANDELIN	3
CG1	15	58	88	168	215	SANDELIN	3
LST1	16	1	62	98	112	HYPO-	1
I6	16	6	36	81	130	HYPO-	1
D491	16	15	52	83	110	HYPO-	1
CG3	16	61	138	156	171	SANDELIN	3
I2	17	5	33	68	114	HYPO-	1
N106	17	9	69	90	122	HYPO-	1
D143	17	13	58	78	105	HYPO-	1
CGALV	17	76	101	149	267	SANDELIN	3
N107	18	6	66	80	106	HYPO-	1
I4	18	9	37	76	123	HYPO-	1

Appendix 1 continued:

Analyses for silicon and phosphorus of all the steels used in this study

STEEL	1000x WT%Si	1000x WT%P	TOTAL COATING THICKNESS (µm) 2 6 & 10 mins @ 455˚C			COATING STRUCTURE	PROJECT ZM-375 CLASS
I12	18	11	33	55	107	HYPO-	1
D571	18	15	53	90	118	HYPO-	1
I13	19	8	37	77	103	HYPO-	1
I10	19	12	42	68	112	HYPO-	1
M109	19	13	68	90	111	HYPO-	1
M108	19	15	60	77	98	HYPO-	1
PASA	19	47	128	296	452	SANDELIN	3
CG2	19	67	156	214	308	SANDELIN	3
I3	20	4	46	65	124	HYPO-	1
D453	20	4	58	83	109	HYPO-	1
D523	20	9	55	87	100	HYPO-	1
D565	20	9	56	79	109	HYPO-	1
M110	20	9	69	77	114	HYPO-	1
SD41	21	20	66	88	110	HYPO-	1
SD42	21	21	60	77	96	HYPO-	1
LR2	23	7	70	83	108	HYPO-	1
I7	23	9	43	71	132	HYPO-	1
SD44	23	9	62	76	99	HYPO-	1
LR1	23	10	69	86	111	HYPO-	1
SD43	23	31	58	75	92	HYPO-	1
CG4	23	87	92	199	314	SANDELIN	3
I1	24	8	30	61	117	HYPO-	1
I5	24	10	41	71	119	HYPO-	1
I8	25	4	41	70	131	HYPO-	1
LR5	25	9	64	93	112	HYPO-	1
LR3	25	13	60	77	98	HYPO-	1
LR4	25	17	65	81	98	HYPO-	1
D208	25	18	55	78	111	HYPO-	1
LR6	25	33	78	92	118	SEMI-SANDELIN	1
I11	26	7	36	58	115	HYPO-	1
WB2	26	9	62	77	95	HYPO-	1
LR8	26	10	66	88	102	HYPO-	1
WB4	27	31	56	79	109	SEMI-SANDELIN	2
WB3	27	43	71	92	118	SEMI-SANDELIN	2
D492	28	14	52	97	128	HYPO-	1
WB5	28	16	67	89	113	HYPO-	1
WB6	28	21	69	95	118	HYPO-	1
R3	29	6	58	89	123	HYPO-	1
CH1	29	7	60	80	100	HYPO-	1
UM1	30	14	61	82	101	HYPO-	1
CH2	30	14	61	83	104	HYPO-	1
LST4	31	17	66	89	121	HYPO-	1
CH4	32	9	58	76	109	HYPO-	1

Appendix 1 continued:

Analyses for silicon and phosphorus of all the steels used in this study

STEEL	1000x WT%Si	1000x WT%P	TOTAL COATING THICKNESS (µm) 2 6 & 10 mins @ 455˚C			COATING STRUCTURE	PROJECT ZM-375 CLASS
CH3	32	19	65	88	105	HYPO-	1
BS-3	34	21	99	135	192	SEMI-SANDELIN	2
CH5	35	11	62	78	103	HYPO-	1
BSCN	37	10	69	101	158	HYPO-	1
TA2	38	10	65	86	116	HYPO-	1
UM2	38	13	71	96	108	HYPO-	1
CH6	38	19	59	82	98	HYPO-	1
CH7	39	13	57	76	106	HYPO-	1
TA1	41	8	65	88	125	HYPO-	1
UM3	41	14	69	88	110	HYPO-	1
WS1	41	15	68	90	110	SEMI-SANDELIN	2
R4	42	9	58	84	107	HYPO-	1
I14	43	10	42	113	157	SEMI-SANDELIN	2
WS2	44	10	81	99	123	SEMI-SANDELIN	2
UM4	44	14	72	93	106	SEMI-SANDELIN	2
I15	45	5	34	109	165	SEMI-SANDELIN	2
BSCP	46	5	129	145	201	SANDELIN	4
WS3	46	14	70	95	106	SEMI-SANDELIN	2
WS4	47	24	89	189	256	SANDELIN	4
UM5	50	14	106	257	358	SANDELIN	4
WS5	50	36	93	238	301	SANDELIN	4
HER3	59	25	99	215	269	SANDELIN	4
UM6	60	14	120	258	309	SANDELIN	4
BS-2	62	7	110	155	206	SANDELIN	4
TUB	63	8	68	112	154	SANDELIN	4
PASC	67	24	93	169	249	SANDELIN	4
BSCG	78	101	102	145	214	SANDELIN	4
WS6	81	8	98	456	569	SANDELIN	4
C6214	89	26	102	156	203	SANDELIN	4
E81	93	47	78	135	247	SANDELIN	4
C6228	95	10	92	154	256	SANDELIN	4
BSCH	96	12	69	101	158	SANDELIN	4
PDC3	97	37	153	321	501	SANDELIN	4
BSCB	105	5	93	141	217	SANDELIN	4
PDC9	111	9	114	171	257	SANDELIN	4
PDC8	118	14	135	199	289	SANDELIN	4
PDC11	124	31	121	191	302	SANDELIN	4
UM7	133	14	85	169	253	HYPER-SANDELIN	5A?
PDC10	136	62	102	178	256	SANDELIN	4?
BSCJ	143	9	82	112	145	HYPER-SANDELIN	5A
PDC19	151	18	86	165	252	HYPER-	5A
BSCR	157	4	67	101	130	HYPER-	5A
E172	158	8	72	83	123	HYPER-	5A

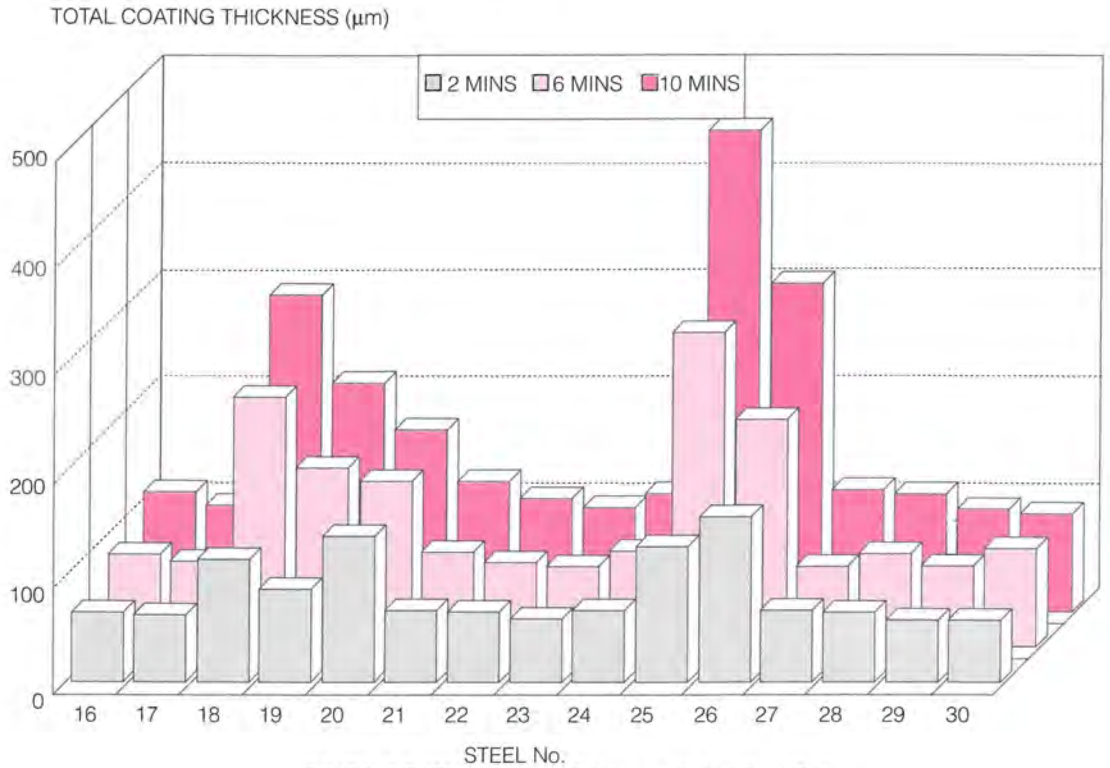
Appendix 1 concluded:

Analyses for silicon and phosphorus of all the steels used in this study

STEEL	1000x WT%Si	1000x WT%P	TOTAL COATING THICKNESS (µm) 2 6 & 10 mins @ 455˚C			COATING STRUCTURE	PROJECT ZM-375 CLASS
BS-7	163	9	65	103	118	HYPER-	5A
UM8	164	15	93	156	233	HYPER-	5A
PDC12	168	31	80	160	240	HYPER-	5B
PDC13	174	12	61	129	159	HYPER-	5A
PDC15	176	53	95	178	265	HYPER-	5B
PDC14	176	80	92	205	319	HYPER-	5B
K213	179	9	89	165	201	HYPER-	5A
B4291	180	9	91	135	162	HYPER-	5A
B4291	179	9	91	135	162	HYPER-	5A
B7351	180	9	69	97	140	HYPER-	5A
PDC16	194	25	90	205	316	HYPER-	5A
UM10	218	15	78	183	253	HYPER-	5A
K107	225	69	78	134	181	HYPER-	5B
PDC17	227	19	78	177	229	HYPER-	5A
D184	230	9	70	115	135	HYPER-	5A
UM11	234	14	78	132	169	HYPER-	5A
PDC18	240	23	88	138	181	HYPER-	5A
UM12	247	14	89	145	181	HYPER-	5A
PDC28	258	21	84	183	249	HYPER-	5A
E170	269	14	69	114	146	HYPER-	5A
D180	280	36	77	140	168	HYPER-	5B
PDC20	286	49	112	197	289	HYPER-	5B
HC	295	13	82	97	164	HYPER-	5A
AS138	301	3	89	148	185	HYPER-	5A
PDC21	302	66	115	201	301	HYPER-	5B
K242	310	52	102	168	223	HYPER-	5B
JD1	319	15	88	165	220	HYPER-	5A
D176	321	31	80	124	160	HYPER-	5B
HD	325	16	91	135	162	HYPER-	5A
JD2	331	23	92	171	210	HYPER-	5A
JD3	346	105	111	145	297	HYPER-	5B
BSCA	360	111	68	132	171	HYPER-	6
K248	369	70	100	150	201	HYPER-	6
JD4	374	84	118	138	250	HYPER-	6
K215	389	46	92	146	188	HYPER-	6
AS135	391	10	78	110	165	HYPER-	6
JD5	393	17	84	145	189	HYPER-	6
JD6	401	68	114	242	368	HYPER-	6
PDC29	413	67	115	235	349	HYPER-	6
PDC26	444	103	125	256	321	HYPER-	6
JD7	449	45	112	240	333	HYPER-	6
JD8	504	56	108	229	293	HYPER-	6
JD9	567	121	109	238	280	HYPER-	6

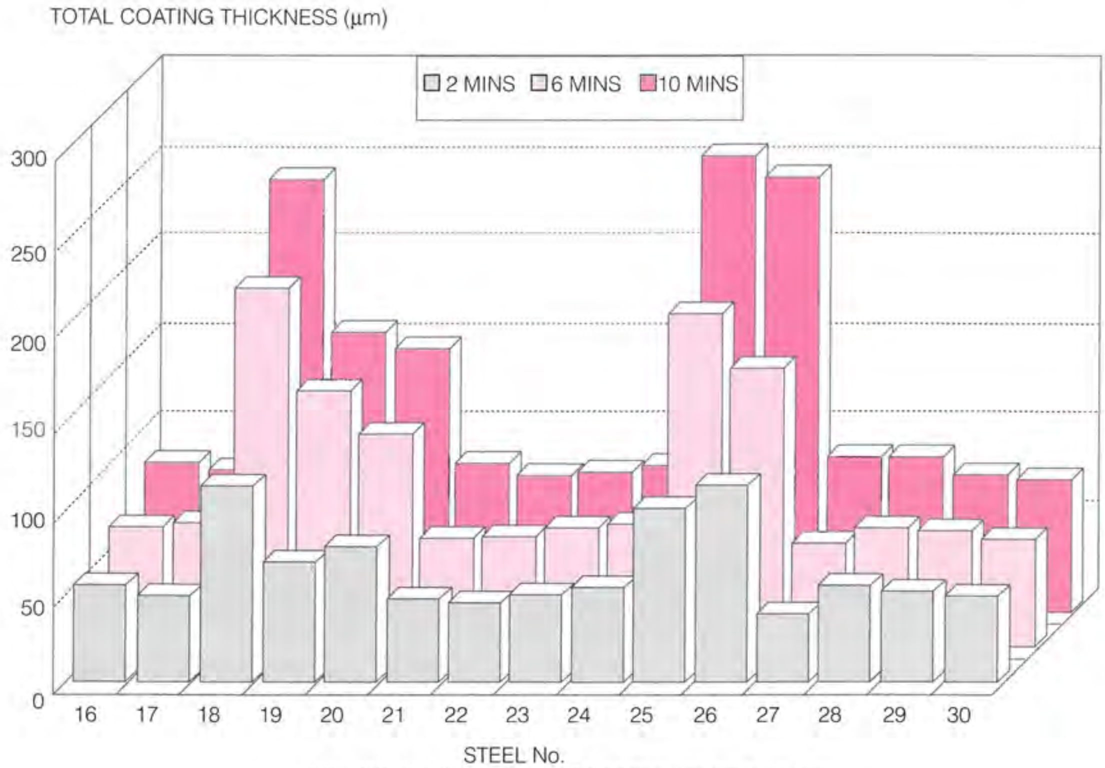
Appendix 2:

a) Comparison of alloy layer thicknesses after dipping for 2, 6, and 10 minutes at 455˚C



COATING DATA: 53μm = 305g\sq.m = 1oz\sq.ft =1.7mil

b) Comparison of alloy layer thicknesses after dipping for 2, 6, and 10 minutes at 440˚C



COATING DATA: 53μm = 305g\sq.m = 1oz\sq.ft =1.7mil

Key to a) and b) above: Steel compositions (refer to Appendix 1)
16: N104; 17: N105; 18: PASB; 19: CG1; 20: CG3; 21: N106; 22: N107;
23: N108; 24: N109; 25: PASA; 26: CG2; 27: M110; 28: SD41; 29: SD42; 30 SD43.

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