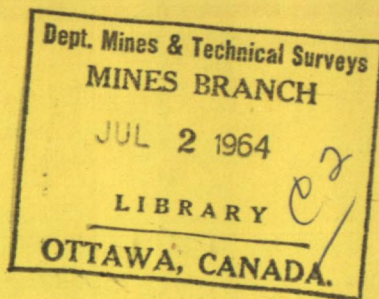




CANADA



HOT-DIP GALVANIZING WITH LESS COMMON BATH ADDITIONS

J. J. SEBISTY & R. H. PALMER

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH

RESEARCH REPORT

R 125

Price 75 cents

PHYSICAL METALLURGY DIVISION

This paper was prepared for presentation at the
Seventh International Galvanizing Conference,
Paris, France, June 1964

FEBRUARY 1964

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Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.

Queen's Printer and Controller of Stationery
Ottawa, Canada

1963

Mines Branch Research Report R-125

HOT-DIP GALVANIZING WITH LESS
COMMON BATH ADDITIONS

by

J.J. Sebisty* and R.H. Palmer**

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ABSTRACT

Galvanized coating formation in "aluminum-free" and "aluminum-containing" baths otherwise alloyed with individual additions of elements not normally encountered in commercial galvanizing practice, has been investigated.

It was revealed that a majority of the fifteen elements studied were retained without difficulty in the experimental baths, although in some cases this involved intermetallic compound formation at higher concentrations of the additions. The remainder, which included some chemically reactive elements, were unstable in the bath because of oxidation, crossing and segregation phenomena.

None of the elements investigated gave indications of commercial promise when combined with aluminum and lead at concentrations applicable to continuous strip galvanizing practice. Coating formation was generally unaffected by small additions, whereas higher levels were detrimental for various reasons, including neutralization of the inhibition of the iron-zinc reaction normally provided by aluminum at short immersion times.

In nominally "aluminum-free" baths, several of the alloying elements contributed to modification of the experimental coatings, principally by influencing iron-zinc alloy growth. For example, silver showed a pronounced accelerating effect, while significant suppression resulted with additions of chromium, manganese, nickel, titanium, and vanadium. Zirconium and silicon were also instrumental in altering the iron-zinc alloy structure, and zinc drag-out and/or drainage were directly affected by the mechanism involved.

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Direction des mines

Rapport de recherches R 125

GALVANISATION PAR IMMERSION DANS UN BAIN
ADDITIONNÉ D'ÉLÉMENTS RARES

par

J.J. Sebisty* et R.H. Palmer**

RÉSUMÉ

On a fait des recherches sur la galvanisation par immersion dans des bains aluminés et non aluminés auxquels ont été ajoutés des éléments non utilisés dans les procédés commerciaux de galvanisation.

On a constaté que la plupart des quinze éléments étudiés ont été facilement retenus dans les bains expérimentaux, mais dans certains cas des composés intermétalliques se sont formés lorsque les additifs étaient en plus fortes concentrations. Les autres éléments, dont quelques-uns sont chimiquement actifs, étaient instables dans le bain à cause de l'oxydation, de l'écémage et de la ségrégation.

Aucun des éléments à l'étude n'a paru susceptible d'utilisation commerciale une fois combiné à l'aluminium et au plomb aux concentrations employées dans les procédés de galvanisation continue. En général, la formation du revêtement n'a pas été affectée par de petites additions, mais de plus fortes doses ont été nuisibles pour diverses raisons, notamment parce qu'elles neutralisent l'inhibition de la réaction fer-zinc que détermine normalement l'aluminium à de courtes périodes d'immersion.

Dans des bains nominalemeut non aluminés, plusieurs des éléments d'alliage ont contribué à modifier les revêtements expérimentaux, surtout en influant sur la croissance de l'alliage fer-zinc. Ainsi l'argent provoque un effet d'accélération prononcé, tandis que l'addition de chrome, de manganèse, de nickel, de titane et de vanadium exerce une action modératrice. Le zirconium et le silicium ont aussi contribué à changer la structure de l'alliage fer-zinc, et le mécanisme résultant a aussi influencé directement l'entraînement et/ou le drainage du zinc.

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INTRODUCTION

In recognition of the importance of bath composition in the hot-dip galvanizing process, many investigators have devoted attention to studying the effect of alloying of the zinc bath. With few exceptions, this considerable effort has been concentrated on additions such as aluminum, lead, tin, cadmium, copper and antimony, which are the most widely encountered secondary elements in normal galvanizing practice. These occur either as a result of deliberate alloying of the bath or because of the use of impure zinc.

Much less is known of the potential value in galvanizing of various other elements which from metallurgical considerations could be expected to have some influence on the galvanizing reaction or on the properties of the galvanized coating. Such less common elements have been largely ignored in recent bath composition studies, or alternatively, the results of investigations made are only superficially documented in the literature. This applies particularly to elements of prime importance in iron or zinc alloy metallurgy and which therefore are of direct interest in the galvanizing process. With this basis for selection, the present investigation was undertaken with the objective of studying the influence of individual additions of other than normally-occurring elements on galvanized coating formation in "aluminum-free" and "aluminum-containing" baths. The concentration of the addition elements and the immersion time were varied widely in the laboratory preparation of coatings by the dry galvanizing technique.

The investigation was carried out with the active co-operation and assistance of the Canadian Zinc and Lead Research Committee and the International Lead Zinc Research Organization.

REVIEW OF PRIOR WORK

As a matter of interest and record, a review of published information on less common galvanizing bath additions has been made. Phillips(1) stated briefly, without giving experimental details, that thorium, indium, calcium, titanium and beryllium had no influence on the alloying behaviour of iron and zinc. Bablik(2) discounted patent claims for the use of bismuth, mercury, sodium and magnesium on the basis of cost. He further condemned magnesium because even in small unstated quantities it promoted excessive bath oxidation and zinc ash formation. Imhoff's tests(3), similarly undefined, also suggested magnesium to be detrimental because of its tendency to dry up the flux cover.

In so far as corrosion performance is concerned, Hiscock(4) reported that coatings prepared from baths containing 0.003% to 2.6% Mg were no better than ordinary coatings, and that magnesium did not appear to be a suitable addition to increase the resistance to hot water attack. Heath(5), on the other hand, claimed improvement in corrosion resistance for magnesium-containing coatings of from 20% to 90% in different environments with, at the same time, elimination of practical difficulties in the operation of a flux-covered bath. The optimum addition of 0.03% to 0.05% Mg in combination with 0.003% to 0.005% Al was also suggested to have no harmful effects on mechanical properties of the coating. Other references to magnesium may be found in Thorley's literature review of prior work(6). In one investigation referred to, the observation was made that 0.5% Mg caused peeling of the coating on cooling, and in another, 0.01% Mg was claimed to provide hardening of the outer zinc layer.

Alloying of the bath with nickel(3) in undefined amounts was indicated to be detrimental for the reasons that the bath appeared to freeze and the coatings obtained tended to crack and peel readily. Another approach tried by Baldwin for introducing nickel in the coating process involved electro-deposition of a thin film on sheet(7) and wire(8) before galvanizing. In addition to the claim that a more desirable surface for galvanizing was provided, the nickel plate prevented oxidation of the base metal when preheating prior to galvanizing.

Silicon has been examined by Gratsiansky(9) by additions of an aluminum master alloy containing 11% to 13% Si (silumin). It was found that 0.2% to 0.3% Al, in combination with silicon not exceeding 0.06%, reduced the amount of aluminum oxide in the bath and resulted in thinner fine-grained coatings. Later work on the same system by Ryabov(10) confirmed that the thickness of the coating and of the iron-zinc alloy layer was a minimum when the bath contained 0.04% Si. The time taken for the alloy layer to form was longest with the silicon-containing bath. The use of silicon is also featured in a patented two-stage dipping process(11) which is claimed to provide attractive high-aluminum coatings having superior resistance to pitting corrosion in hot or cold water. The process involves pregalvanizing in a zinc bath of conventional composition, followed by a second dipping operation in a bath alloyed with 0.1% to 2.5% Al and 0.01% to 0.05% Si. The function of the silicon addition is to suppress the aggressive attack of the primary coating, which would otherwise occur in the secondary high-aluminum bath.

In the review cited earlier(6), reference to studies on other elements may be found. Arsenic had no effect on the rate of growth of the iron-zinc alloy layers, but in excess of 0.01%, it promoted coating embrittlement which was more severe than with antimony. Bismuth, on the other hand, reduced alloy growth

significantly and aided spangle formation. In another brief reference it was noted that steel cleaned with emery could be galvanized in a bath containing 0.05% P.

In so far as noble metals are concerned, Radeker⁽¹²⁾ mentioned that silver improved the corrosion resistance of a galvanized coating. It has also been reported⁽¹³⁾ that 0.01% Au had no effect on coating formation in an aluminum-free bath but did tend to neutralize the inhibiting effect of 0.15% Al, even at short immersion times.

Some work on additions of complex alloy mixtures has been attempted. Imhoff⁽³⁾ referred to several unusual combinations tested by others but without any results being divulged. These comprised the following: Zn-Al-Bi, Zn-Al-Bi-W-Sb, Zn-Al-W-Cu, Zn-Al-Mg and Zn-Al-Mg-Sn-Cu.

MATERIALS AND PROCEDURE

The fifteen elements selected for study in this investigation were chromium, cobalt, lithium, magnesium, manganese, rare earths (mischmetal), nickel, phosphorus, silicon, silver, thorium, titanium, uranium, vanadium and zirconium. Others in the periodic table were considered initially and rejected for various reasons such as cost, availability, toxicity, existence as a gas, high oxidation rate, detrimental corrosion effects, low solid solubility in zinc, and so forth. It will be recognized that individual elements in the group retained are not entirely free of some of these limitations. In a few cases, also, the limited information in the literature suggests further drawbacks to their use in galvanizing. However, these objections were discounted because of the general lack of well documented evidence on the galvanizing application of the selected elements.

Master Alloys

Table 1 lists the form and purity of the bath materials used. As also indicated, most of the alloying additions were introduced into the galvanizing bath as zinc-base binary master alloys which were prepared in the laboratory as water-chilled shot. Other concentrations and other forms of the additions were tried but with lesser success in alloying. In most cases, recoveries were of the order of 90% or higher. Exceptions were vanadium and mischmetal at about 70%, chromium at about 50%, and silicon around 20%. A ternary Zn-Al-Si master alloy yielded much higher silicon recovery but this, of course, could not be utilized in the "aluminum-free" galvanizing tests made. Attempts to produce

a zinc-phosphorus master alloy using zinc-phosphide powder and red phosphorus tablets were unsuccessful, and, because of the lack of alternative simple methods of introduction, further work with phosphorus was discontinued. As is shown in Table 1, silver was added to the galvanizing bath in elemental form, and lithium as a lead-base master alloy. Metallographically, most of the master alloys consisted of a dispersion of intermetallic compounds in a zinc-rich matrix. The size, shape and concentration of the particles varied widely.

Experimental Program

The series of bath compositions comprising the experimental investigation is listed in Table 2. In the main program, galvanizing runs were made (a) in iron-saturated zinc baths alloyed with individual additions of each element, and (b) after further alloying of the same baths with 0.15% Al and 0.3% Pb. Three different concentration levels of each element were generally tried in this manner. Some departures from these sequences can be noted in the table, including the addition of 0.005% Al in the (a) group of tests involving lithium, manganese, mischmetal, silicon, thorium, titanium, uranium, vanadium and zirconium. This addition was found to be necessary to prevent excessive oxidation of the bath which interfered with the production of smooth coatings. Galvanizing immersion times employed in both (a) and (b) were 10 and 60 seconds, and the bath temperature was maintained constant at 450°C (840°F).

In one of the expansions of the original program, supplementary tests were incorporated to permit more extensive study of the influence of magnesium. A total of fifteen different bath compositions were investigated, covering various combinations of magnesium and lead in iron-saturated baths containing 0.005% Al. These tests, identified by single asterisks in Table 2, were run at an immersion time of 60 seconds only and a bath temperature of 450°C (840°F).

From evaluation of the coatings produced in the original series, significant effects of practical interest were apparent with several of the alloying elements studied. Further supplementary tests, identified in Table 2 with double asterisks, were therefore made to establish more conclusively the influence of chromium, manganese, nickel, silver and zirconium in iron-saturated baths, with and without 1.0% Pb. One or, in some cases, two different concentrations were tried. As before, the manganese- and zirconium-containing baths were alloyed with 0.005% Al. Nickel and manganese were also investigated in baths with 0.3% Pb and variable aluminum additions of up to 1.0%. Silicon was another element showing effects of interest and was

re-examined, in combination with 0.15% Al and 0.3% Pb, in essentially iron-free and high-iron (0.3%) baths. Immersion times attempted in this supplementary series were 4, 10 and 35 seconds and 1, 2 and 4 minutes. The temperature of the bath was again maintained at 450°C (840°F).

Coating Procedure and Evaluation

A single grade of open-hearth, 24 gauge (0.025 in., 0.6 mm) rimmed steel sheet, bright annealed and mill finished by temper rolling, was used throughout this investigation. The chemical composition was as follows: 0.07% C, 0.01% P, 0.03% S, 0.34% Mn and 0.002% Si. Test panels were of two sizes: 4 in. x 6 in. (10 cm x 15 cm) and 3 in. x 4 in. (7.5 cm x 10 cm). Twelve of the large panels and three in the smaller size galvanized at each experimental condition in the original series of baths provided specimens for coating evaluation tests and steel weight loss measurements, respectively. Panels for the latter could not be prepared in the supplementary tests described above, because of the limited material available.

The galvanizing procedure was as follows: panels were degreased in trichlorethylene and pickled for 5 minutes in a Rodine-inhibited 5% sulphuric acid solution at 70°C (160°F). The panels were dried in acetone after scrubbing and water rinsing, and then fluxed in an aqueous solution (10.5° Bé) of commercial zinc-ammonium-chloride at 80°C (175°F). Oven drying at 170°C (340°F) was immediately followed by galvanizing in an electrically-heated 40-lb (18 kg) capacity graphite-lined steel pot. The bath temperature was controlled at $\pm 2^\circ\text{C}$ by a graphite-shielded thermocouple. Except for manual handling at the minimum dipping time of 4 seconds, immersion and withdrawal of test panels were controlled by a motor-driven pulley mechanism at speeds of 6 fpm (3 cm/sec) and 3 fpm (1.5 cm/sec) respectively. The small steel weight loss panels were water-quenched after withdrawal.

All baths were sampled for analysis at the beginning and end of each complete run, and also at intermediate stages prior to and after changes in bath composition by alloying. All determinations were made chemically, except for assaying of silver and spectrographic analysis of the following: 0.005% Al, magnesium at 0.10% and less, vanadium at 0.05% and less, and mischmetal and cobalt at all levels.

Evaluation of the experimental coatings comprised the following tests:

- (a) Coating weight measurement (stripping of coating in 20% HCl acid solution).

- (b) Steel weight loss measurement (stripping test on small panels in standard antimony-inhibited HCl acid solution). Where such panels were not prepared, an alternative determination of the iron content of the coating was made in conjunction with (a).
- (c) Forming properties (qualitative rating of behaviour in bending, cupping and seaming tests).
- (d) Metallographic examination of coating microstructures.
- (e) Surface inspection.

Representative panels from the original series of tests in the investigation have been set out at a fully instrumented site in a semi-industrial atmosphere, and information on the atmospheric corrosion evaluation in progress will be published at a later date. Panels from the subsidiary tests with magnesium additions were also exposed for a 1-year period at three different sites comprising marine, rural and industrial environments. These were evaluated by weight loss measurements.

RESULTS AND DISCUSSION

For convenience in discussion, the results obtained with the various elements studied are divided into five sections: bath composition, stripping tests and coating microstructures, surface appearance of coatings, forming properties and corrosion tests. It is to be noted that the designation "aluminum-free" coating refers to the nominally aluminum-free series of tests, some of which were actually run with 0.005% Al. Similarly, the "aluminum-containing" coating designation applies to the tests made with 0.15% or higher aluminum in the bath.

Bath Composition

For the concentrations investigated, nine of the fourteen elements studied were satisfactorily retained in the galvanizing bath at or near the nominal levels attempted; stable retention of the basic elements, iron, aluminum and lead, was also indicated. An exception was 0.2% Ni in combination with aluminum at and above 0.3% in the supplementary tests. Wide nickel variations were recorded, duplicating similar trends with the iron analyses. The stability of the remaining five elements, comprising lithium, mischmetal, silicon, thorium and uranium, was generally poor at all levels tried, because of segregation, oxidation or dross formation.

Depletion of lithium from the bath by oxidation was rapid and continuous, proceeding at a somewhat slower rate when 0.15% Al was present. The oxidation products varied from a tenacious grey film at a high-lithium sampling stage (0.03%) to a grey powdery crust at a much lower level of 0.004%. Only in the latter case, and in combination with 0.15% Al, could coatings free of adhering oxide products be produced.

Thorium was found to be stable except at the highest level of 0.5% in combination with 0.005% Al. Approximately 40% of this addition was lost, most probably by oxidation, since the retained concentration of about 0.3% was effectively maintained after the aluminum content of the bath was increased from 0.005% to 0.15%.

Mischmetal retention was variable and erratic with either 0.005% or 0.15% Al present, and the results suggested that segregation was responsible. In this connection, gross inter-metallic compounds were present in the zinc-mischmetal master alloy prepared and these were found to be essentially unchanged in galvanizing bath samples examined metallographically.

Uranium analyses in preliminary trial melts were lower than the nominal additions by a factor of about ten. Reaction with the graphite-lined galvanizing crucible was suspected and a protective alumina coating was applied. A considerable improvement was obtained, but the uranium retained in the melts listed in Table 2 was still two to three times less than that added. Various experiments later confirmed that segregation of uranium to the bottom of the bath was principally responsible. A corresponding movement of either iron, aluminum or lead in the bath was not detected by analysis.

At all concentrations tried, silicon retention in iron-containing baths was of the order of 0.02% or less even with additions of up to 0.2%. This was accompanied by a marked reduction in the iron content from the saturation value (0.03% Fe) down to 0.01% Fe with 0.05% Si, and to 0.003% Fe with 0.2% Si. With the high-iron (0.3%) bath run, 0.05% Si was proportionately less effective, reducing the iron content to 0.17%. A characteristic effect on alloying of all iron-containing baths with silicon was the formation of a viscous top dross of very high iron and silicon content, which thus accounts for the losses reported. With "aluminum-containing" baths, it was indicated that the aluminum present was not involved in this dross formation, since the nominal additions of 0.15% and 0.3% were effectively retained during dipping. However, general bath depletion by removal of the large quantities of dross formed could explain the apparently better retention of aluminum.

Zirconium additions of 0.3% and 0.5% in the original test program were of interest because of a steadily increasing concentration of iron in the bath during the course of dipping. This trend was not affected by increasing the aluminum content from 0.005% to 0.15%, and final sampling of these zirconium-containing baths analysed around 65% higher in iron than that introduced initially to produce the saturated condition of 0.03%. The lower zirconium addition of 0.1% in the supplementary tests produced a similar trend and the iron concentration at the end of the relevant run was twice as high as the original saturation level. Possible explanations for these increases are discussed in a following section.

Stripping Tests and Coating Microstructures

The stripping test data of principal practical interest and importance are plotted in Figures 1 to 4. Figures 1 and 2 cover the coating weight and steel weight loss measurements, respectively, for the "aluminum-free" tests in the main program, and in Figures 3 and 4 the results of coating weight and iron content determinations, respectively, are presented for the supplementary extended-immersion-time series of tests. The corresponding data for the "aluminum-containing" coatings prepared in the main program were less amenable to graphical presentation, and the results are listed in Table 3, as are also those for the magnesium-containing coatings in the supplementary tests.

Representative samples covering the wide variety of experimental coatings produced were examined metallographically after treatment with Rowland's etchants(14).

(a) Main Program: "Aluminum-free" Coatings

From Figure 1 it can be seen that, for the conditions investigated, nominal alloying additions of 0.01% to 0.1% Co, 0.1% to 0.5% Th and 0.01% to 0.4% U generally yielded only minor changes in coating weight. The coating microstructures were similar to that of the typical alloy-free control coating shown in Figure 5(a), and the steel weight loss curves in Figure 2 also suggest the absence of any significant change in the iron-zinc reaction. This type of response was repeated with 0.015% Li and with mischmetal in the range of 0.1% to 0.5%. The minimum addition of 0.005% Mg also failed to have any effect, but at and above 0.04%, well-defined vertical fissuring and related non-uniformity in the eta layer were much the same as in the microstructure in Figure 5(b). These features, which suggest a change in the solidification mechanism of the zinc layer, were much more pronounced at 10 seconds immersion and appeared to account for a coating weight reduction approaching 15% at these higher magnesium levels.

Additions of 0.1% and 0.3% Zr in the "aluminum-free" baths produced substantial coating weight reductions as indicated in Figure 1. This behaviour could not be accounted for by the steel weight loss data in Figure 2 which reveal a distinct, but moderate, downward trend in weight loss only with higher zirconium at 60 seconds immersion. Metallographically, the iron-zinc alloy structure in the coatings was of normal thickness but was otherwise distinguished by a sharply-defined boundary at the zeta-eta interface as shown in Figure 5(c). A dissolution mechanism is suggested because of the rounded edges of the individual zeta crystals forming the smooth boundary. This modification presumably facilitated lower zinc drag-out and/or better drainage of the zinc layer, thereby resulting in the thinner coatings found with zirconium at and below 0.3%. A dispersion of very fine intermetallic compound particles was observed in the eta layer.

Another distinctive feature of the zirconium data in Figure 1 is the return to more or less normal coating weight with 0.5% Zr. An excessively thick coating was obtained at 10 seconds but, at both immersion times, the reversed trend was observed to be related to an irregularly thick zinc layer. Gross intermetallic compounds, dispersed as in Figure 5(d), were responsible. These were entirely different in form and etching behaviour from the small, angular $ZrZn_{14}$ compounds found in the zinc-zirconium master alloy used.

Reference was made, in the previous section on bath composition, to an increase in the iron content of the zirconium-containing baths during dipping. This behaviour, and the coating microstructure modification described above, appear to be connected since dissolution of the zeta iron-zinc phase, which is apparently involved, would increase the iron content of the bath. The indicated non-equilibrium state between the zeta phase and the bath suggests a higher solubility limit for iron in the zinc melt owing to the presence of zirconium. An alternative possibility is that iron in solution in the bath is effectively depleted by formation of intermetallic compounds rich in iron and zirconium, and the unstable condition arising from incomplete iron saturation results in more aggressive attack of the zeta phase boundary crystals. In either case, the total iron content of the bath would tend to increase to some limit not defined in the present experiments.

Despite the characteristically poor retention of silicon in the bath, coating weight in the relevant tests (bath 44) was reduced approximately 20% and 30% at 10 and 60 seconds, respectively. These reductions were again related to a thin eta layer and not to a decrease in steel attack (Figure 2) or iron-zinc alloy growth. Closer examination of the coating microstructures revealed the same zeta-eta interface smoothing as was

found with the zirconium-containing coatings -- although to a less exaggerated degree as illustrated in Figure 5(e). In this case, the condition of incomplete iron-saturation of the bath leading to dissolution of the zeta-phase boundary is more readily explained. As noted earlier, it was impossible to hold iron in the bath, owing to its rapid and continuous loss by combination with silicon to form a floating dross. An unstable equilibrium at the zeta-melt interface was thus continuously maintained so long as some iron or silicon remained in uncombined form.

With the exception of silver, all the remaining elements investigated, comprising chromium, manganese, nickel, titanium and vanadium, contributed to modification of the "aluminum-free" coatings, primarily as a result of reduced attack of the steel base. A decrease in iron-zinc alloy thickness was a characteristic feature, although this was not apparent in the coating weight measurements in all cases because of the compensating effect of intermetallic compounds on zinc drag-out and/or drainage. Manganese represented a typical case of this behaviour. For example, Figure 2 reveals a significant reduction of about 15% in steel weight loss with manganese at and above 0.5%, but according to Figure 1 coating weight was only moderately reduced at 60 seconds and not at all at 10 seconds. A thick eta layer, contaminated with fine intermetallic compounds as in Figure 6(a), accounted for these discrepancies. The particles were again totally different from the dendritic-type compounds present in the zinc-manganese master alloy.

Titanium-containing coatings in the higher end of the range studied were unsatisfactory, for various reasons as described later, and it was possible to produce uniformly coated panels with an addition of 0.01% and to a limited extent with 0.05%. The stripping test results in Figures 1 and 2 reflected this behaviour and consistent data were associated only with the minimum addition of 0.01% Ti. Contrary to Phillips' claim(1) that titanium does not influence the alloying behaviour of iron and zinc, it was found that both of the above concentrations decreased growth of iron-zinc alloy appreciably, and of the zeta phase in particular. The typical compound formation and iron-zinc alloy modification due to titanium can be seen by comparison of the microstructure in Figure 6(b) with that of the control coating in Figure 5(a). A resemblance to the smooth zeta-eta interface boundary observed with zirconium and silicon additions can be noted. As a matter of interest, the unique structure obtained with 0.10% Ti in the bath is shown in Figure 6(c). An extremely thin zeta layer, caused either by restricted growth or by melt dissolution, is apparent and is combined with distinctive dispersions of intermetallic compounds in the eta layer. Some eutectic is also present. As illustrated, the floating band of semi-detached crystals generally followed a wave pattern through the very non-uniform zinc layer and was suggestive of a reaction layer initially formed at the steel surface, which was subsequently undermined and floated off as a coherent band.

A prominent feature of the "aluminum-free" data plotted in Figures 1 and 2 is the marked influence and generally similar behaviour of chromium, nickel and vanadium. These elements were most consistently effective in direct suppression of steel attack and iron-zinc alloy growth, and maximum reductions in weight loss, exceeding 20% at 60 seconds immersion, were obtained with 0.2% Ni and 0.2% Cr. A lower value of 15% applied with 0.1% V, but the similar trend of all three curves in Figure 2 is to be noted. The coating weight results in Figure 1 followed the same pattern, although in a less consistent manner at the short immersion time of 10 seconds, and with nickel additions at 60 seconds. Of particular note is the pronounced decrease in coating weight of around 40% obtained with 0.2% Cr at 60 seconds immersion. Corresponding values for 0.1% V and 0.2% Ni were 30% and 20% respectively. Metallographic examination confirmed that these differences were principally caused by variations in the thickness of the eta layer and to the nature and distribution of inter-metallic compounds contained therein. Particles of larger size, and in greater number, were usually characteristic of the nickel-containing coatings. Photomicrographs illustrating the typically thin alloy layer common to the coatings prepared with these alloying additions are given in Figures 6(d), 7(a) and 7(b).

Silver was distinguished from all the other elements studied by the fact that it tended to promote exaggerated attack of the steel base and the formation of much thicker coatings. These effects were absent with 0.2% Ag, and with all concentrations tried at 10 seconds immersion. However, the pronounced influence of 0.7% and 1.2% Ag at 60 seconds immersion is clearly apparent in Figures 1 and 2. A maximum increase in steel weight loss of 95% was recorded, and in the case of coating weight the corresponding increase was 65%. An explanation of the reaction mechanism accounting for this spectacular influence of silver could not be found, but the typical microstructure reproduced in Figure 7(c) indicates that extremely active growth of the zeta iron-zinc phase was a predominant factor. From economic considerations it would appear that the observed behaviour of silver is only of academic interest. However, this conclusion is premature until a study of the practical value of silver in galvanizing can be made on a more intensive scale than has been possible in the present work. In this connection, Radeker's observation⁽¹²⁾ that silver improved the corrosion resistance of a galvanized coating is pertinent, although this behaviour was possibly related solely to an increase in coating thickness.

(b) Main Program: "Aluminum-containing" Coatings

The results of the stripping tests for the alloyed coatings prepared with 0.15% Al and 0.3% Pb also present in the bath are given in Table 3. Depending on the concentration of the addition element and the immersion time, various effects were revealed. These are discussed below in conjunction with observations made in metallographic studies of the coatings.

In contrast to its behaviour in "aluminum-free" baths, silver in the range 0.2% to 1.2% had no effect on coating thickness and structure. This applied also with 0.1% to 0.5% Th and with up to 0.1% U. Higher uranium additions of 0.2% and 0.4% resulted in moderate increases in coating weight, more notably at 60 seconds immersion. A corresponding change in steel weight loss suggested some modification of the iron-zinc reaction but this was not distinguishable in the coating structures. Similar increases with 0.015% Li and 0.1% to 0.5% mischmetal were associated with significant non-uniformity in the eta layer. Oxide drag-out in the former case and the presence of intermetallic compounds particles in the mischmetal-containing coatings were responsible. Irregularity in the eta layer, featured by a tendency to marked local thinning, was also characteristic of the silicon-containing coatings. This was reflected in erratic thickness variations in some cases but, in general, the influence of silicon on coating formation was otherwise indicated to be slight for the range of conditions investigated. It will be recalled that unstable retention in the bath was common to all of the above elements except for silver.

In the case of magnesium, inconsistent coating weight trends found were, to some extent, again caused by non-uniformity in the eta layer. The development of ridge-shaped formations originating from attachment of residues during withdrawal of the experimental panels was a major contributing factor. These were generally scattered on the panel surface, and affected areas could not be entirely avoided in sampling for the stripping tests. From microscopic examination, it was established that the higher additions of 0.04% and 0.3% Mg tended to promote steel attack in the form of small local outbursts. This could account for the moderate increases in steel weight loss indicated in Table 3. The presence of eutectic in the eta layer was a typical feature of the high-magnesium (0.3%) coatings and a gross formation is illustrated in Figure 8(a). The more usual distribution was in scattered small patches or as a stringer discontinuity. At the intermediate level of 0.04% Mg, fine hairline cracks, generally running perpendicular to the surface through the eta layer, also appeared to represent eutectic formation.

The data in Table 3 suggest that all of the remaining elements were significantly detrimental in high-aluminum baths, generally at the higher end of the concentration range and at the longer immersion time of 60 seconds. These comprised chromium, cobalt, manganese, nickel, titanium, vanadium and zirconium. The predominant effect was more or less complete neutralization of the inhibition of the iron-zinc reaction normally provided by 0.15% Al. At the extreme, all of the iron-zinc phases were developed in the usual layer-type formation characteristics of "aluminum-free" coatings. A secondary factor contributing to increase in coating thickness was contamination of the eta layer with intermetallic compounds.

At 10 seconds immersion, the minimum concentrations of all elements in the above group failed to have any apparent effect on coating formation. This applied equally to nickel at 0.1% and to vanadium at all levels tried. Intermediate concentrations of chromium, cobalt, manganese, titanium and zirconium were effective in producing small coating weight increases, but only in the case of cobalt, and to a lesser extent with zirconium, was it evident that more vigorous attack of the steel base was involved. The maximum alloying additions in all cases, exclusive of vanadium, reflected this latter trend and appreciable increases in steel weight loss were instrumental in the development of thicker coatings ranging from 0.8 to 0.9 oz/sq ft. More prominent local alloy outbursts indicating some degree of neutralization of aluminum were characteristic of these coatings formed at 10 seconds immersion. Such increased iron-zinc alloy growth is illustrated by the zirconium-containing coating in Figure 8(b). The gross compounds present, which contributed to non-uniformity in the eta layer, were identical to those in the high-zirconium "aluminum-free" coating shown in Figure 5(e).

At 60 seconds immersion, pronounced modifications in coating structure were produced with the maximum concentrations of all of the above group of elements, and this applied also to the intermediate levels of chromium, cobalt, titanium and zirconium. The stripping test data in Table 3 emphasize the detrimental neutralization of aluminum associated with these additions and the representative microstructures in Figure 9 show that, with respect to iron-zinc alloy growth, the coatings were not unlike those produced in an unalloyed zinc bath. Attention is drawn to the typical compound contamination in the manganese- and titanium-containing coatings in Figures 9(c) and 9(d), respectively.

(c) Supplementary Tests: "Aluminum-free Coatings"

The supplementary galvanizing tests with magnesium-containing coatings were primarily made to provide samples for corrosion testing. Magnesium additions at three levels in the range 0.005% to 0.2% were tried in combination with five lead levels in the range 0.002% to 1.0%. All baths were iron-saturated and contained 0.005% Al.

From the stripping tests results given in Table 3, only minor variations in the thickness and iron content of the coatings can be noted. Direct comparison with the prior tests was not possible because of bath composition differences but, in general, similar effects were revealed and it was confirmed that magnesium primarily affected the eta layer. Figure 5(b) reveals the characteristic non-uniformity caused by vertical fissuring in a low-lead coating containing 0.2% Mg. Hairline cracks at the base of the fissures were found to represent eutectic formation, even though only 0.005% Al was present. It was observed that coatings containing 0.3% and higher lead were less susceptible to fissuring, and the eta layer was more uniform.

In Figures 3 and 4 are plotted the stripping test data for the extended immersion tests with chromium, manganese, nickel, silicon, silver and zirconium. As mentioned earlier, material was not available for galvanizing separate steel weight loss panels in this series, and determination of the iron content in the coating was used as a substitute test. Data for the minimum immersion time of 4 seconds were not included in the graphs, because these were generally erratic as a result of manual handling of the panels during immersion and withdrawal.

The relevant curves in Figures 3 and 4 provide well-defined confirmatory evidence of the substantial reductions in steel attack and coating weight to be expected from alloying of an "aluminum-free" zinc bath with 0.2% Cr or 0.2% Ni or 0.5% Mn. The trends suggest that all three additions were more or less equally effective in reducing attack of the steel base. In each case, significantly greater response was obtained with increasing immersion time in the range investigated. Coating weight reductions with nickel and manganese were smaller than with chromium, apparently because the nickel- and manganese-containing inter-metallic compounds formed promoted increased thickness in the eta layer. For unexplained reasons, the further addition of 1% Pb to the bath lessened the effect of 0.2% Ni on attack of the steel base, as shown in Figure 4(c). An opposite, but less pronounced, reaction was obtained with 0.5% Mn, but in both cases the corresponding coating weight changes were negligible. The influence of lead with 0.2% Cr was not established since a comparable lead-free bath was not run. Typical coating microstructures obtained at 4 minutes immersion, and shown in Figures 10(a) to 10(c),

illustrate the relative effectiveness of 0.2% Ni and 0.5% Mn in suppressing iron-zinc alloy growth, and of the zeta phase in particular. Characteristic intermetallic compound dispersions can be seen in the eta layer of the alloyed coatings. It is to be noted that the compounds in the nickel-containing coatings appeared to originate by reaction at the zeta-eta interface boundary. The number and size of the particles increased with immersion time, and a distinctive hexagonal crystal form was evident.

The behaviour of other concentrations of chromium, nickel and manganese is also apparent from the graphs. Chromium at 0.05% was much less effective than at 0.2%. On the other hand, the iron content trends in Figures 4(b) and 4(c) indicate that the influence of 0.5% Ni and 1.0% Mn was the same as the lower levels of these additions when the respective baths contained 1% Pb. These similarities were not duplicated in the coating weight curves of Figures 3(b) and 3(c), and, with the higher nickel addition of 0.5% particularly, coating thickness was significantly increased and exceeded that of the nickel-free control coatings at longer immersion times. This was explained by gross intermetallic compound formation in the eta layer, combined with a sluggish zinc solidification mechanism as described later.

The distinctive alteration in coating characteristics associated with silver was again realized, as shown in Figures 3(e) and 4(e). It is also apparent that a proportionately larger effect can be expected as the dipping time is prolonged. Metallographically, comparison of Figures 10(a) and 10(d) illustrates the highly activated zeta phase growth and the accompanying coating thickness increase resulting from the addition of 0.7% Ag. At 4 minutes immersion, this coating was over 45% thicker than the control. The further addition of 1% Pb lowered this value somewhat, although the change could not be readily distinguished or explained from the respective coating microstructures.

The coating modification observed with zirconium in the main program was also duplicated in the relevant supplementary tests made. Figure 10(e) illustrates the typical sharp definition of the zeta-eta interface, which is combined with a thin compound-free eta layer. These features explain the significant coating weight reduction shown in Figure 3(f) since, as in Figure 4(f), the corresponding change in iron content of the coating was generally negligible for the dipping times used. The minor effect of the further addition of 1% Pb is also to be noted. Despite the contrasting mechanisms involved in coating weight reduction, zirconium reflected the behaviour of 0.2% Cr, 0.2% Ni and 0.5% Mn in being more effective with increasing immersion time. This trend was in fact emphasized with 0.1% Zr, and the coating weight of 2 oz/sq ft at 4 minutes immersion was a minimum for this series of tests.

(d) Supplementary Tests: "Aluminum-containing" Coatings

In the supplementary "aluminum-containing" tests made with 0.2% Ni and 1.0% Mn, it was re-established that these additions neutralized the normal inhibiting effect of 0.15% Al at short immersion times. The relevant curves in Figures 3 and 4 also indicate that, at longer immersion times, steel attack and coating build-up were significantly greater than with the "aluminum-free" control bath. These effects are characteristic of a lower aluminum level of around 0.10% and it is apparent that the nickel and manganese additions reduced the effective aluminum content of the bath by direct combination or some other mechanism. A typical coating microstructure is illustrated in Figure 11(a).

With higher aluminum additions of 0.3% and 0.5%, in combination with either 0.2% Ni or 1.0% Mn, effective inhibition of the iron-zinc reaction was retained at all immersion times in the range investigated. The detrimental effect of nickel and manganese was counteracted by the excess aluminum present, and the irregularly thin coatings showed negligible alloy formation except for small isolated Fe_2Al_5 growths at the higher aluminum level of 0.5%. To a limited extent, the same response was obtained with 1.0% Al as shown in the graphs and by the representative microstructure in Figure 11(b). However, with prolonged immersion, the aggressive nature of such a high-aluminum bath was revealed, and exaggerated Fe_2Al_5 growths as in Figure 11(c) were common.

From Figures 3(d) and 4(d), it can be seen that the presence of 0.05% Si in a high-iron (0.3%) bath containing 0.15% Al was instrumental in delaying the onset of severe steel attack at short immersion times; as a result, the coatings formed remained relatively thin. Longer immersion times reflected the same aggressive attack and heavy coating build-up as with the nickel- and manganese-containing baths described above, and the effect of silicon for these conditions was negligible. The aggressive nature of these high-iron baths was, of course, related to depletion of aluminum by combination with the excess iron present. Attention is drawn to the claim by Ryabov(10) that silicon tends to reduce iron-zinc alloy growth in aluminum-containing baths. Although this behaviour was to some extent confirmed in the above tests, the practical value of silicon additions would appear to be uncertain because of bath composition instability as discussed earlier.

With the comparable iron-free tests made, the predominant feature observed was the retained effectiveness of 0.15% Al through the full range of immersion times used. According to Figure 3(d), the addition of 0.05% Si was indicated to be somewhat detrimental, but a higher iron build-up found with the relevant bath was probably a more important factor. The increase in dross formation and zinc drag-out to be expected, probably accounts for the thicker coatings developed in this case.

It is emphasized that the various effects described above cannot be considered fully substantiated, in view of the inherent discrepancies associated with the iron content stripping test used. This substitution for the more accurate steel weight loss test was unavoidable, as explained previously. Also, in the case of the nickel-containing baths in this series, both nickel and iron varied widely in bath samples analysed and the influence of these effects on coating formation is uncertain. Further tests with nickel and silicon in "aluminum-containing" baths are to be attempted.

Surface Appearance of Coatings

(a) "Aluminum-free" Coatings

The aluminum- and lead-free control coatings produced in the main program were smooth and bright, apart from oxide streaking, and showed a faintly outlined polygonal pattern of very small grains. Except for oxidation effects, this characteristic appearance was generally unaltered by the minimum additions of most of the alloying elements tried, and significant modifications were restricted to higher concentrations. Attention is again called to the fact that 0.005% Al was added to some of the alloyed baths for the purpose of suppressing excessive oxidation at the bath surface.

Uranium, thorium and cobalt, at the higher levels used, tended to promote a finer grain structure and a pebbled texture owing to depression of the grain boundaries. The coatings had a bright appearance which, in the case of those containing uranium and thorium, could be related to the aluminum addition referred to above. Mischmetal at and above 0.3% caused some loss in reflectivity. With the single addition of 0.015% Li tried, the coatings were covered by a grey oxide skin picked up during withdrawal and the drainage interference due to this adhering skin resulted in pronounced ridging of the surface. Grey oxidation patches were also apparent on the silicon-containing coatings but, in combination with 0.005% Al, a brilliant mirror-like metallic finish was obtained. On these latter coatings, dross particles picked up on withdrawal appeared as randomly-scattered raised pimples.

With titanium in the bath, preparation of uniformly coated panels was possible only with an addition of 0.01% Ti. At 0.05% Ti and higher concentrations, the coatings were covered by numerous bare spots as well as flux and oxide residues. The suggested interference with the fluxing reaction was confirmed by absence of the normal flux boil at these higher titanium levels.

Manganese additions of up to 0.5% significantly improved coating smoothness and reflectivity. This latter effect was presumably influenced by the presence of 0.005% Al in the bath since, at 1.0% Mn, a dull, matte finish was produced. Chromium tended to increase coating grain size and, at the highest level of 0.2%, an improvement in coating brightness was also noticed. An associated effect, suggestive of non-uniform zinc drainage, was a mild form of "curtain" formation. In the case of nickel, the only change observed was slight depression of the grain boundaries with an addition of 0.2%. Zirconium up to 0.3% also provided bright fine-grained coatings showing evidence of a pebbled texture. In contrast, 0.5% Zr was indicated to be detrimental and resulted in a pattern of wide vertical streaks on the panels having a coarse sandpaper-like texture. The affected areas consisted of closely-spaced pimple projections originating from pick-up of the gross intermetallic compound particles described previously and illustrated in Figure 5(e).

Magnesium, vanadium and silver all tended to whiten the coating and to reduce the grain size, so that at higher levels in the ranges investigated, a smooth, metallic finish was obtained. The magnesium-containing coatings had a frosty appearance which contrasted with the reflective finish produced by 1.2% Ag and by vanadium at and above 0.05%. In the latter case, the coatings were marred by light oxide streaking and pimple defects. From the subsidiary tests made, it was found that the characteristic frosty finish due to magnesium was retained with up to 0.02% Pb in the bath. In this lead range, deterioration to a dull grey surface was observed with increase in magnesium. At higher lead levels, a typically smooth coating featuring large well-defined spangle crystals was obtained. Reflectivity was again reduced with increasing magnesium, and a reversion to the frosty type of finish was combined with formation of irregularly outlined spangles.

The additions of nickel, chromium, manganese, silver and zirconium in the lead-free supplementary tests essentially reproduced the various surface effects described above for each of these elements. Smooth fine-grained metallic finishes were generally obtained, even at 4 minutes immersion. It was again noted that 0.5% Mn and 0.05% Cr also, tended to improve coating brightness.

In combination with 1.0% Pb, each of the particular additions tried altered the normal spangling behaviour associated with high-lead baths in varying degrees. With 0.2% Ni, and manganese at 0.5% and 1.0%, large irregular-shaped flowery spangles were observed. A somewhat similar pattern of smaller crystals, showing good contrast, was apparent with zirconium and silver, whereas with chromium, the grains were large and had a mirror-like finish. From the point of view of surface appearance,

coatings prepared in this series with an addition of 0.5% Ni were unsatisfactory. The polygonal pattern of intermediate-sized grains showed pronounced depression of the grain boundaries, and an exaggerated pebbled appearance resulted.

(b) "Aluminum-containing" Coatings

The "aluminum-containing" coatings obtained in the main program had a characteristic bright finish with a lightly-outlined small spangle pattern. This appearance was in general unaltered by silver, thorium and uranium and by the lower concentrations of most of the other alloying elements. As described earlier, higher additions of chromium, cobalt, manganese, titanium, vanadium and zirconium at the longer immersion time of 60 seconds tended to neutralize the inhibiting effect of 0.15% Al, and this was reflected in the surface appearance of the respective coatings. A smooth contrasty spangle finish was generally evident, as would be expected from the appreciable iron-zinc alloy layer growth and the relatively thick outer zinc layer found with these coatings.

Several of the additions had a detrimental influence on coating appearance. Magnesium, for example, caused marked deterioration in uniformity and smoothness, because of pronounced ridge formations running horizontally across the panels. The effect of this on coating uniformity has already been noted. Similar defects on a lesser scale were produced by high mischmetal additions and by silicon. In both cases, pimple projections were also present, owing to pick-up of intermetallic and dross compounds in the eta layer. The presence of gross compounds formed with 0.5% Zr in the bath was again reflected in a rough, sandpaper-like finish, and in a more extreme case the addition of 0.5% Ti resulted in a severely wrinkled surface.

In the supplementary tests combining 0.2% Ni and aluminum in the range 0.15% to 1.0%, it was shown that an addition of 0.3% Al was required to restore the bright, low-contrast, spangled finish normally obtained with 0.15% Al. This conforms with the relevant stripping data trends defined in Figures 3 and 4. It was also observed that with 0.3% and higher aluminum, the surface was roughened by embedded intermetallic compounds and by ridge-type streaking across the panels. Thus, the production of satisfactory high-aluminum coatings with the aid of nickel additions, which was the objective of this series of tests, was not fully realized. Somewhat similar effects were encountered with the duplicate tests made with 1.0% Mn. In this case also, aluminum at and above 0.3% counteracted the neutralizing effect of manganese and the high-aluminum type of finish was again apparent.

In the iron-free supplementary tests made, 0.05% Si in combination with 0.15% Al appeared to be of questionable value. The coatings had an uneven streaky appearance, which suggested non-uniform zinc drainage. However, with a high-iron condition, the better retention of aluminum resulting from the same silicon addition was reflected in restoration of the normal high-aluminum type of finish.

Forming Properties

Attempts were made to compare the bending and forming behaviour of all coatings produced in the main program, by subjecting samples to bending and cupping tests and to formation of an "S" bend in a lock-seaming machine. From the qualitative performance ratings obtained, it was found that none of these methods was sufficiently sensitive to show the effect of other than moderately large changes in coating structure and thickness. Thus, the reduced iron-zinc alloy growth apparent in the "aluminum-free" coatings containing nickel, chromium, vanadium, etc., was not reflected in the forming tests. Similarly, no significant change in performance could be associated with the silicon- and zirconium-containing coatings which had a characteristically thin outer zinc layer.

As related to the cupping and bend tests, the ductility and adherence properties of the entire "aluminum-free" series of coatings were classified as being inferior. Equally poor were the "aluminum-containing" group which featured appreciable iron-zinc alloy growth and exceeded about 1.2 oz/sq ft in thickness. All of these exhibited severe flaking in formation of the lock seam bends. The opposite extreme was apparent with the remaining "aluminum-containing" coatings which had a coating weight of 0.70 oz/sq ft and less; these were rated as having excellent ductility and adherence and the behaviour in the seam test was completely satisfactory. Lower ratings were applied in the intermediate thickness range of around 0.90 oz/sq ft, but for all practical purposes the performance of this group was also considered acceptable.

Corrosion Tests

The corrosion behaviour of the magnesium-containing coatings in the supplementary tests was evaluated by weight loss measurements after exposure of representative 4 in. x 6 in. (10 cm x 15 cm) panels for one year in rural, industrial, and marine environments.

The extremes in weight loss were associated with the industrial and rural exposures, averaging around 2.1 g and 0.36 g, respectively, per panel. More or less complete disappearance of the eta layer was evident on the industrial panels. In each series, the weight losses were found to be independent of the magnesium and/or lead content of the coatings, and comparable results were obtained with magnesium-and-lead-free control coatings, as well as with additional rolled zinc panels of 99.99% purity.

In the marine environment, also, the influence of magnesium was again negligible, but a moderate advantage appeared to be connected with the low-lead panels (0.002% and 0.02% Pb). The respective weight losses were 0.65 g and 0.7 g as compared to the range of 0.9 to 1.1 g for the remaining coatings in this group which contained 0.2% and higher lead. A possible relationship with coating surface finish is suggested by this variable influence of lead, since the low-lead coatings had a metallic, spangle-free finish which reverted to a characteristic spangled surface with higher lead. Surface smoothness was otherwise good in both cases. As described earlier, coating reflectivity was altered by increasing magnesium content, but this change does not appear to be relevant in view of the negligible effect of the magnesium level on corrosion weight loss in the marine environment.

SUMMARY AND CONCLUSIONS

Galvanized coating formation in "aluminum-free" and "aluminum-containing" baths alloyed with individual additions of elements not normally encountered in commercial galvanizing practice has been investigated. From evaluation of the experimental coatings produced, various reaction effects and other data of practical interest and value were revealed.

Additions of chromium, cobalt, magnesium, manganese, nickel, silver, titanium, vanadium and zirconium were generally retained without difficulty, at or near the nominal concentrations tried in the experimental flux-free baths. At higher concentrations in the ranges studied, several of these elements tended to form a dispersion of intermetallic compound particles in the bath, which, in some cases, originated from products of the galvanizing reaction. The stability of the remaining elements, comprising lithium, mischmetal, silicon, thorium and uranium, was generally poor because of oxidation, segregation or drossing phenomena. Phosphorus can also be included in this group, since it could not be added to zinc by any simple method of introduction.

The poor retention of silicon resulted from its tendency to combine with iron in the bath to form a viscous top dross. This iron scavenging effect was apparent with "aluminum-free" and "aluminum-containing" baths, and in the latter case the effective depletion of iron appeared to promote better retention of aluminum. The experiments made suggest that silicon additions offer a method of reducing the iron content of a galvanizing bath. However, the practical value or limitations of this approach are uncertain, since more intensive study of the phenomena involved was not possible.

From the point of view of coating formation, none of the fifteen elements examined gave indications of a promising nature when combined with aluminum and lead at concentrations applicable to continuous strip galvanizing practice. Small additions generally had no effect on the galvanizing reaction and, depending on the immersion time, higher concentrations were detrimental for various reasons. For example, chromium, cobalt, manganese, nickel, titanium, vanadium and zirconium all tended to neutralize the inhibiting effect of 0.15% Al, thereby promoting active iron-zinc alloy growth. Intermetallic compound formation was excessive with some of these and other elements, and was instrumental in causing heavy zinc drag-out or non-uniformity in the eta layer. Poor coating appearance, due to drag-out of oxidation and other reaction products, was usually apparent with additions of magnesium, mischmetal, lithium, and silicon.

In the absence of aluminum, or with an aluminum addition of 0.005% as applicable in some tests, various phenomena of interest and significance to general galvanizing practice were observed. Excluding cobalt, lithium, mischmetal, thorium and uranium, which showed small effects or were otherwise detrimental, all of the remaining elements contributed to modification of the experimental coatings in different degrees, depending on the concentration and immersion time. This was primarily achieved by changes in the iron-zinc alloying reaction rate and the principal mechanisms involved could be classified as follows:

- (a) Alteration in iron-zinc alloy growth:
Silver accelerated growth of the zeta iron-zinc phase to a pronounced degree and coating thickness was correspondingly increased. In a reverse manner, chromium, manganese, nickel, titanium and vanadium were effective in producing thinner coatings by moderate but direct suppression of iron-zinc alloy growth. Maximum response was obtained with chromium.

- (b) Zeta-phase modification:
Zirconium, and silicon to a lesser extent, were instrumental in promoting the formation of a smooth zeta-eta interfacial boundary, thereby reducing the thickness of the outer zinc layer and of the coating as a whole.
- (c) Change in zinc fluidity:
Zinc drag-out from baths containing high concentrations of nickel, manganese, titanium and zirconium tended to increase because of intermetallic compound formation.

From limited atmospheric corrosion tests run in rural, industrial and marine environments, weight loss measurements failed to indicate any significant advantage for magnesium-containing coatings. Variations in behaviour were found in the case of marine exposure, but these appeared to be related to the lead content of the coatings tested.

ACKNOWLEDGEMENT

The authors are indebted to the Director of the Mines Branch, Department of Mines and Technical Surveys, to the Canadian Zinc and Lead Research Committee, and to the International Lead Zinc Research Organization, for permission to publish this paper. The contributions of the Consolidated Mining and Smelting Company of Canada, Limited, the Hudson Bay Mining and Smelting Company, Limited, and The Steel Company of Canada, Limited, with respect to material supplies and assistance in various phases of the investigation, are also acknowledged with gratitude.

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TABLE 1
 Bath Addition Elements, and Composition
 of Master Alloys

Element	Form and Purity	Master Alloy Shot
Aluminum	Sheet (99.99%)	Zn + 4% Al
Chromium	Powder (99.0%)	Zn + 0.9% Cr
Cobalt	Ingot (99.95%)	Zn + 1.85% Co
Iron	Electrolytic (99.98%)	Zn + 0.3% Fe
Lead	Sheet (99.99%)	-
Lithium	Bar (99.9%)	Pb + 5.0% Li
Magnesium	Ingot (99.99%)	Zn + 4.4% Mg
Manganese	Electrolytic (99.9%)	Zn + 2.0% Mn
Mischmetal	Pellets (98.6% R.E.)	Zn + 2.8% R.E.
Nickel	Electrolytic (99.99%)	Zn + 4.0% Ni
Silicon	Powder (97.85%)	Zn + 0.35% Si
Silver	Shot (99.99%)	-
Thorium	Pellets (98.0%)	Zn + 1.3% Th
Titanium	Sponge (99.99%)	Zn + 1.9% Ti
Uranium	Sheet (99.99%)	Zn + 1.9% U
Vanadium	Chips (99.7%)	Zn + 0.4% V
Zirconium	Sponge (99.99%)	Zn + 1.8% Zr
Zinc	Ingot (99.99%)	-

TABLE 2
Experimental Program

Bath No.	Test No.	Fe %	Al %	Pb %	Others %
<u>Main Program</u>					
1	1-4	0.03	-	-	-
"	"	"	0.15	0.3	-
14	53-56	"	-	-	-
"	"	"	0.15	0.3	-
33	123-126	"	-	-	-
"	"	"	0.15	0.3	-
27-29	99-110	0.03	-	-	0.05, 0.1, 0.2 Cr
"	"	"	0.15	0.3	" " "
11-13	41-52	0.03	-	-	0.01, 0.05, 0.1 Co
"	"	"	0.15	0.3	" " "
60	235,236	0.03	0.005	0.3	0.015 Li
"	237,238	"	0.15	"	"
"	239,240	"	"	1.0	0.05 Li
5-7	17-28	0.03	-	-	0.005, 0.04, 0.3 Mg
"	"	"	0.15	0.3	" " "
30-32	111-122	0.03	0.005	-	0.1, 0.5, 1.0 Mn
"	"	"	0.15	0.3	" " "
57-59	223-234	0.03	0.005	-	0.1, 0.3, 0.5 mischmetal
"	"	"	0.15	0.3	" " "
8-10	29-40	0.03	-	-	0.05, 0.1, 0.2 Ni
"	"	"	0.15	0.3	" " "
44	163,164	0.03	-	-	0.05 Si
45	167,168	"	0.005	-	"
46,52,53	173,208	"	0.15	0.3	0.05, 0.1, 0.2 Si
18-20	69-80	0.03	-	-	0.2, 0.7, 1.2 Ag
"	"	"	0.15	0.3	" " "
41-43	151-162	0.03	0.005	-	0.1, 0.3, 0.5 Th
"	"	"	0.15	0.3	" " "
37-40	(139-150)	0.03	0.005	-	0.01, 0.05, 0.1, 0.5 Ti
"	(197-200)	"	0.15	0.3	" " " "
4,47-51	(13-16)	0.03	0.005	-	(0.01, 0.02, 0.05, 0.1)
" "	(177-196)	"	0.15	0.3	(" 0.2, 0.4 U)
15-17	57-68	0.03	0.005	-	0.01, 0.05, 0.1 V
"	"	"	0.15	0.3	" " "
34-36	127-128	0.03	0.005	-	0.1, 0.3, 0.5 Zr
"	"	"	0.15	0.3	" " "

continued

TABLE 2 (cont'd)
Experimental Program

Bath No.	Test No.	Fe %	Al %	Pb %	Others %	
<u>Supplementary Tests</u>						
23	86-88	0.03	0.005	0.002	0.05, 0.1, 0.2 Mg	*
24	89-91	"	"	0.02	" " "	*
25	92-94	"	"	0.2	" " "	*
22	83-85	"	"	0.3	" " "	*
56	219-221	"	"	1.0	" " "	*
66	301-306	0.03	-	-	0.05 Cr	**
"	307-312	"	-	1.0	"	**
72	480-484	"	-	"	0.2 Cr	**
64	337-342	0.03	0.005	-	0.5 Mn	**
"	343-348	"	"	1.0	"	**
"	349-354	"	"	"	1.0 Mn	**
65	355-360	"	0.15	0.3	"	**
"	361A-366A	"	0.3	"	"	**
"	361-366	"	0.5	"	"	**
"	367-372	"	1.0	"	"	**
61	241-246	0.03	-	-	0.2 Ni	**
"	247-252	"	-	1.0	"	**
"	253-258	"	-	"	0.5 Ni	**
62	259-264	"	0.15	0.3	0.2 Ni	**
"	259A-264A	"	0.3	"	"	**
"	265-270	"	0.5	"	"	**
"	271-276	"	1.0	"	"	**
68	441-446	-	0.15	0.3	-	**
"	447-452	0.3	"	"	-	**
69	453-459	-	"	"	0.05 Si	**
"	460-464	0.3	"	"	"	**
63	277-282	0.03	-	-	0.7 Ag	**
"	283-288	"	-	1.0	"	**
67	373-378	0.03	0.005	-	0.1 Zr	**
"	379-384	"	"	1.0	"	**

*60 seconds immersion time only.

**4, 10 and 35 seconds; 1, 2 and 4 minutes immersion time.

All others 10 and 60 seconds.

TABLE 3

Coating Test Results*

Bath No.	Nominal** Addition, %	Coating Weight, oz/sq ft - sheet		Steel Wt. Loss, g/m ² - sheet	
		10 Sec	60 Sec	10 Sec	60 Sec
<u>Main Program</u>					
1, 14, 33	Control bath	0.37 (114)	0.44 (136)	2.9	3.7
27-29	0.05 Cr	0.42 (129)	0.46 (142)	3.0	4.4
"	0.1 "	0.63 (194)	1.27 (391)	4.2	20.2
"	0.2 "	0.83 (256)	1.57 (484)	9.2	26.4
11-13	0.01 Co.	0.42 (129)	0.69 (213)	4.2	7.5
"	0.05 "	0.70 (216)	1.40 (431)	11.1	22.1
"	0.1 "	0.96 (296)	1.46 (450)	12.7	25.4
60	0.015 Li	0.60 (185)	0.53 (163)	3.0	5.2
5-7	0.005 Mg	0.67 (206)	0.92 (283)	3.0	6.1
"	0.04 "	0.94 (290)	0.81 (250)	3.5	6.4
"	0.3 "	0.47 (145)	0.59 (182)	4.0	5.4
30-32	0.1 Mn	0.37 (114)	0.52 (160)	3.0	4.6
"	0.5 "	0.63 (194)	0.66 (203)	3.2	3.9
"	1.0 "	0.94 (290)	1.92 (592)	15.2	27.7
57-59	0.1 R.E.	0.61 (188)	0.63 (194)	3.2	4.2
"	0.3 "	0.57 (176)	0.63 (194)	3.8	4.0
"	0.5 "	0.56 (173)	0.71 (219)	2.9	3.7
8-10	0.05 Ni	0.42 (129)	0.47 (145)	3.6	4.2
"	0.1 "	0.42 (129)	0.64 (197)	3.9	7.7
"	0.2 "	0.86 (265)	1.48 (456)	11.8	24.3
46, 52, 53	0.05 Si	0.43 (132)	0.55 (169)	3.8	5.1
"	0.1 "	0.51 (157)	1.05 (324)	3.1	4.6
"	0.2 "	0.59 (182)	0.75 (231)	3.0	4.1
18-20	0.2 Ag	0.33 (102)	0.39 (120)	2.4	2.9
"	0.7 "	0.32 (102)	0.40 (123)	2.6	3.9
"	1.2 "	0.36 (111)	0.40 (123)	2.5	3.9
41-43	0.1 Th	0.42 (129)	0.49 (151)	1.6	4.1
"	0.3 "	0.42 (129)	0.49 (151)	2.8	4.4
"	0.5 "	0.43 (132)	0.47 (145)	3.3	4.3

continued

TABLE 3 (cont'd)
Coating Test Results*

Bath No.	Nominal** Addition, %	Coating Weight, oz/sq ft - sheet		Steel Wt. Loss, g/m ² - sheet	
		10 Sec	60 Sec	10 Sec	60 Sec
37-40	0.01 Ti	0.36 (111)	0.47 (145)	4.1	4.0
"	0.05 "	0.59 (182)	1.25 (385)	5.5	25.6
"	0.1 "	0.85 (262)	1.70 (524)	14.0	24.7
4,47,51	0.01 U	0.39 (120)	0.55 (169)	2.5	3.8
"	0.02 "	0.36 (111)	0.46 (142)	3.0	4.6
"	0.05 "	0.41 (126)	0.43 (132)	3.7	4.2
"	0.1 "	0.40 (123)	0.48 (148)	2.8	4.2
"	0.2 "	0.50 (154)	0.67 (206)	4.1	8.9
"	0.4 "	0.50 (154)	0.69 (213)	3.9	7.7
15-17	0.01 V	0.43 (132)	0.43 (132)	2.7	3.8
"	0.05 "	0.44 (136)	0.70 (216)	3.0	4.5
"	0.1 "	0.54 (166)	1.42 (437)	4.2	13.0
34-36	0.1 Zr	0.46 (142)	0.91 (280)	5.0	12.5
"	0.3 "	0.56 (173)	1.34 (413)	7.0	24.7
"	0.5 "	0.87 (268)	1.78 (548)	7.5	17.7

Supplementary Tests***

23	0.05 Mg, 0.002 Pb	-	1.72 (530)	-	29.4
"	0.1 " "	-	1.70 (524)	-	29.4
"	0.2 " "	-	1.75 (539)	-	30.1
24	0.05 Mg, 0.02 Pb	-	1.74 (536)	-	29.7
"	0.1 " "	-	1.74 (536)	-	30.9
"	0.2 " "	-	1.78 (548)	-	31.9
25	0.05 Mg, 0.2 Pb	-	1.82 (561)	-	28.8
"	0.1 " "	-	1.76 (542)	-	29.1
"	0.2 " "	-	1.85 (570)	-	29.4
22	0.05 Mg, 0.3 Pb	-	1.82 (560)	-	28.8
"	0.1 " "	-	1.76 (542)	-	29.1
"	0.2 " "	-	1.85 (570)	-	29.4
56	0.05 Mg, 1.0 Pb	-	1.92 (592)	-	28.7
"	0.1 " "	-	1.88 (579)	-	29.0
"	0.2 " "	-	1.87 (576)	-	27.2

*Averages of at least three determinations. Coating weight values in brackets are in g/m².

**Basic bath composition: Main program (Zn + 0.03% Fe + 0.15% Al + 0.3% Pb)
Supplementary tests (Zn + 0.03% Fe + 0.005% Al)

***The iron content of the coating is given in the steel weight loss column.

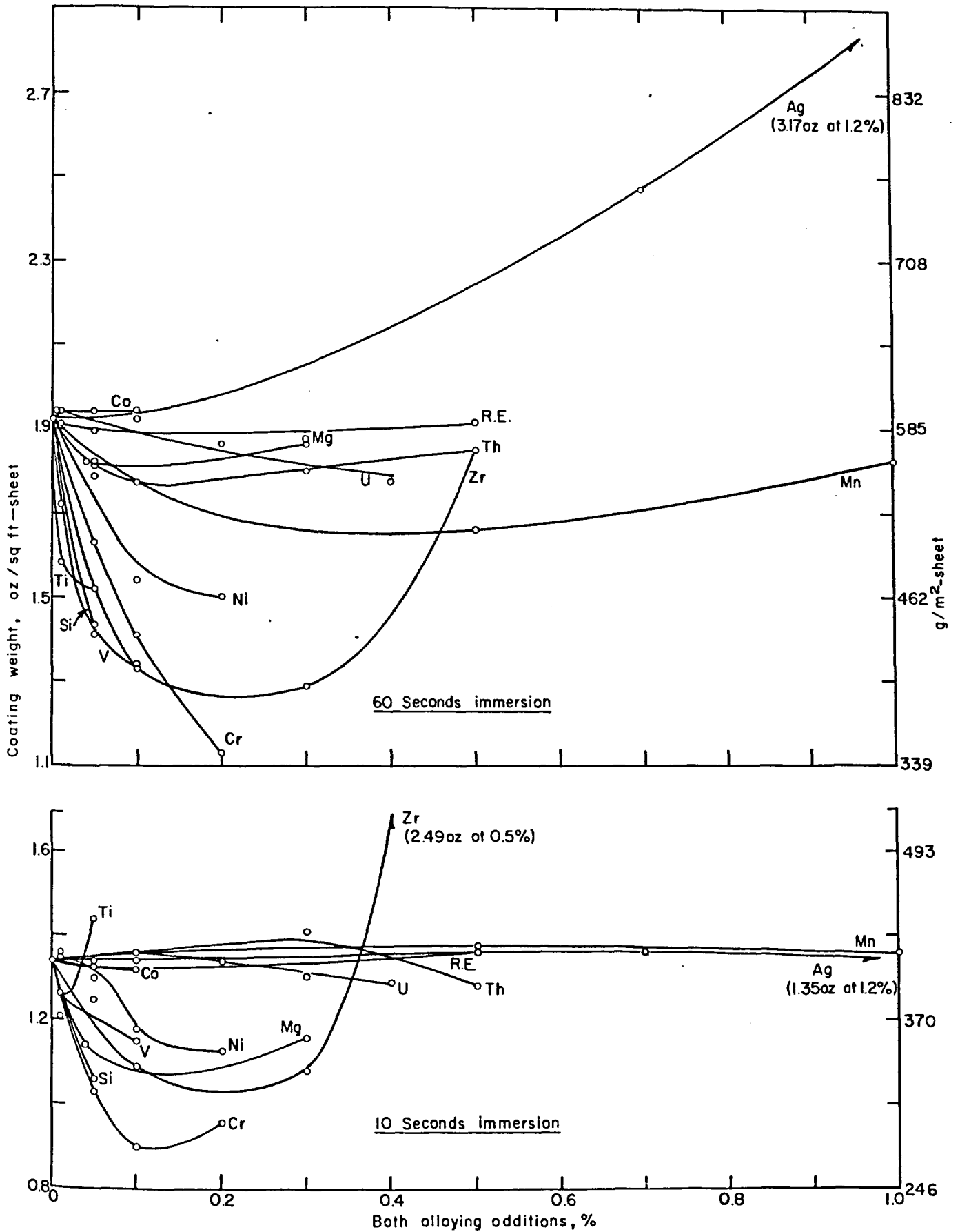


Figure 1. Influence of bath alloying additions on coating weight.

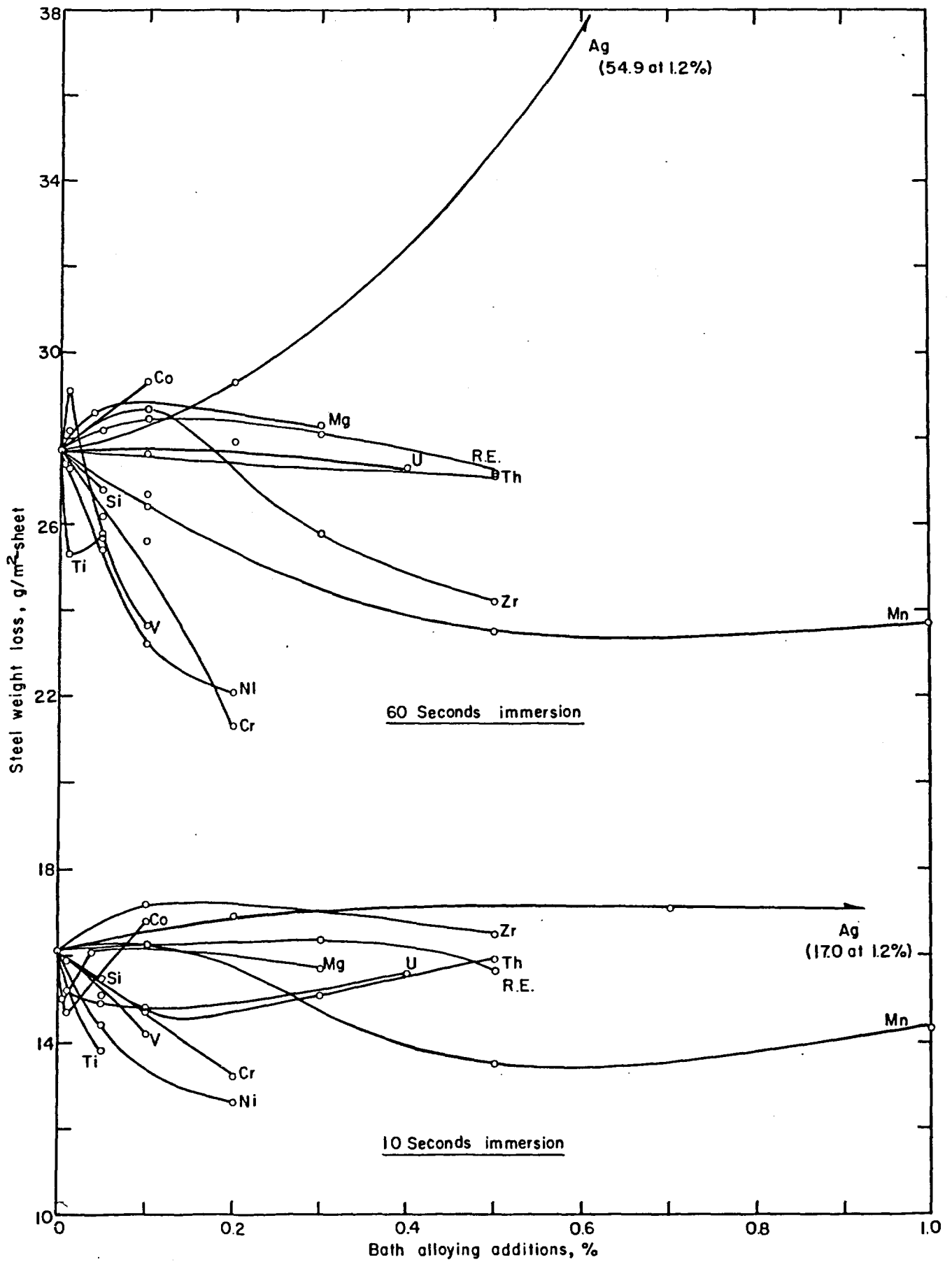


Figure 2. Influence of bath alloying additions on steel weight loss.

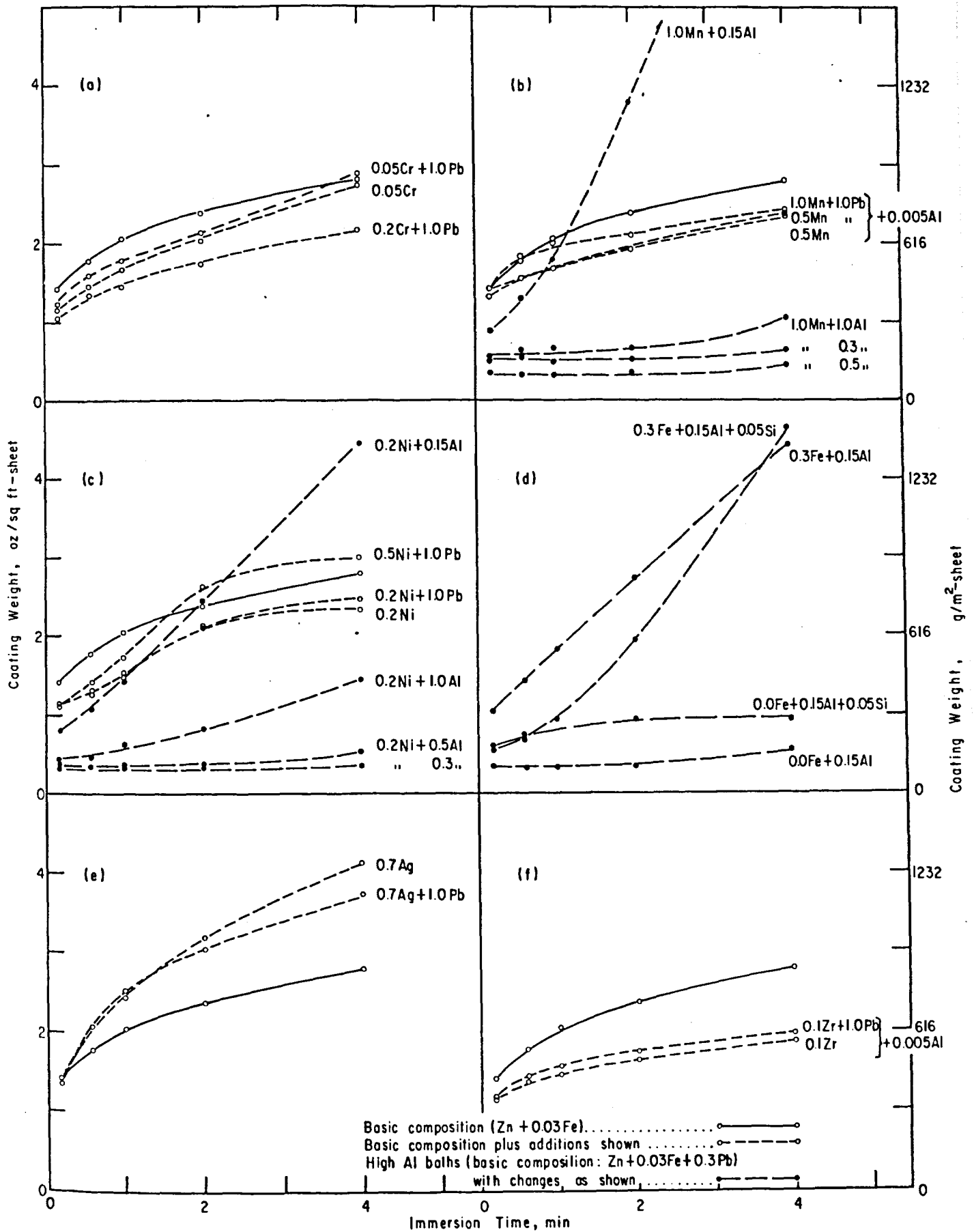


Figure 3. Influence of immersion time and bath composition on coating weight.

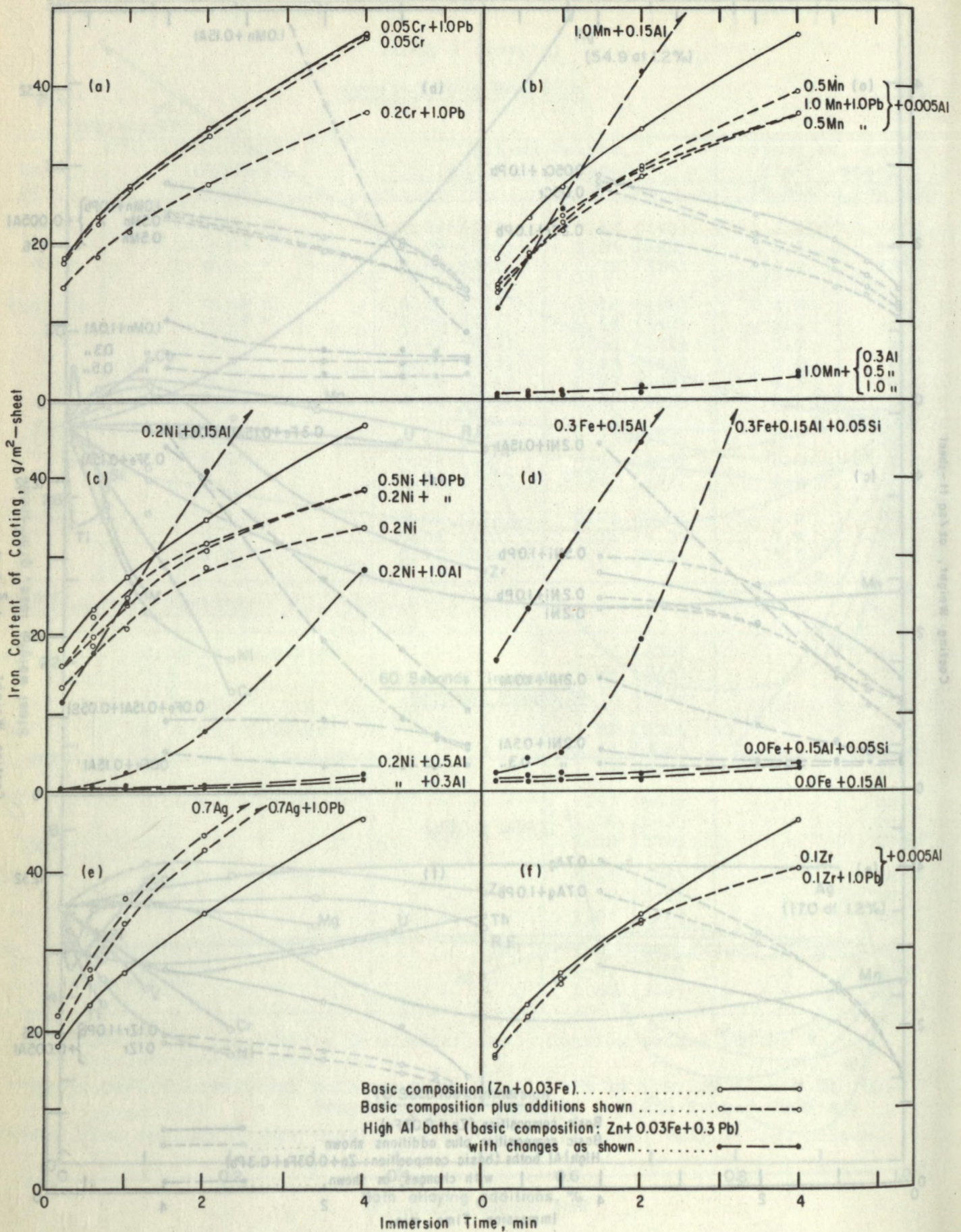
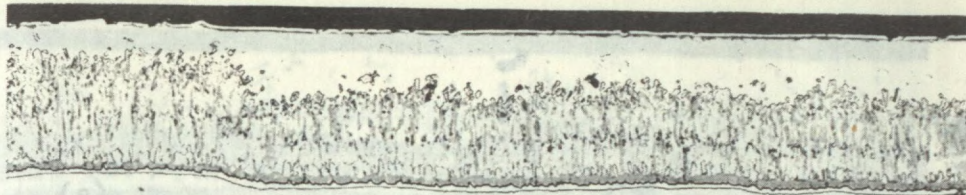
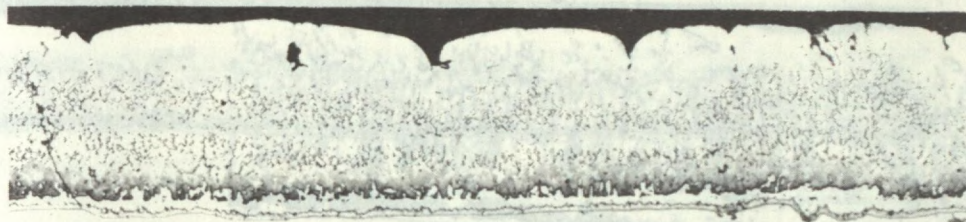


Figure 4. Influence of immersion time and bath composition on iron content of coating.

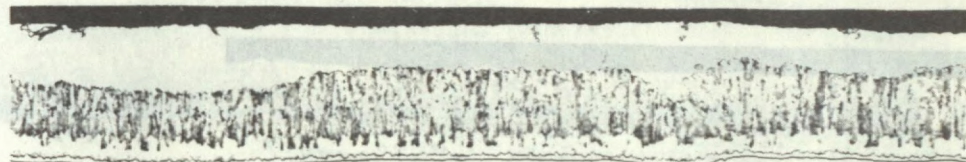


(a)
Basic bath composition

+ 100 X
IA 3000.0

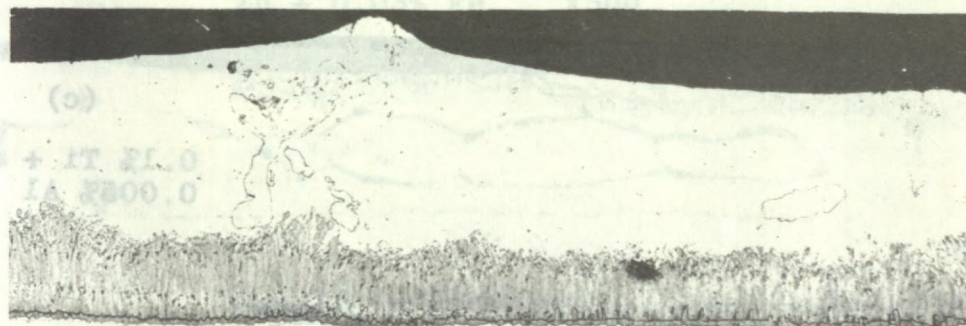


(b)
0.2% Mg +
0.005% Al +
0.02% Pb



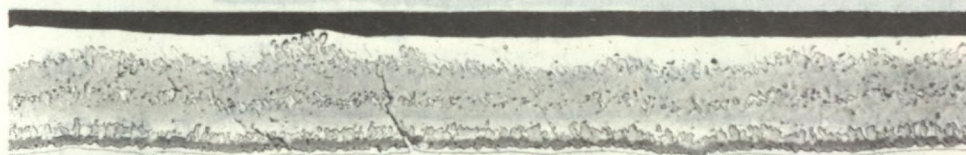
(c)
0.1% Zr +
0.005% Al

+ 100 X
IA 3000.0



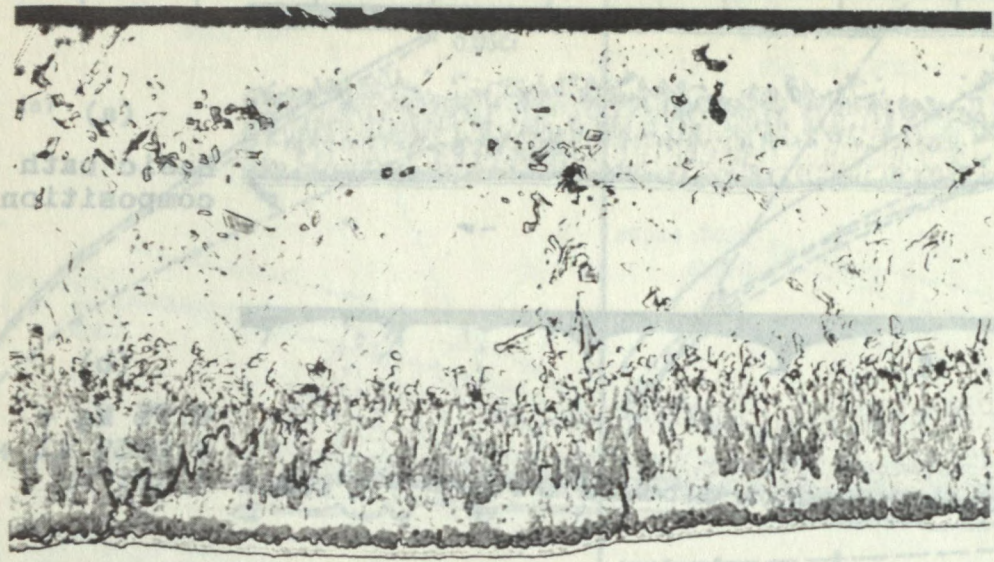
(d)
0.5% Zr +
0.005% Al

+ 100 X
IA 3000.0



(e)
0.05% Si

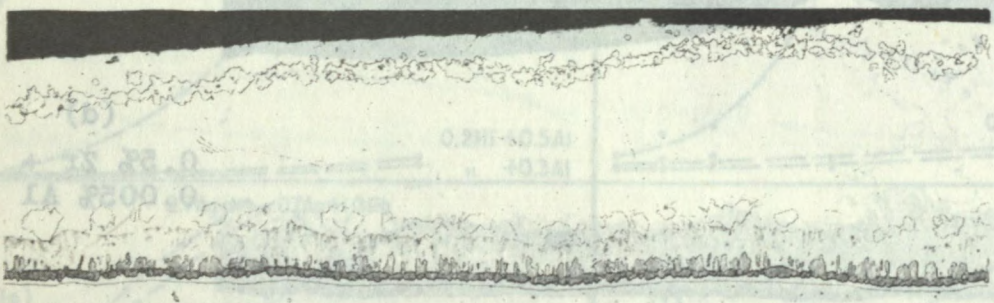
Figure 5. Microstructures of "aluminum-free" coatings obtained at 1 minute immersion. Basic bath composition: Zn + 0.03% Fe. X500



(a)
1.0% Mn +
0.005% Al
X1500.



(b)
0.05% Ti +
0.005% Al



(c)
0.1% Ti +
0.005% Al



(d)
0.2% Cr

Figure 6. Microstructures of "aluminum-free" coatings obtained at 1 minute immersion. Basic bath composition: Zn + 0.03% Fe. X500, except in (a).

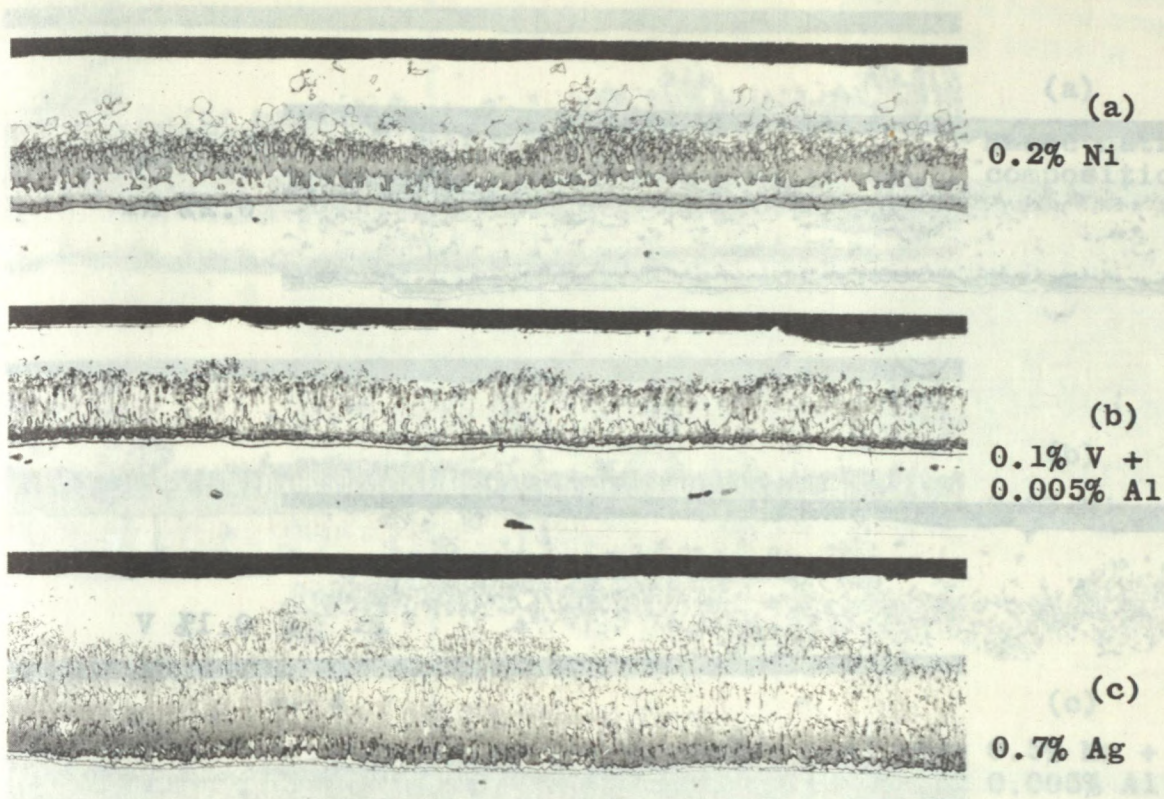


Figure 7. Microstructures of "aluminum-free" coatings obtained at 1 minute immersion. Basic bath composition: Zn + 0.03% Fe. X500

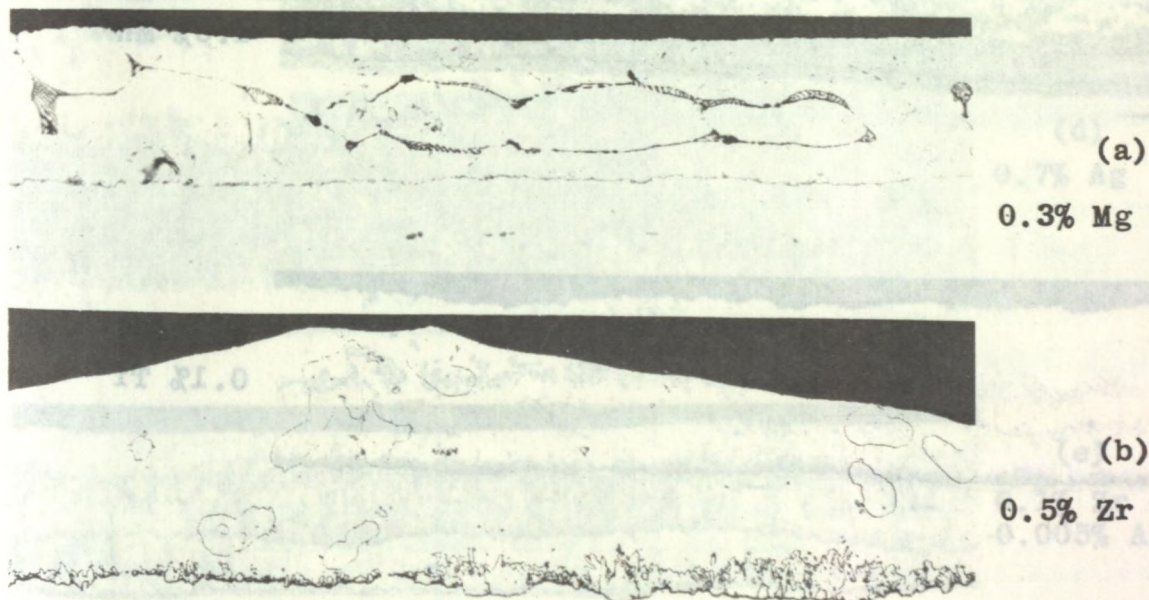
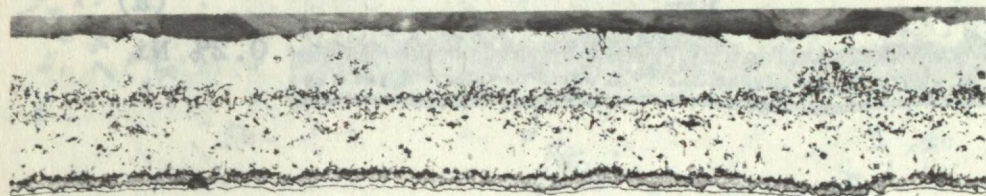
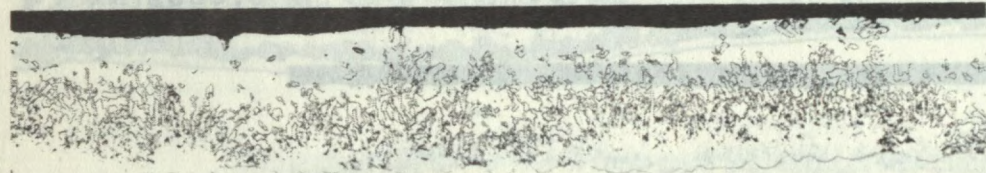


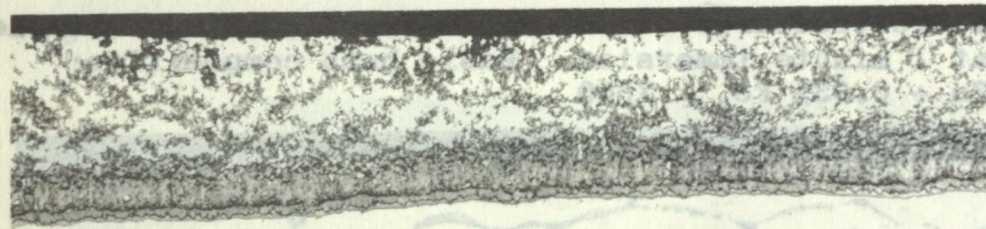
Figure 8. Microstructures of "aluminum-containing" coatings obtained at 10 seconds immersion. Basic bath composition: Zn + 0.03% Fe + 0.15% Al + 0.3% Pb. (a) at X750; (b) at X500



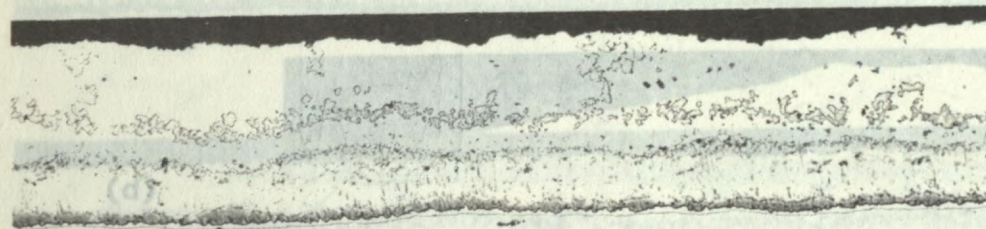
(a)
0.2% Ni



(b)
0.1% V

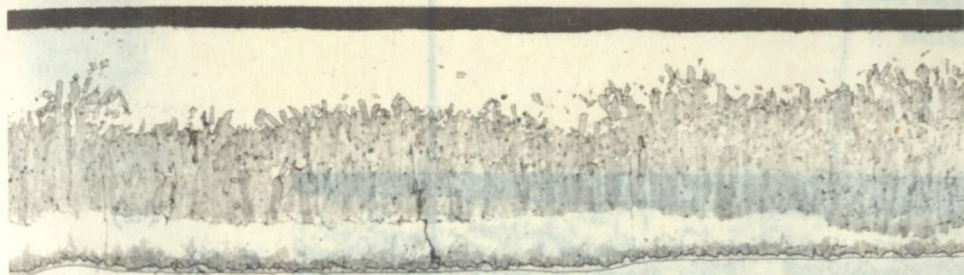


(c)
1.0% Mn

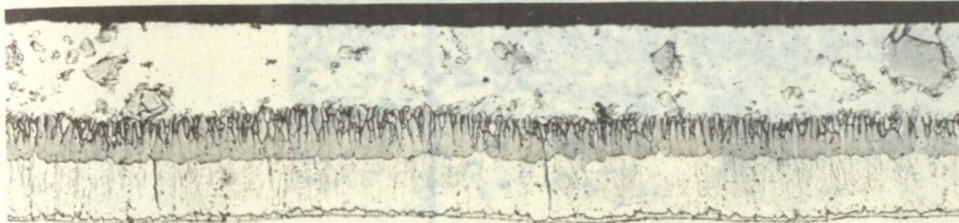


(d)
0.1% Ti

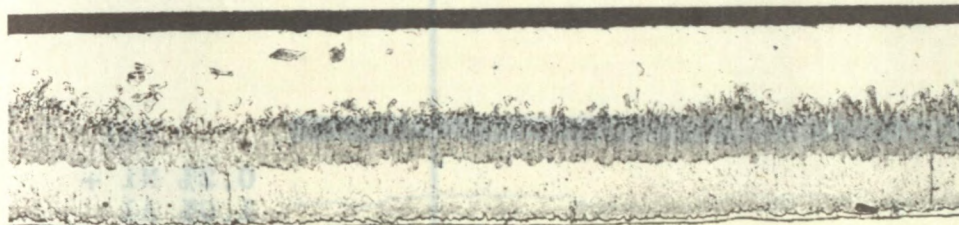
Figure 9. Microstructures of "aluminum-containing" coatings obtained at 1 minute immersion. Basic bath composition: Zn + 0.03% Fe + 0.15% Al + 0.3% Pb. X500.



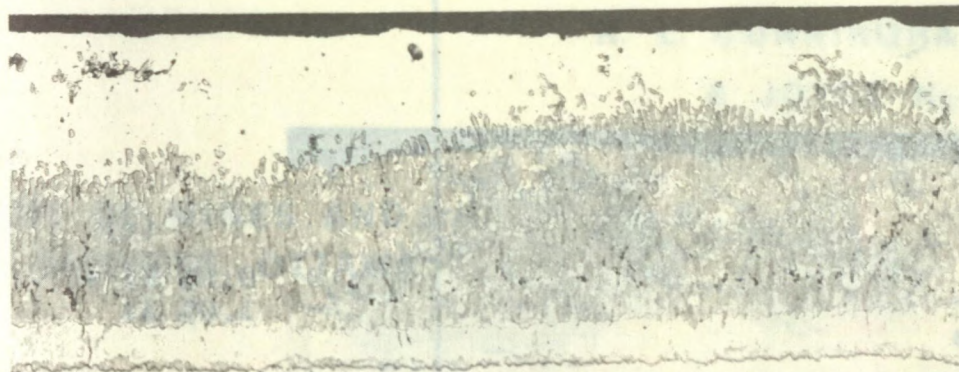
(a)
Basic bath
composition



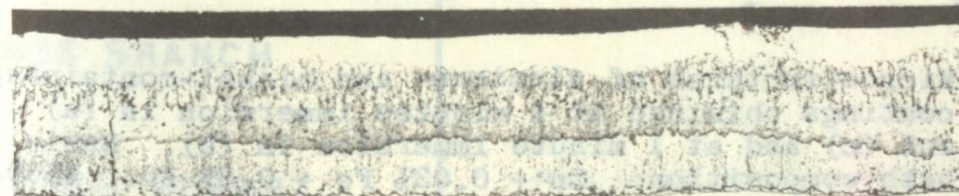
(b)
0.2% Ni



(c)
0.5% Mn +
0.005% Al



(d)
0.7% Ag



(e)
0.1% Zr +
0.005% Al

Figure 10. Microstructures of "aluminum-free" coatings obtained at 4 minutes immersion. Basic bath composition: Zn + 0.03% Fe + 1.0% Pb. X500.

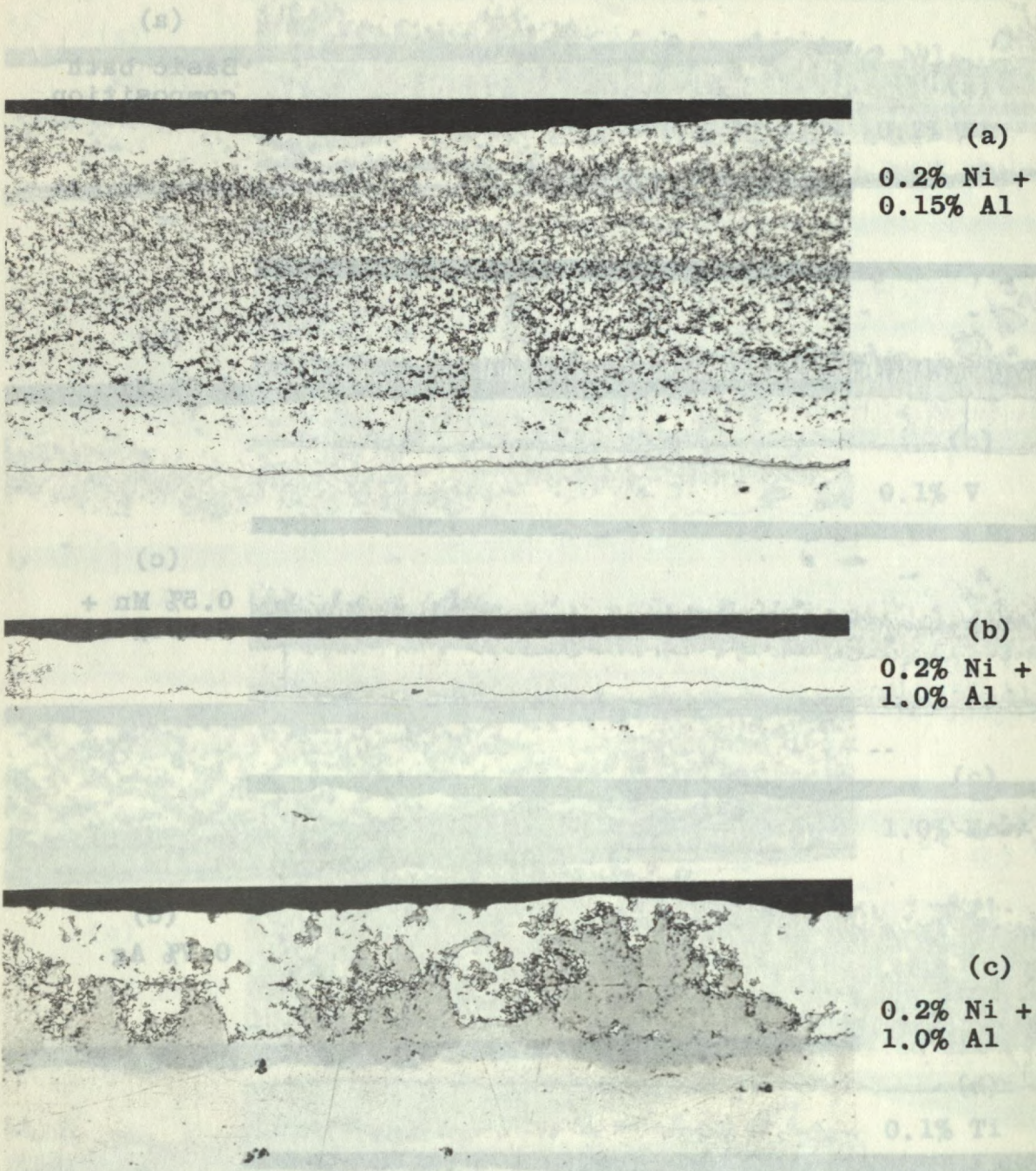


Figure 11. Microstructures of aluminum- and nickel-containing coatings obtained at 4 minutes immersion in (a) and (c) and at 1 minute immersion in (b). Basic bath composition: Zn + 0.03% Fe + 0.3% Pb. X500.

Figure 9. Microstructures of "aluminum-containing" coatings obtained at 1 minute immersion. Basic bath composition: Zn + 0.03% Fe + 0.15% Al + 0.3% Pb. X500.

Figure 10. Microstructures of "aluminum-containing" coatings obtained at 4 minutes immersion. Basic bath composition: Zn + 0.03% Fe + 1.0% Al + 0.3% Pb. X500.