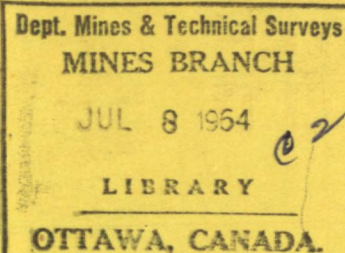




CANADA



THE GALVANIZING BEHAVIOUR OF COMMERCIAL STEEL SHEET MATERIALS

J. J. SEBISTY & R. H. PALMER

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

PHYSICAL METALLURGY DIVISION

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THE GALVANIZING BEHAVIOUR OF COMMERCIAL
STEEL SHEET MATERIALS

by

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

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ABSTRACT

A statistically designed investigation has been made of the hot-dip galvanizing characteristics and behaviour of several commercially produced steel sheet materials, comprising a series of low-carbon mild steels and a representative group of low-alloy high-strength steels. Both continuous strip and general galvanizing practice were considered in selection of the laboratory galvanizing conditions.

Coating formation on the mild steels in aluminum-free zinc baths was largely influenced by the physical roughness of the steel surface, whereas in baths alloyed with aluminum and under conditions approximating to continuous strip practice effective inhibition of the iron-zinc reaction was more dependent on the inherent chemical activity of the steel surface. As this increased, the beneficial effect of aluminum was lessened and especially so in the case of heavily-worked mild steel sheet.

The galvanizing response of low-alloy high-strength type steels in aluminum-free baths varied according to steel composition. High-silicon materials showed an extremely aggressive, linear rate of attack with time which was reflected in the formation of very thick coatings having an unsatisfactory surface appearance. In aluminum-alloyed baths, suppression of zinc attack of the alloy steels was somewhat less effective than with mild steels, except under certain conditions where the effect of aluminum was enhanced with the high-silicon type steels. Coatings on the latter were prone to the development of bare or uncoated spots when the aluminum concentration in the bath was high. Tensile properties of the alloy steels were affected in varying degrees by galvanizing and most significantly in the case of yield strength.

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Direction des mines

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COMPORTEMENT À LA GALVANISATION D'ACIERS
À TÔLES UTILISÉES DANS LE COMMERCE

par

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

RÉSUMÉ

On a fait une étude statistique des caractéristiques de galvanisation par immersion à chaud ainsi que du comportement de plusieurs tôles d'acier produites dans le commerce, notamment une série d'aciers doux à faible teneur en carbone et un groupe représentatif d'aciers très résistants mais faiblement alliés. Dans le choix des conditions de galvanisation au laboratoire, on a tenu compte tant du procédé par bandes continues que du procédé général de galvanisation.

La formation de l'enduit sur les aciers doux plongés dans des bains de zinc sans aluminium était en grande partie influencée par la rugosité physique de la surface de l'acier, alors que dans le cas des bains contenant de l'aluminium et dans des conditions presque identiques à celles du procédé par bandes continues, l'inhibition de la réaction entre le fer et le zinc dépendait davantage de l'activité chimique inhérente de la surface de l'acier. A mesure que croissait cette activité, l'avantage de l'emploi de l'aluminium s'atténuait, tout particulièrement dans le cas de tôles d'acier doux soumises à de nombreux traitements.

Le comportement à la galvanisation d'aciers très résistants et faiblement alliés dans les bains sans aluminium variait d'après la composition de l'acier. Les matériaux riches en silicium dénotaient une vitesse d'attaque linéaire extrêmement agressive à mesure que le temps s'allongait, et, comme résultat, il se formait des enduits très épais d'aspect peu satisfaisant en surface. Dans les bains contenant de l'aluminium, la suppression de l'attaque au zinc des aciers alliés était un peu moins efficace que dans le cas des aciers doux, sauf dans certaines conditions où l'effet de l'aluminium était plus marqué sur les aciers riches en silicium. Les enduits sur ces derniers aciers étaient sujets à la formation de points dénudés ou sans enduit lorsque la concentration en aluminium du bain était élevée. La galvanisation influait à divers degrés sur les propriétés de traction des aciers alliés, et ce phénomène était très marqué dans le cas de la limite apparente d'élasticité.

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INTRODUCTION

It is generally assumed that composition and other variations within the range of mild steel sheet materials normally supplied to the galvanizer have little influence on the galvanizing process. This is based on numerous published investigations, reviewed elsewhere(1-3), which have examined the role of the steel base with respect to the effect of such factors as chemical composition, surface condition, metallographic structure, etc. As a result, recent studies have paid scant attention to the sheet materials the galvanizer is or may be confronted with, despite the significant changes and improvements made in recent years in steel sheet processing and quality. Advances in this direction are of concern to the galvanizing industry, since they can influence the success achieved in meeting the increasing demand for higher quality coatings and the competition of other protective systems. For this reason, and in the interest of the widespread effort towards new and expanded use of zinc coatings, an appraisal of the galvanizing performance of sheet materials currently available was considered to be of importance.

These considerations motivated the present investigation which was undertaken at the Physical Metallurgy Division of the Department of Mines and Technical Surveys, Ottawa, Canada, in cooperation with the Canadian Zinc and Lead Research Committee and the International Lead Zinc Research Organization. This involved a statistically-designed laboratory study made to compare the galvanizing characteristics and behaviour of a series of commercially-produced steel sheet materials which are or could be used for galvanizing purposes. Mill-finished materials, comprising various mild steel grades and low-alloy high-strength steels, were experimentally coated by the dry galvanizing technique in aluminum and/or lead-containing baths. Coating formation and properties were evaluated by various tests.

STEEL SHEET MATERIALS

The mild steels selected for study included the materials broadly classified as (a) Armco iron, (b) rimmed galvanizing grade, (c) aluminum-killed deep-drawing grade, (d) hot-rolled normalized grade, (e) full hard grade and (f) bottle-top tin-plate grade; all of these were mill-finished by cold rolling to 24 gauge (0.025 in., 0.6 mm), except for the hot-rolled normalized sheet which was 14 gauge (0.077 in., 2 mm). Two of the three low-alloy steels tested were also hot-rolled to 14 gauge, whereas the third was cold-rolled to 16 gauge (0.061 in., 1.5 mm). These discrepancies in gauge and surface finish were unavoidable because of material availability.

The chemical composition, mechanical properties, grain size and surface roughness data for the materials tested are given in Table 1. Variations between the as-received mild steels reflected the effects of steelmaking and processing history, but were within normal limits. The heavily worked structure of the full hard steel (No. 10) and the larger grain size combined with marked smoothness of the Armco iron (No. 4) distinguished these materials from the other four grades. The latter were all fine-grained and had a rougher surface texture which tended to show wider variation around the average values given in the table. A distinctive feature of the aluminum-killed steel (No. 6) was an irregular distribution of coarse angular-shaped cementite particles; these were much less numerous in the Armco (No. 4), normalized (No. 8) and rimmed (No. 1) grades, in that order. In the bottle top steel (No. 11), the cementite was scattered in the form of fine spheroidized particles.

One of the hot-rolled alloy steels was a high-silicon type (No. 13), a second was a high-manganese grade (No. 14), and the third, cold-rolled grade (No. 15), was high in both silicon and phosphorus. Other variations in composition as well as in mechanical properties of these higher strength materials can be seen in Table 1. All were fine-grained, but were otherwise differentiated by the fine spheroidized particles at the grain boundaries in Steel No. 15 and the lamellar pearlite distribution in Steel No. 13 and 14. Distinctive features of the hot-rolled high-manganese steel (No. 14) were an increased amount of pearlite, greater prominence of stringer-type inclusions, and a markedly rougher surface finish.

In order to examine the effect of cold working and surface smoothness on galvanized coating formation, six additional steel grades were obtained by laboratory rolling (polished rolls) of the mild steels, exclusive of the full hard sheet. This accounts for the total of fifteen steels listed in Table 1. As indicated, reductions of 5 or 15% were applied, followed by stretcher straightening. This treatment increased the tensile strength, yield strength and hardness significantly, at the same time reducing elongation and Erichsen cup depth, as shown by the results. Improvement in the measured surface smoothness (Talysurf) was variable, being greatest with the bottle top sheet (No. 12) and least with Armco iron (No. 5), which had by far the smoothest surface in the as-received condition. It is to be noted that metallographic evidence of the smoothing due to rolling, as seen on samples after galvanizing, was frequently much more pronounced than that indicated by the Talysurf measurements. In this connection, it is emphasized that the latter represent averaged values which were affected by occasional wide variations in the measured roughness on the same and different pieces of the same material, particularly in the as-received condition. Insofar as steel base microstructure was concerned, no changes in any of the re-rolled materials were observed.

EXPERIMENTAL PROCEDURE

The statistically-designed experimental galvanizing program is given in Table 2. In an initial series of tests, designated Experiment "A", the various steels were dipped in the sequence shown at immersion times of 10, 35 and 60 seconds in iron-saturated zinc baths alloyed with 0.3% Pb and either nil, 0.075% or 0.15% Al. Experiment "B" was added later and involved lead additions of 0.3% and 1.0% and immersion times of 1, 2 and 4 minutes. In both series, duplicate baths were run to provide sufficient samples for testing. A constant bath temperature of 450°C (840°F) was maintained throughout.

Details of the laboratory galvanizing apparatus and procedure used may be found elsewhere^(4,5) and can be briefly summarized as follows:

Test 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 followed by galvanizing in a 40-lb (18 kg) capacity graphite-lined steel pot under controlled conditions of immersion and withdrawal (6 fpm-3 cm/sec, and 3 fpm-1.5 cm/sec, respectively). 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). Four panels of each steel in the larger size and two in the smaller size were galvanized in each bath and provided specimens for coating evaluation tests and steel weight loss measurements, respectively. The small panels were water-quenched after withdrawal.

Materials used in making up the experimental baths were of 99.99% or higher purity. Lead was added directly, and iron and aluminum were introduced as master alloys which had been prepared as shot by casting into water. All baths were sampled for chemical analysis at the beginning and end of each run, and also after galvanizing of 16, 32 and 48 of the large panels. The results showed little variation in iron, aluminum and lead from the nominal levels, probably for the reason that periodic replenishment of each bath from a reserve melt of the same nominal composition was carried out. This was necessary because of sampling and skimming losses, and the otherwise normal bath depletion due to the large number of panels dipped in each bath.

Contamination of the experimental baths by alloying elements dissolved from the alloy steels was considered to be worthy of investigation. To this end, chill-cast disc samples

were taken at the beginning and end of galvanizing runs with baths 19 to 28 in Experiment "B". These involved the longest dipping times and were therefore expected to show maximum effects. Spectrographic analysis of the discs revealed contamination to be slight and thus of negligible importance insofar as formation of the experimental coatings was concerned. Average values before and after dipping for the three elements which increased in concentration in the baths were: 0.0007% - 0.0015% Cu, 0.0001% - 0.0006% Mn, 0.0001% - 0.0003% Ni. Other elements present at similarly low concentrations remained at a constant level throughout dipping.

Evaluation of the experimental coatings was based on tests essentially similar to those used in prior work(4). These included the following:

- (a) Coating weight and iron content of coating (stripping test in 20% HCl acid solution).
- (b) Coating ductility (qualitative rating of behaviour of thinner-gauge mild steels in Erichsen cupping test).
- (c) Coating adherence (qualitative rating of behaviour of thinner-gauge mild steels in bend test).
- (d) Coating structure (microscopic examination, measurement of thickness and proportion of iron-zinc alloy in coating).
- (e) Steel weight loss (stripping test on smaller panels with standard antimony-inhibited HCl acid solution).
- (f) Surface appearance evaluation (measurement of spangle size, spangle contrast, coating brightness and coating roughness qualitatively rated against arbitrary standards).

Other tests made included examination of the pickling behaviour of all steels and of the effect of galvanizing on the mechanical properties of the alloy grades. Evaluation of the atmospheric corrosion behaviour of test panels set out at an instrumented semi-industrial site was also undertaken and information of interest will be published at a future date. In addition, attempts were made to compare the storage-stain susceptibility of the experimental coatings by humidity and water film stack tests. However, the data obtained failed to yield conclusive information and the tests are being reappraised. A principal difficulty in this connection was the lack of flatness of the test panels, which consistently developed a slight curl across the shorter dimension during galvanizing.

OBSERVATIONS AND RESULTS

From statistical evaluation of the quantitative and qualitative coating test data obtained, graphical plots were prepared showing the trend of the relationships between the dependent and independent variables investigated. For reasons of space, this paper contains only some of the more significant plots. Those pertaining to Experiment "A" are illustrated in Figures 1 to 4 and to Experiment "B" in Figures 5 to 7. A more complete compilation may be found in a separate report⁽⁵⁾ which also gives a full description of the statistical treatment of the results. In the same report, all experimental and coating test data pertinent to the investigation are tabled.

For plotting and comparative purposes, the fifteen grades of steel were separated into six groups as indicated in the graphs. In the following discussion, the designation "aluminum-containing" refers to coatings prepared with aluminum in the bath in Experiment "A". The designation "aluminum-free" applies to all others and covers tests in both Experiments "A" and "B".

Coating Weight

The graphs in Figure 1 apply to Experiment "A" and show coating weight for the various steel groupings plotted against aluminum content of the bath and immersion time. Taking the as-received mild steels first, it can be seen that the rimmed (No. 1), Armco iron (No. 4) and bottle top (No. 11) grades behaved similarly and showed expected response to both increasing aluminum in the bath and to immersion time. Thicker aluminum-free coatings were developed on the aluminum-killed (No. 6) and normalized (No. 8) steels and these were otherwise distinguished by the increased effectiveness of aluminum in the bath, as shown by the similarity in coating weight for all five steels at 0.15% Al. The full hard steel (No. 10) also yielded aluminum-free coatings of comparable thickness to the Armco iron, rimmed and bottle top grades despite its heavily work-hardened state. However, the effect of aluminum additions was minimal in this case as shown in Figure 1 (g).

The results for the aluminum-free tests in Experiment "B", given in Figure 5, show better definition of the normal curvilinear or parabolic relationship with immersion time. The formation of thicker coatings on the as-received normalized and aluminum-killed steels at the extended immersion times used was again evident, as was also the otherwise similar behaviour of the other four grades including the full hard steel. In general, the variation in lead content from 0.3% to 1.0% had very little effect on coating weight for the individual steels in the entire group. Such minor effects as were significant appear in Figures 5(b) and 5(f).

With the exceptions described below, the improvement in surface smoothness provided by the pre-rolling of the mild steels was reflected in significant reductions in coating weight. This was largely confined to the aluminum-free coatings and was more pronounced at immersion times of 1 minute and over, as revealed in Figures 1 and 5. An opposite effect was found with the hot-rolled normalized steel and Figure 1(g) shows that the aluminum-free as well as aluminum-containing coatings tended to be thicker on the re-rolled sheet (No. 9). The trend was somewhat erratic and actually disappeared with the longer dipping times in Experiment "B". Figure 1(h) indicates a similar reversal with the aluminum-containing coatings on the bottle top steel (No. 12). These anomalies suggest an increased steel surface activity, due to work hardening, which apparently overshadowed the smoothing effect of rolling on coating formation. In this connection it is not known to what extent the lesser mass of the rolled, normalized steel samples may have altered the rate or degree of the galvanizing reaction.

It is apparent from these observations that, for the range of conditions and materials studied, coating formation in aluminum-free baths was influenced to a greater degree by the physical roughness than by the chemical activity of the as-received steel surface, at other than very short immersion times. In aluminum-containing baths, the reverse was true and steel surface activity as influenced by the work hardening history of the steel base was a more dominant factor. From a practical standpoint, and ignoring other factors, realization of optimum inhibition of the iron-zinc reaction would thus appear to necessitate higher aluminum additions with a heavily worked steel sheet. Also, with a rough steel surface, as exemplified by the normalized and aluminum-killed grades tested, more frequent alloying of the bath with aluminum will be necessary to maintain the concentration at or near the optimum level; otherwise the coating weight will rise rapidly.

Figures 1 (i), 1 (l), and 5(f) show the coating weight trends with the three alloy-grade steels in Experiments "A" and "B", respectively. In the absence of aluminum and with immersion times up to 1 minute, all three materials behaved similarly and yielded coatings significantly thicker than on the most active mild steels. However, more prolonged dipping resulted in retention of the normal parabolic relationship with time only on the high-manganese steel (No. 14), Figure 5(f). In contrast, coating thickness on the other two grades continued to increase with time, revealing the characteristic linear relationship which is typical of such high-silicon steels. At 4-minute immersion, the coatings were in excess of 7 oz/sq ft (2100 g/m^2). The steep trend of the curves in Figure 5(f) gives an indication of the practical difficulties involved in coating thickness control with such materials. Varying the lead content of the bath appears to offer little assistance in this connection since its effect on coating formation in Experiment "B" was found to be relatively insignificant.

Coating weight build-up on the alloy steels with aluminum in the bath was variable, as shown in Figure 1(i). The usual downward trend with increasing aluminum was indicated, but this was consistently retained over the range investigated only with the high-manganese grade (No. 14). The high-silicon steel (No. 13) showed maximum reduction in coating weight, thus confirming the well-known enhanced effect of aluminum with silicon-containing steels. This grade in fact yielded the thinnest 0.075% Al coatings for the complete range of steels tested. It is remarkable that coating thickness on the same material, and also on the high-silicon high-phosphorus grade (No. 15), tended to increase again beyond this intermediate aluminum level. This reversal cannot be explained, but, if real, it suggests that the effectiveness of aluminum in the bath is limited with materials of this type and maximum inhibition appears to be confined to a narrow range of aluminum concentration and short immersion times.

Steel Weight Loss

The relative activity of the different steels, as measured by weight loss due to galvanizing attack, is illustrated in Figures 2 and 6 for Experiments "A" and "B", respectively. Under all conditions studied, markedly similar results were indicated for the as-received mild steels, exclusive of the full hard sheet (No. 10) in aluminum-containing baths. Attack of the aluminum-killed steel (No. 6) at extended immersion times was slightly greater than on the other grades, possibly because of the absence of a decarburized rim at the surface. The small increase could account in part only for the thicker aluminum-free coatings formed on this material and the rougher surface texture appeared to be the principal factor responsible. This could apply equally to the normalized sheet (No. 8), although in this case the increased gauge thickness was a secondary factor of undetermined importance.

In general, variable but small reductions in weight loss resulted from the rolling treatment applied to the mild steels. The improved surface smoothness of the rolled samples must therefore have been responsible for the appreciable aluminum-free coating thickness reductions found with the Armco iron (No. 5), rimmed (No. 3), aluminum-killed (No. 7) and bottle top (No. 12) steels. A consistent and apparently significant increase in steel attack was apparent with the high-aluminum coatings only on the normalized (No. 9) and bottle top (No. 12) steels, as illustrated in Figures 2(g) and 2(h). The indicated trends duplicate the effects found in the coating weight tests and support the prior observation that increased surface activity due to work hardening overshadowed the smoothing effect of the rolling treatment. Much more exaggerated evidence of the same phenomena in aluminum-containing baths is indicated by the high and uniform rate of attack of the full hard steel (No. 10) in Figure 2(g). In this case, negligible inhibition by aluminum is apparent within the range of additions used. The predominant effect of steel surface activity on the formation of coatings on mild steels in aluminum-alloyed baths is thus confirmed, as is also the contrasting importance of steel surface roughness with aluminum-free coatings.

As in the case of coating weight, the effect of increasing the lead content of the bath from 0.3% to 1.0% in Experiment "B" did not significantly alter zinc attack of the mild steels. This applied equally to the tests with the alloy-type steels.

Among the group of alloy steels, the high-manganese grade (No. 14) most nearly reflected the mild steel weight loss trends under all conditions, although losses were generally higher. In contrast, the two silicon-containing steels revealed extreme activity and very high weight losses with prolonged dipping in aluminum-free baths. The identical and pronounced linear rate of attack can be seen in Figure 6(f). This activity was counteracted by aluminum in the bath with the silicon steel (No. 13), and the weight loss results duplicated the trends evident in the corresponding coating thickness tests. However, as illustrated in Figure 2(i), attack was inhibited at a decreasing rate as the aluminum concentration was increased, so that weight losses tended to rise again at the higher end of the range investigated. The limited effectiveness of aluminum, referred to in the previous section, thus appears to be confirmed. The negligible response of the high-silicon high-phosphorus steel (No. 15) in Figure 2(i) is also to be noted. The lack of a consistent relationship with other coating tests made suggests that the trend of the relevant graphs is questionable. Experimental error associated with the high activity of this steel in the stripping operation is suspected.

Proportion of Iron-Zinc Alloy

Variations in the amount of iron-zinc alloy in the experimental coatings, calculated from microscopic thickness measurements and the coating weight stripping tests, are plotted in Figures 3 and 7. In consideration of the iron-zinc alloy microstructure irregularities found as described later, it will be appreciated that the thickness measurements are at best approximate estimates only.

Aluminum-free coatings on the mild steels varied from about 50% to 70% iron-zinc alloy for the immersion time range of 10 seconds to 4 minutes. Small differences between the different grades can be seen in the graphs, but of greater note is the consistently higher proportion of alloy on the re-rolled materials at and beyond 1-minute immersion as shown in Figure 7. The effect of a smoother steel surface in promoting more uniform iron-zinc alloy growth and less zinc drag-out is well defined, and is apparently confirmed by the minimal values associated with the rough, normalized steel (No. 8) in Figure 7(d). However, the increased gauge thickness in this case remains as a probable contributing factor. Similarly increased zinc drag-out, and for the same reasons, is apparent with the hot-rolled high-manganese alloy steel (No. 14) in Figure 7(f). In the same figure, the contrasting behaviour of the extremely active high-silicon steels (No. 13, 15) can be seen. Iron-zinc alloy represented in excess of 95% of the coating at 4-minute immersion.

As indicated in Figure 3, the mild steels responded in a characteristic manner to increasing aluminum in the bath, and the thickness of iron-zinc alloy was reduced to less than 10% of the total coating with 10 seconds immersion. An exception was the full hard steel (No. 10), which was essentially unaffected and yielded iron-zinc alloy in excess of 40% under all conditions. In general, immersion time effects were minor for most of the mild steels, and the influence of the rolling pretreatment was also reflected in small but erratic variations in the iron-zinc alloy measurements as can be seen in Figure 3. A more significant and apparently real effect was the unusual initial upward trend of the curves, reaching a peak at around 0.05% Al. Metallographically, this was suggested to be related to the influence of the intermediate aluminum addition of 0.075% in promoting better overall uniformity in the zeta phase layer, thereby contributing to a thinner and more uniform outer zinc layer. At the same time, the total thickness of iron-zinc alloy was only moderately reduced. Thus, an effective increase in the proportion of alloy around this intermediate aluminum range could be expected, and within the limitations of the alloy thickness measurements the upward trend in the graphs appears to represent consistent behaviour.

Microstructural irregularities were relatively pronounced on the high-aluminum coatings on the high-manganese (No. 14) and the high-silicon high-phosphorus (No. 15) steels, and iron-zinc alloy growth could be estimated only. For this reason the trend of the respective curves in Figure 3(h) can be considered as approximate only, although the behaviour indicated is consistent with that apparent in the prior coating tests. Much more reliable measurements were possible on the high-silicon steel (No. 13), and the effect of aluminum is well defined in the above figure. The characteristic curvature, tending to show a minimum with increasing aluminum instead of a maximum as with the mild steels and the high-manganese alloy steel, duplicates the trends found in the coating weight and steel weight loss tests. A narrow aluminum range, where inhibition of iron-zinc alloy formation was most effective, is again suggested.

Metallographic Structures

All samples prepared for microstructural examination were treated with etchants recommended by Rowland(6).

(a) Aluminum-free Coatings

Metallographically, the aluminum-free coating microstructures on the as-received mild steels were not greatly dissimilar and such differences as were apparent were related to immersion time and to the nature and roughness of the steel base. The zeta iron-zinc phase was the predominant layer in the coatings, and varied from the normal dense packing at short immersion times to well-defined columnar-oriented growth as the immersion time was

increased. For the same change in conditions, the expected faster rate of growth of the delta prime phase was also evident. Roughness of the steel base was reflected in non-uniform but reciprocal growth of these phases, as illustrated in Figure 9(a). The resultant irregularity in thickness of the eta layer can also be seen.

In most cases, marked improvement in uniformity of the individual layers, and of the coating as a whole, was achieved when the materials were pretreated by rolling before galvanizing. The rolling reduction of 15% applied had the greatest smoothing effect on the bottle top steel (No. 12), and the coatings obtained at lengthier immersion times represented the nearest approach to the exceptional iron-zinc alloy and coating uniformity found on corresponding samples of the mill-finished full hard steel (No. 10). A typical microstructure on this heavily worked material is shown in Figure 9(b). At shorter immersion times, the usual irregular zeta phase growth found with the other grades was observed.

In the group of mild steels mill-finished by cold rolling, thickest coatings were obtained on the aluminum-killed sheet (No. 6), particularly at longer immersion times. Apart from the effect of surface roughness, this behaviour was to some extent also affected by local surface irregularities of unknown origin. As illustrated in Figure 9(c), this material was prone to greater unevenness in the zeta phase layer and, in the extreme, gaps formed where steel attack and iron-zinc alloy formation were largely inhibited at short immersion times. This was not related to exposure of cementite particles on the steel surface. Increasing the dipping time initiated development of the normal phases at such gaps, but this was combined with formation of characteristic mushroom outbursts of zeta crystals. Such reaction variations could be expected to increase zinc drag-out and overall thickness of the coating. All of the above effects were much less exaggerated on the re-rolled aluminum-killed sheet (No. 7), thereby accounting for the relatively marked coating weight reduction achieved by the rolling treatment applied.

Typical aluminum-free coatings on the three low-alloy steels are illustrated in Figure 10. It can be seen that the very thick coatings developed at 4 minutes immersion on the high-silicon (No. 13) and the high-silicon high-phosphorus (No. 15) grades were similar and consisted largely of gross individual crystals of the zeta phase, embedded in a zinc matrix. These appeared to nucleate near the steel base within the delta prime phase, which was otherwise made more irregular by its tendency to break up into a fine granular mass in areas of easy access to zinc. The gamma iron-zinc phase was absent and another feature was the very thin covering layer of zinc at the surface. Shorter immersion times produced the same essential features, although in more compacted form and with a much thicker outer zinc layer containing a heavy dispersion of small zeta crystals. Coatings on the high-manganese

grade (No. 14) were not unlike those observed on the rimmed (No. 1) and normalized (No. 8) mild steel materials. More pronounced and irregular zeta phase growth was apparent, and a heavier dispersion of fine zeta crystals in a thick eta layer was another difference. However, the basic features of a normal coating microstructure were otherwise retained and clearly distinguished this material from the other two more chemically active alloy steels.

No significant changes in microstructure of the complete series of aluminum-free coatings were observed due to increase in lead content of the bath from 0.3 to 1.0%. At the higher concentration, the lead could be seen distributed as fine particles in the outer zinc layer, and also scattered throughout the thick zeta layer formed at extended immersion times. In these thicker coatings, the zeta-delta prime interface appeared to represent the limit of lead penetration, and particles of lead could not be distinguished in the latter phase.

(b) Aluminum-containing Coatings

(i) 0.075% Al

With 0.075% Al in the bath, the characteristic layered microstructure on the mild steels was retained, but with somewhat reduced total thickness of iron-zinc alloy and of the coating as a whole. Much less pronounced local irregularities in zeta phase growth contributed to better uniformity in the alloy band as a whole. This modification due to aluminum was more striking with the relatively rough aluminum-killed (No. 6) and normalized (No. 8) steels in the as-received condition, and was thus responsible for the greater overall coating weight reductions achieved with 0.075% Al in these cases.

Because of the more even iron-zinc alloy growth, the influence of surface roughness of the mild steels was principally reflected in thickness variations in the outer zinc layer only. Such variations were largely eliminated by the laboratory rolling treatment applied, which thereby promoted better total coating uniformity. This effect was general on the different steels, being most marked with the bottle top grade (No. 12). On the aluminum-killed steel, the tendency to form gaps in the alloy layer, and in rare cases breaks open to the surface, was retained in both the as-received and rolled conditions, although coating uniformity was improved by rolling.

A typical microstructure representative of the above coatings is shown in Figure 11(a). At short immersion times, the effect of the aluminum addition was to promote increased growth of the delta prime phase as a duplex-structured layer. This consisted of a thin dark-etching continuous band adjacent to the gamma phase, and a much thicker featureless layer showing little response to etching. Above this, zeta phase growth was confined to a loosely

packed band of angular crystals. Marked growth of the zeta crystals was a predominant effect at longer immersion times. These frequently penetrated well down into the delta prime phase, as massive individual crystals or as a continuous close-packed band of such crystals showing the same well-defined columnar growth. Variations between these extremes were common on the same steel and between the different mild steel grades at 60 seconds immersion, but the particular factors accounting for the variable amounts of the delta prime and zeta phases could not be resolved metallographically. The similarity in iron content of the zeta phase and the major portion of the adjacent delta prime phase found by electron micro-probe analysis (7) would appear to be involved.

Microstructural features of the coatings on the high-manganese alloy steel (No. 14) were much the same as those on the mild steels except for more irregular iron-zinc alloy growth and total coating uniformity. The particularly rough hot-rolled steel surface was seen to be largely responsible. The same basic coating microstructure, somewhat superior in uniformity and of increased thickness, was also found on the high-silicon high-phosphorus steel (No. 15). The typical band of columnar-oriented zeta crystals was particularly well-defined even at 10 seconds immersion and was again combined with a thick eta layer showing a heavy dispersion of small zeta crystals, Figure 11(b). For unexplained reasons, an occasional sample of Steel 15 exhibited an exceptionally thin coating on both surfaces. Only a thin continuous band of iron-zinc alloy crystals had formed, indicating much more effective aluminum inhibition. This erratic behaviour, which reduced the coating weight by up to 50%, was a more prominent feature of the high-aluminum tests described in the next section.

The response of the high-silicon steel (No. 13) was different from all others in the 0.075% Al series of tests. The enhanced inhibition by aluminum, referred to earlier, was reflected in marked suppression of iron-zinc alloy growth and a moderately thin continuous band of alloy only was formed even at 60 seconds immersion as in Figure 11(c). However, uniformity in the eta layer, which constituted the bulk of the coating, was generally poor because of the rough steel base.

(b) 0.15% Al

Suppression of iron-zinc alloy growth with 0.15% Al in the bath was the principal effect observed with all of the as-received mild steels except the full hard sheet (No. 10). The coating structure consisted of the normal thin fringe of alloy crystals and a thin eta layer cover showing some irregularity depending on the roughness of the steel base. Microstructural differences were otherwise minor at 10 seconds immersion, but more prominent at longer times, being distinguished by variable general growth in the alloy fringe and in development of local alloy outbursts at the sites of vigorous steel attack. Such

growths, in combination with a rougher steel surface, contributed to thicker and more non-uniform coatings on the normalized (No. 8) and aluminum-killed (No. 6) steels. The Armco iron (No. 4), rimmed (No. 1) and bottle top (No. 11) grades were somewhat superior in this respect, presumably because of lower chemical activity at the reacting surface.

The variable steel response described above was better defined on the rolled samples, and local attack was much more prevalent on the normalized and aluminum-killed grades. Also, in opposition to its behaviour in the prior series of tests, the bottle top steel in the rolled condition (No. 12) exhibited more aggressive general and local attack at 1 minute immersion. This accounts for the reversed effect of rolling on coating weight in Figure 1(h). More conclusive evidence showing the effect of cold working on coating formation was provided by the full hard steel. Development of all the iron-zinc alloy phases in the normal layered structure was retained and the only effect of the 0.15% Al addition, even at 10 seconds immersion, was to reduce the total thickness of alloy slightly.

The characteristic suppression of steel attack by 0.15% Al was evident with the high-silicon (No. 13) and also with the high-manganese steel (No. 14). Extensive areas were covered by the usual fringe layer of alloy crystals but numerous local outbursts and roughness of the steel base contributed to significant non-uniformity in the coating as a whole. Stringer-type inclusions open to the surface on Steel 14, which were undermined and forced upwards as crescent-shaped slivers, also contributed to uneven zinc drag-out in this case. With respect to the silicon-containing steel (No. 13), the effect of 0.15% Al in the bath was not markedly different from that with 0.075%. Somewhat less pronounced development of the alloy fringe, as shown in Figure 11(d), was essentially the only change observed.

The erratic behaviour of the high-silicon high-phosphorus alloy steel (No. 15) previously described was repeated and exaggerated with the 0.15% Al addition. Iron-zinc alloying activity varied haphazardly on opposite sides of a sample and on different samples given the same treatment. Areas of inhibited attack were frequently broken by pronounced local outbursts and by more widespread patches showing development of a thick continuous band of alloy. A heavy dispersion of particles in the irregularly thick eta layer was a feature common to all samples. Some additional galvanizing tests were made on this particular steel and the same erratic response to aluminum in the bath was observed. To what extent the high-silicon high-phosphorus content, the cold-rolled nature of the steel surface or other unknown factors were responsible for this behaviour remains unexplained. A more intensive examination is in progress.

Composition of Coatings

As a matter of interest, the iron content of the coatings was determined in conjunction with the coating weight stripping tests. In general, the trend of the curves derived duplicated the steel weight loss results, with the characteristic exception of lower attack being indicated by the iron determinations for the high-aluminum series of coatings. Because of the generally limited iron-zinc alloy formation in such coatings, particularly at short immersion times, the absolute differences observed are probably not of great practical significance. However, there would appear to be some justification for the criticism that the uninhibited acid stripping technique does not completely remove the thin iron-zinc alloy layers normally formed in high-aluminum baths. A further study in this direction is in progress.

The aluminum-containing and aluminum-free coatings were analysed for aluminum and lead, respectively, on separately stripped samples. In agreement with results of other investigators, it was found that the aluminum content of the coatings was three to four times higher than the nominal bath additions of 0.075% and 0.15%. The spread was related to immersion time and the higher concentration was always found in the thicker coatings formed at 1-minute immersion. Wider variation in the results for the different steels was apparent with the 0.15% Al addition, again at the longer immersion times, but the lack of any consistent trend indicated that the grade and composition of the steel base were not significant. The aluminum content of the coatings tended to decrease as steel weight loss increased but this relationship, also was not consistent.

The lead content of the aluminum-free coatings generally varied from about 35% to 45% of the nominal additions of 0.3% and 1.0%. This discrepancy is accounted for by the fact that the entire coating was stripped for analysis. It also explains the decrease in lead content observed within the above limits with increasing immersion times, since thicker coatings would contain a proportionately smaller volume of the lead-containing eta layer. As to be expected because of its effect on zinc pick-up, steel surface roughness also influenced the lead content of the coatings. It was found that the rough, hot-rolled normalized (No. 8) and high-manganese alloy steel (No. 14) grades yielded consistently higher lead values than all others. The opposite extreme was represented by the two chemically active, high-silicon materials (No. 13, 15) on which the coatings consisted largely of iron-zinc alloy crystals embedded in a zinc matrix and covered by a thin outer zinc layer only.

Coating Ductility and Adherence

The ductility and adherence properties of the coatings on the thinner-gauge plain carbon steels only were evaluated by Erichsen cupping tests and simple bend tests, respectively. The statistically derived relationships for the coatings obtained in Experiment "A" are reproduced in Figure 4.

In consideration of the variations in mechanical and forming properties of the different steels, as well as the relatively large coating thickness spread between aluminum-free and high-aluminum coatings, only a rough sorting of these properties was possible or intended. According to the performance standards set up, the expected superiority of the high-aluminum coatings was realized and, as indicated in Figure 4, these were generally classified as having good to excellent ductility and adherence even in the case of coatings formed at 1-minute immersion. Within this series, only the coatings on the full hard steel (No. 10) were graded as less satisfactory.

Coatings prepared with 0.075% Al in the bath were distinctly inferior to those described above and only slightly better than the aluminum-free coatings, which were all rated as having poor ductility and adherence. Because of the excessive severity of the tests as applied to these relatively thick coatings, it was not possible to distinguish any significantly important effects due to steel grade or surface condition as affected by rolling.

Tests run with an electrically operated lock-seaming machine confirmed the marked superiority of the high-aluminum coatings. These withstood the stresses applied in forming the "S" bend without any deterioration, whereas all others flaked and peeled severely.

Coating Surface Appearance

Surface appearance of the experimental coatings was evaluated on the basis of estimated average spangle size and by qualitative rating of spangle contrast, coating brightness and coating roughness.

Samples galvanized in the aluminum-free baths containing 0.3% Pb had a characteristic dull, low-contrast finish with well-defined spangle grains varying in average diameter from 1/4 in. to 1/2 in. (6 to 12 mm). The size of the spangles increased only moderately with immersion time. A more dominant factor was the thickness or mass of the steel base, as shown by the development of largest spangles on the heavier gauge normalized (No. 8, 9) and alloy-grade (No. 13, 14, 15) steels. This must be related to the slower coating solidification rate and also, in the case of the rougher hot-rolled normalized and high-manganese grades, to increased zinc drag-out.

Grey coating formation distinguished the high-silicon (No. 13) and high-silicon high-phosphorus (No. 15) steels from all others. At very short immersion times this occurred in randomly distributed solid patches, to be followed at longer immersion times by general development of a characteristic diffused spangle boundary pattern and, finally, a uniformly grey finish over the entire surface. For the conditions studied, this deterioration in appearance, which is due to penetration of iron-zinc alloy to the surface, appeared to develop more rapidly and reached a more advanced stage with the high-silicon steel. Increasing the lead content of the bath to 1% in Experiment "B" appeared to reduce the degree of greyness on both materials but the effect was not entirely consistent, particularly with the high-silicon sheet.

A more prominent effect of the higher lead addition was a marked increase in spangle size with all steels. This change was again more pronounced with the heavier-gauge steels, on which spangle grains exceeding 1 in. (25 mm) in diameter were normal. By comparison, the maximum spangle diameter on the thin-gauge mild steels was less than 3/4 in. (18 mm). On all high-lead coatings, the characteristic dull, low-contrast surface finish was retained.

Coatings produced with aluminum in the bath in Experiment "A" were typically bright and smooth, except for occasional raised ridges with the higher addition of 0.15% Al. Spangle contrast was uniformly low but from etching of the surface it was revealed that spangle formation on all steels was much finer than on the aluminum-free coatings. Maximum spangle diameter at 60 seconds immersion was generally less than 3/16 in. (4.5 mm) and around 1/16 in. (1.5 mm) at 10 seconds. In this connection both 0.075% and 0.15% Al were equally effective. The effects of steel grade, grain size and surface condition on coating appearance were all indicated to be minor factors except for increased roughness and lower reflectivity of coatings on the heavier gauge steels. Another exception was the consistently finest spangle formation on the bottle top steels (No. 11, 12) under all conditions in the aluminum-containing series of tests. No explanation for this behaviour was found.

The occurrence of ridge-type formations on the high-aluminum coatings has already been mentioned. Another defect, encountered principally with the two high-silicon alloy steels (No. 13, 15), was non-uniform wetting of the surface and resultant development of uncoated areas or black spots. These were most prominent on coatings formed at the minimum immersion time of 10 seconds and with 0.15% Al in the bath. Additional galvanizing tests made, involving modifications in pickling and fluxing practice, as well as increase in lead content of the bath to 1%, failed to provide noticeable elimination of this defect. It is to be noted that the high-manganese alloy steel (No. 14) was also susceptible to bare spotting, but to a minor degree by comparison with the other two alloy steels.

Miscellaneous Tests

(a) Pickling Behaviour

In preliminary work to the main investigation, the pickling behaviour of the complete series of steels was examined in a Rodine-inhibited 5% sulphuric acid solution. Various immersion times and temperatures were used, and the more pertinent results of practical interest are plotted in Figure 8. Armco iron (No. 4) was the least active of the as-received mild steels, followed by the rimmed (No. 1), aluminum-killed (No. 6) and bottle top (No. 11) grades which behaved similarly as a group. The full hard steel (No. 10) was still more active and the upper extreme was represented by the hot-rolled normalized steel (No. 8). With the latter, scale removal presumably contributed significantly to the high losses indicated. Pickling attack was moderately reduced by rolling of the aluminum-killed (No. 7) and bottle top (No. 12) steels but lesser to negligible effects were apparent with the rimmed (No. 3), normalized (No. 9) and Armco iron (No. 5) grades in that order. The relatively low pickling activity of the high-manganese steel (No. 14), and the much higher level of attack on the high-silicon steel (No. 13), which did not vary markedly with temperature, can also be seen in Figure 8(e). The contrasting temperature response of the high-silicon, high-phosphorus steel (No. 15), as well as the marked increase in weight loss with time at a higher temperature, indicates the more critical pickling control required by a material of this type.

(b) Tensile Tests

Tests to compare the effect of galvanizing on the mechanical properties of the steel base were confined to the three alloy steels. The particular galvanizing conditions selected and the results obtained are given in Table 3. The data show that where changes were produced, these were independent of the galvanizing bath composition and immersion time ranges studied. The ultimate tensile strength of the three steels was not altered by galvanizing, and elongation also was affected only in the case of the cold-rolled high-silicon high-phosphorus grade (No. 15). This amounted to an approximate reduction of 15%. Yield strength, on the other hand, was increased significantly without exception, with Steels 13 and 14 showing a somewhat larger gain in excess of 5000 psi (3.5 kg/mm^2). Proportionate increases in the yield-tensile ratio resulted. Such changes in properties caused by heating during galvanizing cannot be explained by normal ageing effects, in view of the killed nature of the materials involved. More complex precipitation phenomena, possibly related to copper content of the steels, are indicated to be responsible.

SUMMARY AND CONCLUSIONS

A statistically designed investigation has been made of the hot-dip galvanizing characteristics of several commercially produced steel sheet materials, comprising a series of low-carbon mild steels and a representative group of low-alloy high-strength steels. Both continuous strip and general galvanizing practice were considered in selection of the laboratory galvanizing conditions. From the extensive study made, evidence has been obtained confirming and supplementing previously available information on galvanized coating formation as affected by variations in the steel base and in composition of the bath. The principal findings and conclusions made are discussed and considered in terms of their significance and importance to the practical galvanizer.

Without aluminum in the bath, zinc attack and coating formation on the mild steels examined were found to be primarily influenced by the physical roughness of the steel surface. Apart from immersion time, other factors such as structure, composition and chemical activity of the steel base, as well as lead content of the bath, were apparently of lesser or negligible importance. It is thus indicated that the surface roughness characteristics of such materials must be considered as a significant variable in any practical attempt to improve on control of coating structure and uniformity.

An addition of aluminum to the bath in the intermediate range around 0.075%, while beyond the limits permissible in flux-covered baths, also appears to be of significant value in improving coating uniformity control with mild steel materials. However, some sacrifice in coating thickness is involved at relatively short immersion times.

In the region of high-aluminum additions approximating to continuous strip galvanizing practice, effective inhibition of the iron-zinc reaction with mild steel materials was indicated to be dependent on the inherent chemical activity of the steel surface. As this increased, the beneficial effect of aluminum was lessened and markedly so in the case of a heavily worked surface. Exclusive of galvanizing controls, mechanical or otherwise, the galvanizing response of such materials in aluminum-alloyed baths is thus largely determined by the work-hardened state of the steel surface as affected by steelmaking and processing history.

The galvanizing behaviour of low-alloy high-strength type of steels in aluminum-free baths was shown to be significantly dependent on the steel composition. High-silicon materials characteristically exhibited an extremely aggressive, linear rate of attack with time which was reflected in very thick coatings and in grey-coating deterioration of the coating surface. Rigid coating

thickness control would thus appear to be a major requirement in the galvanizing of such materials if excessively thick aluminum-free coatings are to be avoided. In aluminum-alloyed baths, suppression of attack of the alloy steels was marked but was somewhat less effective than with mild steels. Under certain conditions, the effect of aluminum was enhanced with the high-silicon steels. Although not conclusively established, this behaviour was suggested to be restricted to a narrow range of aluminum concentration and short immersion time. A further limitation on the use of aluminum with the alloy steels was the tendency for development of bare or uncoated spots in the coating, due to incomplete wetting of the surface.

The mechanical properties of the alloy grade steels were affected in varying degrees by galvanizing. Tensile strength was unaltered but yield strength was, in general, significantly increased and combined with an appreciable drop in elongation in the case of the high-silicon high-phosphorus material tested. These changes are possibly related to an interdependence between steel composition and precipitation phenomena induced by heating during galvanizing.

Galvanizing bath contamination due to solution of elements from the alloy steels during dipping was negligible and of no significance in the formation of the experimental coatings. To what extent this might still apply in a commercial-scale extended galvanizing run on such materials is not known.

The influence of lead in the bath was primarily restricted to alteration in coating surface appearance and notably to a marked increase in spangle grain size. This was most evident on the heavier steel gauges at extended immersion times. The mechanism of this effect of lead remains unexplained.

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TABLE 1
Steel Grade, Composition, Mechanical Properties, Grain Size and Surface Roughness*

Steel No.	Grade of Steel and Condition	Gauge	%										UTS, kpsi	YS, 0.2% offset, kpsi	Ratio YS to UTS	El., % in 2 in.	Rockwell Hardness, R _B	Erichsen Cup Depth, in.	ASTM Grain Size No.	C.L.A. Roughness, micro in.
			C	P	S	Mn	Si	Cu	Cr	Ni	Al	V								
1	Rimmed grade, as-received	24	0.05	0.010	0.026	0.30	<0.01	-	-	-	0.007	-	45.6	35.7	0.78	36.6	44	0.331	8	40
2	Rimmed grade, cold rolled - 5% reduction												50.1	45.3	0.90	26.7	73	0.294	-	-
3	Rimmed grade, cold rolled - 15% reduction												49.6	47.6	0.96	15.6	78	0.278	-	20
4	Armco iron, as-received	24	0.019	0.010	0.017	0.03	0.03	-	-	-	-	-	-	-	-	-	38	0.382	5	15
5	Armco iron, cold rolled - 15% reduction												-	-	-	-	67	0.296	-	13
6	Aluminum-killed, as-received	24	0.07	0.009	0.024	0.28	0.01	-	-	-	0.060	-	45.0	27.1	0.60	39.8	39	0.413	7	45
7	Aluminum-killed, cold rolled - 15% reduction												50.4	48.0	0.95	21.6	70	0.315	-	20
8	Hot-rolled normalized, as-received	14	0.04	0.003	0.024	0.26	0.01	-	-	-	0.006	-	51.7	41.4	0.80	38.0	60	-	8	50
9	Hot-rolled normalized, cold rolled - 15% reduction												62.1	61.0	0.98	11.1	81	-	-	42
10	Full hard, as-received	24	0.06	0.019	0.025	0.31	<0.01	-	-	-	0.004	-	103.0	99.2	0.96	2.0	99	0.200	-	38
11	Bottle top, as-received	24	0.09	0.012	0.028	0.58	0.02	-	-	-	0.002	-	52.1	37.4	0.72	34.3	54	0.386	9	65
12	Bottle top, cold rolled - 15% reduction												59.8	59.9	1.0	8.9	82	0.294	-	15
13	Alloy steel A, as-received	14	0.09	0.025	0.029	0.49	0.38	0.27	0.29	0.32	-	-	72.4	55.9	0.77	30.6	81	-	10	58
14	Alloy steel B, as-received	14	0.15	0.006	0.020	1.10	0.03	0.36	-	-	0.05 sol 0.01 insol	0.08	83.8	64.4	0.77	25.6	92	-	10	85
15	Alloy steel C, as-received	16	0.08	0.075	0.031	0.38	0.29	0.31	0.45	0.30	-	-	67.9	53.8	0.79	29.7	81	-	8	42

*Tensile and hardness values are averages of six or more determinations.
Diameter of ball and die orifice: 0.875 in. and 1.0 in., respectively.

TABLE 2

Experimental Galvanizing Conditions*

Bath No.	Fe %	Al %	Pb %	Immersion Time, sec	Steel Dipping** Sequence
<u>Experiment "A"</u>					
1	0.03	0.15	0.3	35	11,14,13,9,6,1,4,15,8,10,3,7,12,2,5
2	"	0.15	0.3	60	5,3,6,11,2,15,8,7,13,9,1,14,10,4,12
3	"	0.075	0.3	60	8,9,3,2,14,1,5,11,15,10,13,12,4,6,7
4	"	0.0	0.3	10	7,4,2,12,1,13,15,3,14,9,5,6,10,11,8
5	"	0.075	0.3	35	1,8,10,12,3,14,2,6,9,15,4,13,7,5,11
6	"	0.0	0.3	35	13,7,15,3,9,4,2,5,12,1,11,8,6,10,14
7	"	0.15	0.3	10	8,2,4,3,14,7,13,10,6,5,9,11,12,15,1
8	"	0.0	0.3	60	5,6,10,2,12,1,15,11,7,14,8,4,13,3,9
9	"	0.075	0.3	60	1,10,14,4,8,2,6,12,5,7,9,3,15,11,13
10	"	0.075	0.3	35	13,8,7,9,11,15,1,2,10,3,12,5,6,4,14
11	"	0.15	0.3	10	3,14,11,15,10,1,13,9,8,4,2,5,6,7,12
12	"	0.075	0.3	10	12,6,14,13,15,1,11,4,8,10,3,7,2,9,5
13	"	0.15	0.3	60	10,7,5,2,8,1,3,13,6,14,15,12,9,11,4
14	"	0.0	0.3	10	1,2,8,13,5,15,3,11,10,7,4,12,6,9,14
15	"	0.15	0.3	35	8,10,4,11,12,3,6,14,13,2,15,5,7,9,1
16	"	0.075	0.3	10	2,11,5,12,1,9,8,3,15,4,10,6,7,14,13
17	"	0.0	0.3	60	13,2,7,11,5,15,8,14,9,4,10,12,3,6,1
18	"	0.0	0.3	35	10,9,5,2,14,3,4,11,13,8,12,15,6,7,1
<u>Experiment "B"</u>					
19	"	0.0	1.0	240	7,4,2,12,1,13,15,3,14,9,5,6,10,11,8
20	"	0.0	1.0	120	13,7,15,3,9,4,2,5,12,1,11,8,6,10,14
21	"	0.0	1.0	60	5,6,10,2,12,1,15,11,7,14,8,4,13,3,9
22	"	0.0	1.0	240	1,2,8,13,5,15,3,11,10,7,4,12,6,9,14
23	"	0.0	1.0	60	13,2,7,11,5,15,8,14,9,4,10,12,3,6,1
24	"	0.0	1.0	120	10,9,5,2,14,3,4,11,13,8,12,15,6,7,1
25	"	0.0	0.3	240	7,4,2,12,1,13,15,3,14,9,5,6,10,11,8
26	"	0.0	0.3	120	13,7,15,3,9,4,2,5,12,1,11,8,6,10,14
27	"	0.0	0.3	240	1,2,8,13,5,15,3,11,10,7,4,12,6,9,14
28	"	0.0	0.3	120	10,9,5,2,14,3,4,11,13,8,12,15,6,7,1

*Bath temperature for all tests: 450°C (840°F).

**Four 4 in. x 6 in. (10 cm x 15 cm) and two 3 in. x 4 in. (7.5 cm x 10 cm) panels of each grade of steel were galvanized in order indicated in each bath. For tensile testing, three extra panels of each of the alloy steel grades (No. 13, 14 and 15) were galvanized in baths 2, 3, 4, 7, 8 and 12.

TABLE 3
Mechanical Properties of Alloy Steels*

Steel No. and Grade	Bath No.	Al %	Pb %	Immersion Time, sec	UTS, kpsi	YS, 0.2% offset, kpsi	Ratio YS to UTS	El., % in 2 in.
<u>13, Alloy Steel A</u>								
As-received	-	-	-	-	72.4	55.9	0.77	30.6
Galvanized	4	0.0	0.3	10	72.0	60.9	0.85	29.8
"	8	0.0	0.3	60	70.0	60.9	0.87	29.0
"	12	0.075	0.3	10	72.8	62.0	0.85	28.2
"	3	0.075	0.3	60	74.0	63.6	0.86	28.6
"	7	0.15	0.3	10	73.1	61.9	0.85	31.1
"	2	0.15	0.3	60	73.9	62.9	0.85	30.2
<u>14, Alloy Steel B</u>								
As-received	-	-	-	-	83.8	64.4	0.77	25.6
Galvanized	4	0.0	0.3	10	81.7	69.3	0.85	25.0
"	8	0.0	0.3	60	80.8	68.0	0.84	24.9
"	26	0.0	1.0	120	83.4	71.3	0.86	24.6
"	27	0.0	1.0	240	83.7	70.8	0.84	22.8
"	12	0.075	0.3	10	82.8	70.4	0.85	24.9
"	3	0.075	0.3	60	83.4	70.0	0.84	25.4
"	7	0.15	0.3	10	82.9	69.7	0.84	25.5
"	2	0.15	0.3	60	82.7	69.0	0.84	25.3
<u>15, Alloy Steel C</u>								
As-received	-	-	-	-	67.9	53.8	0.79	29.7
Galvanized	4	0.0	0.3	10	68.0	57.5	0.85	24.9
"	8	0.0	0.3	60	66.6	57.5	0.87	25.6
"	26	0.0	1.0	120	64.6	56.2	0.87	25.2
"	27	0.0	1.0	240	63.2	55.5	0.88	24.8
"	12	0.075	0.3	10	66.5	57.8	0.87	25.0
"	3	0.075	0.3	60	67.2	58.1	0.87	26.5
"	7	0.15	0.3	10	68.4	59.8	0.87	25.0
"	2	0.15	0.3	60	66.1	56.0	0.85	25.5

*As-received values are averages of 36 tests.
Galvanized values are averages of 6 to 12 tests.

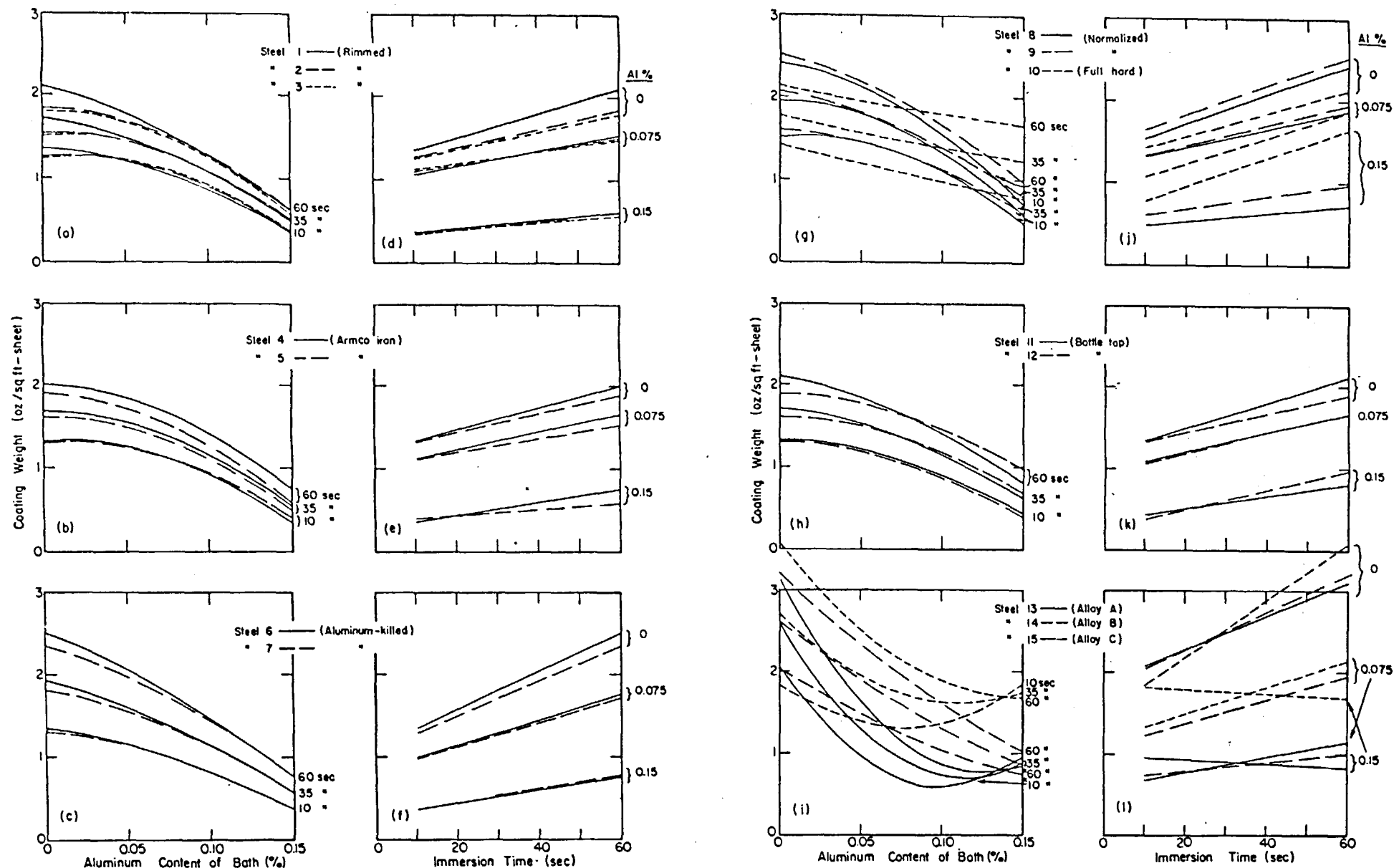


Figure 1. Coating weight versus aluminum content of bath, immersion time and steel grade.

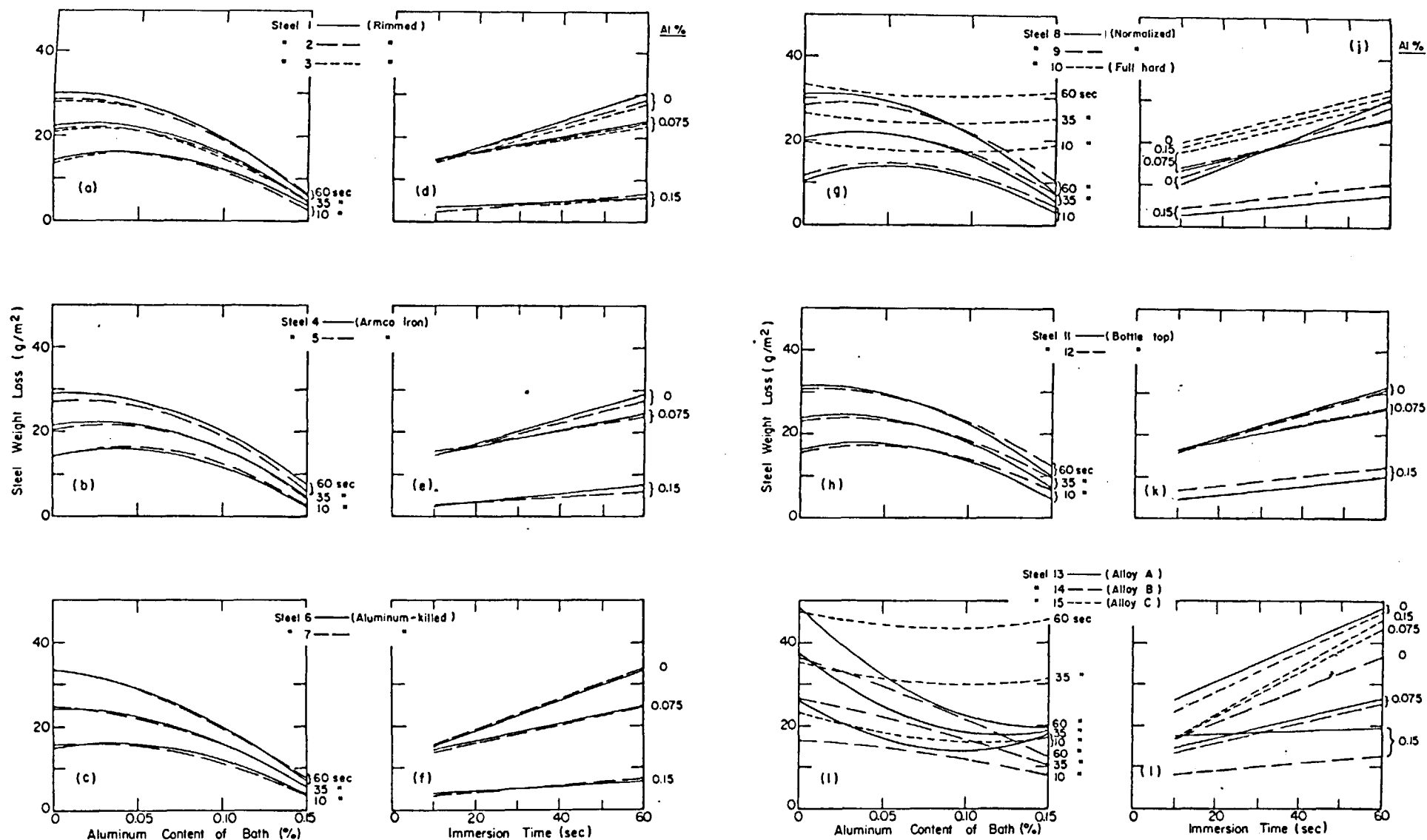


Figure 2. Steel weight loss versus aluminum content of bath, immersion time and steel grade.

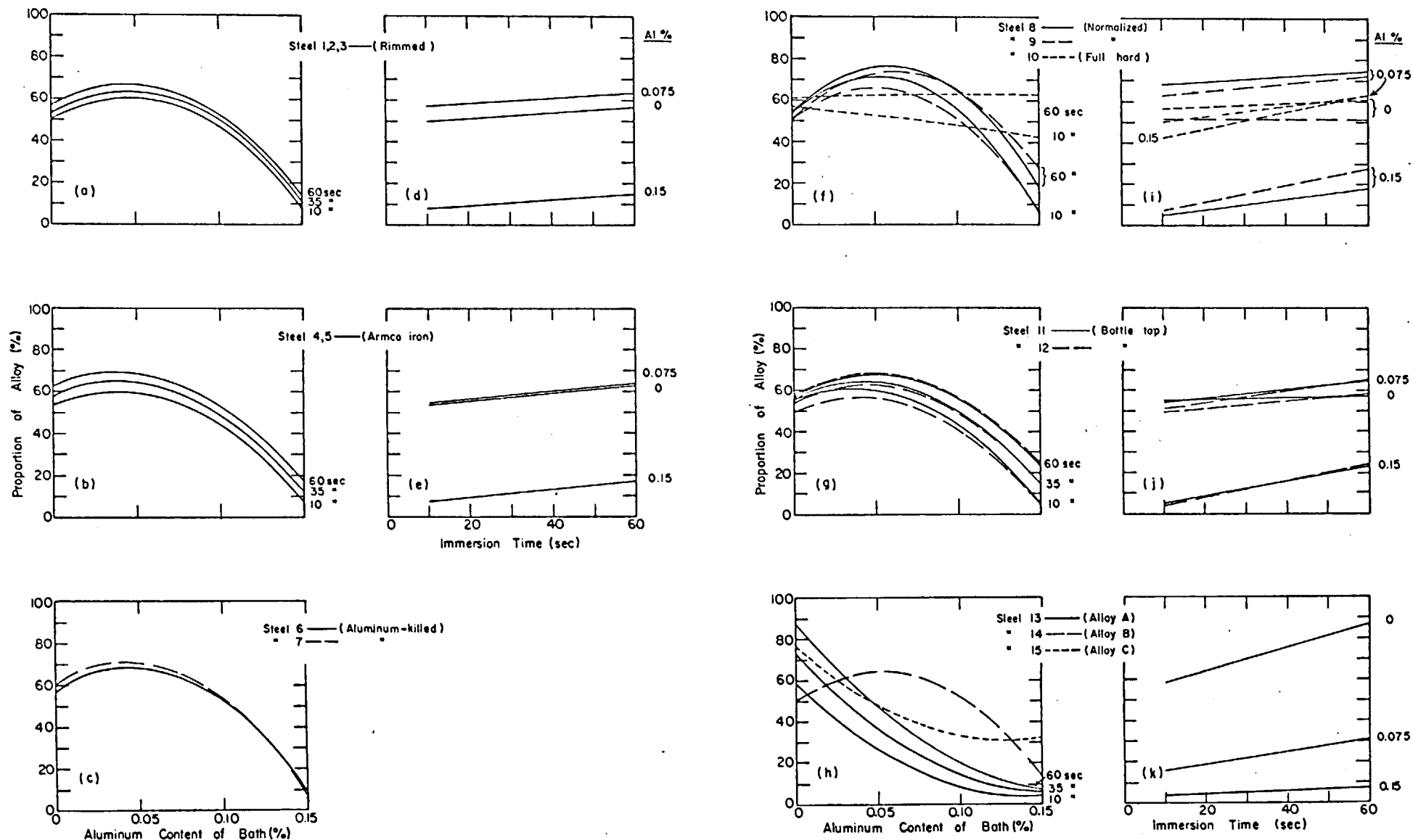
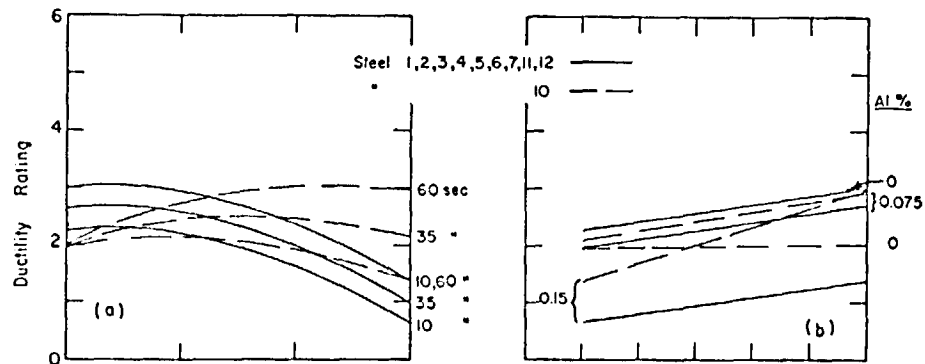


Figure 3. Proportion of iron-zinc alloy in coatings versus aluminum content of bath, immersion time and steel grade.



Ductility Evaluation : 1-no cracks ; 2-fine cracks ; 3-wide cracks ; 4-gross crack separation.

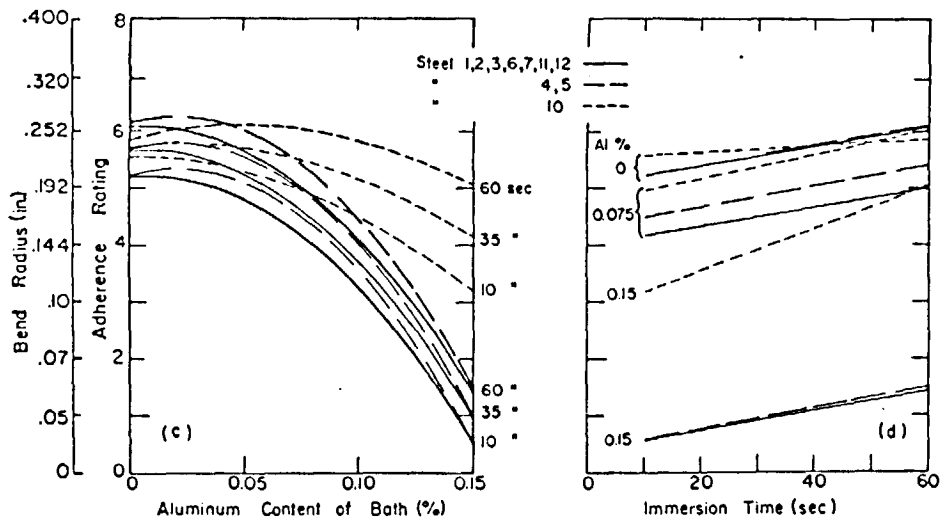


Figure 4. Coating ductility and adherence ratings versus aluminum content of bath, immersion time and steel grade.

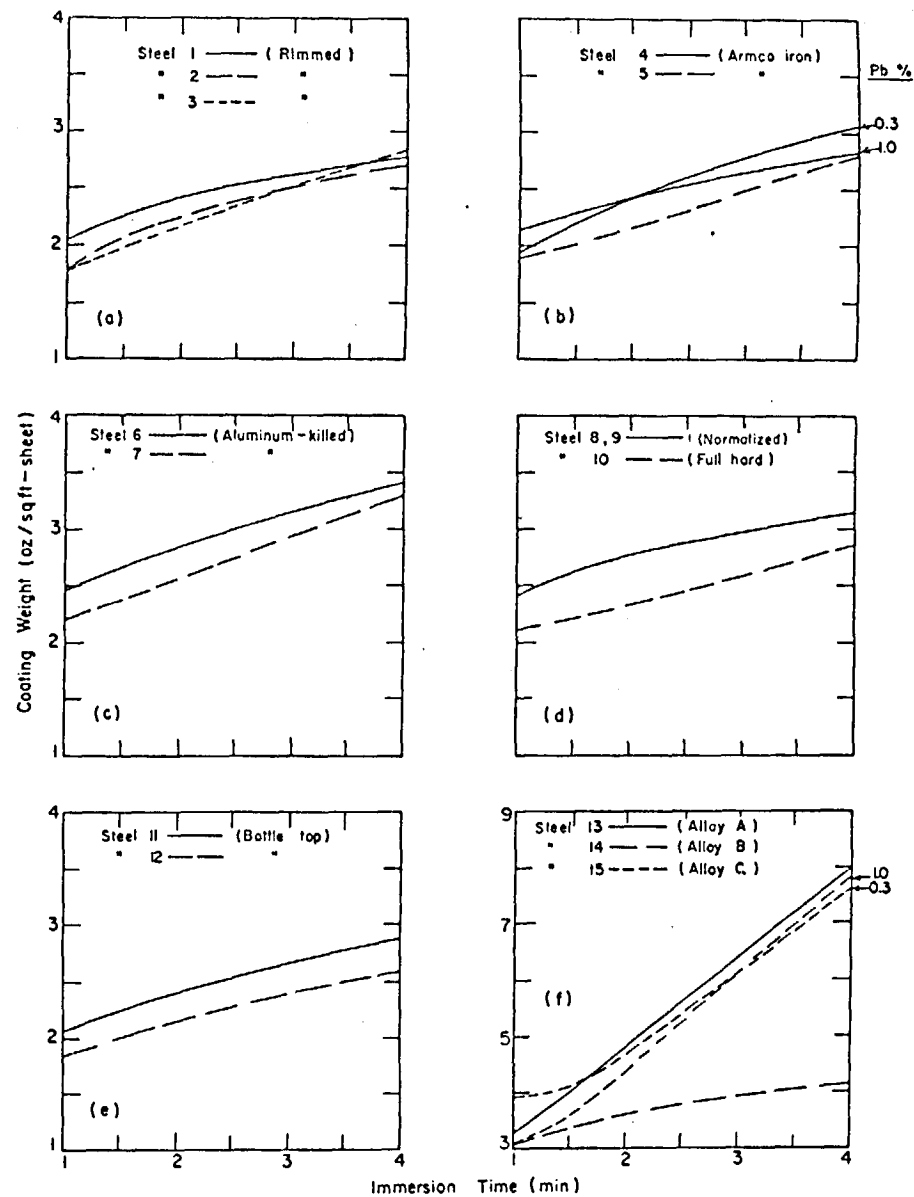


Figure 5. Coating weight versus immersion time, steel grade and lead content of bath (aluminum-free).

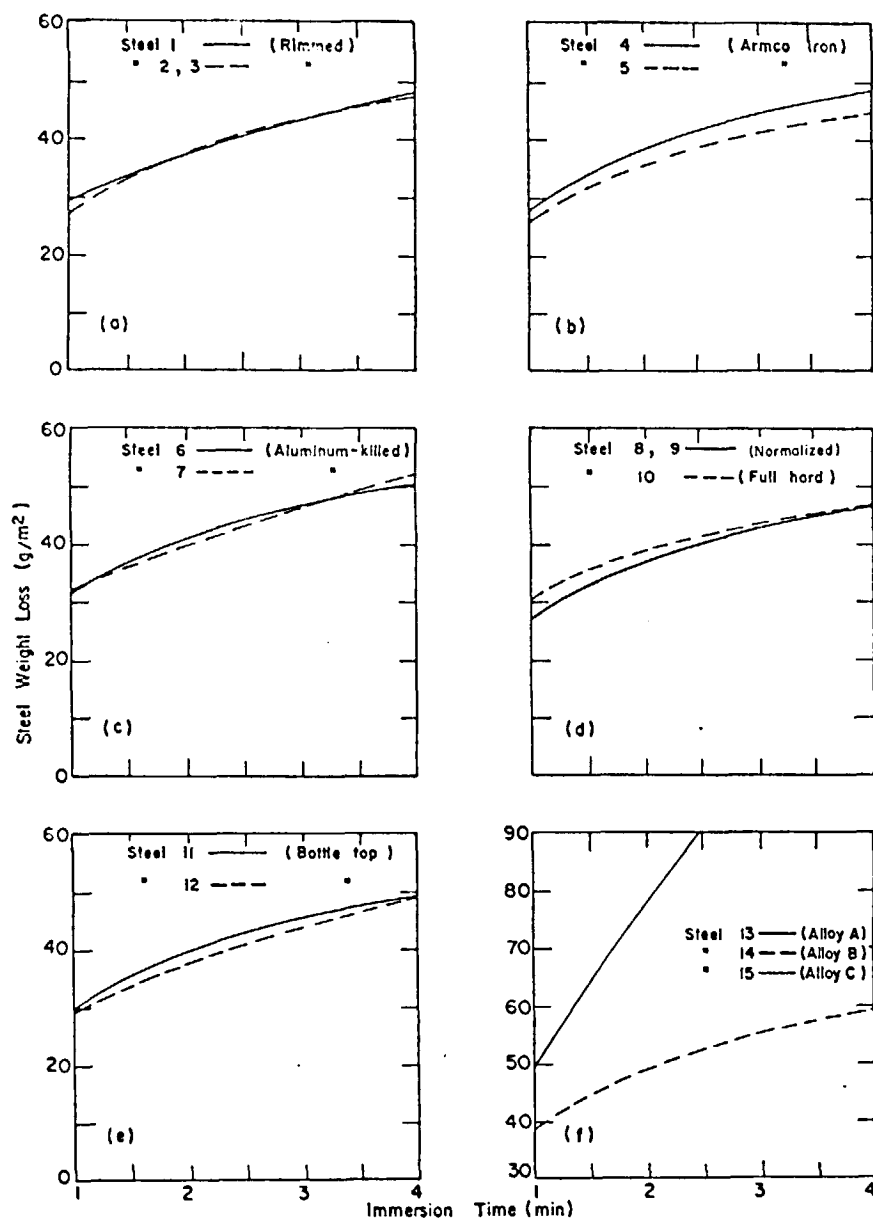


Figure 6. Steel weight loss in aluminum-free baths versus immersion time and steel grade.

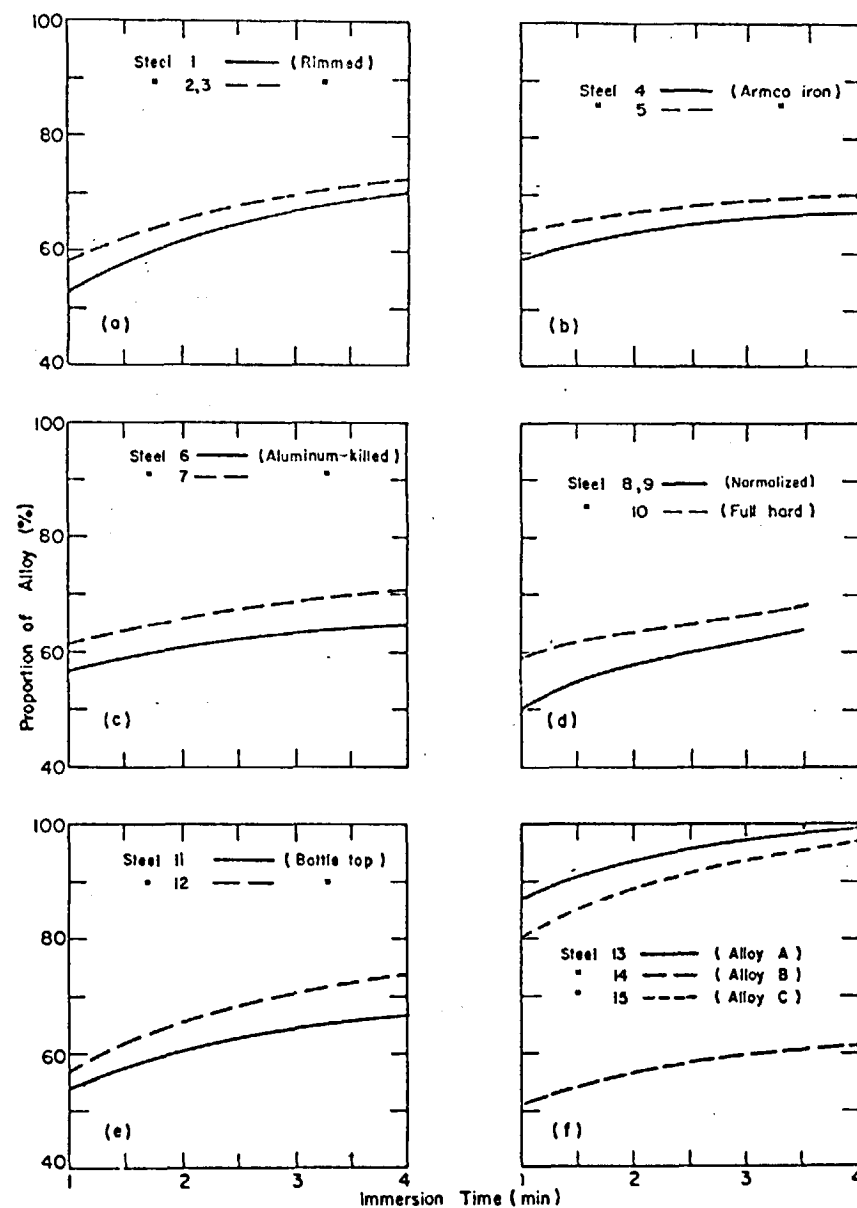


Figure 7. Proportion of iron-zinc alloy in aluminum-free coatings versus immersion time and steel grade.

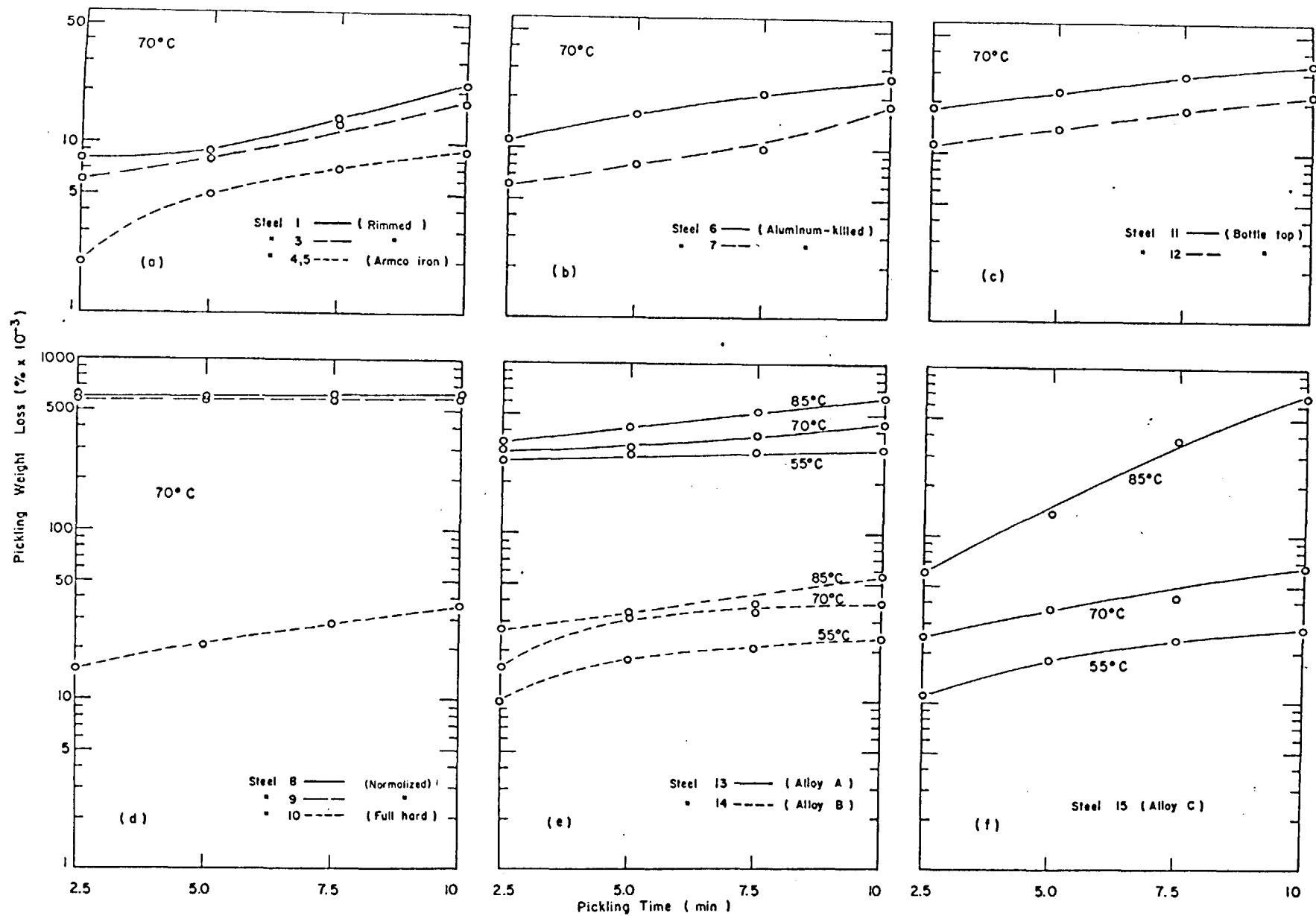
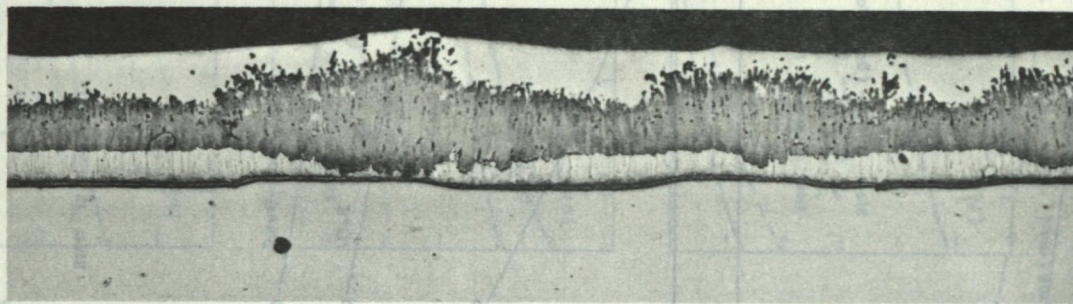
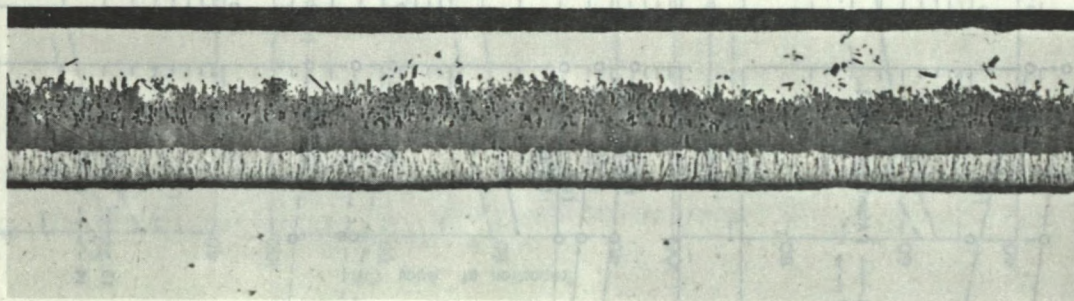


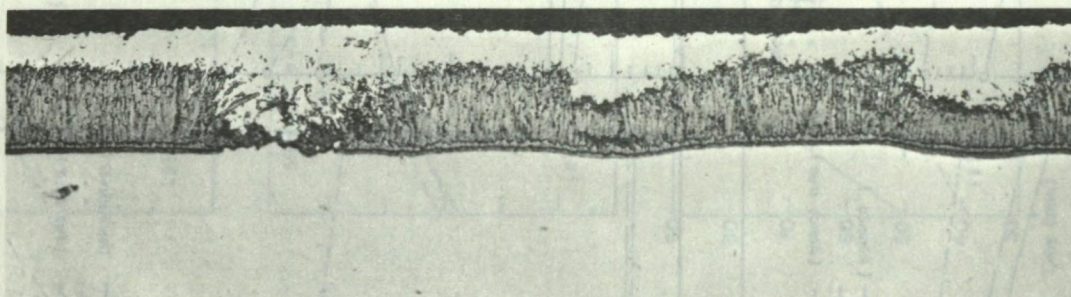
Figure 8. Pickling behaviour of mild steels and low-alloy high-strength steels for conditions indicated.



(a) As-received rimmed steel, No. 1 (0.3% Pb, 4 minutes immersion) X300.

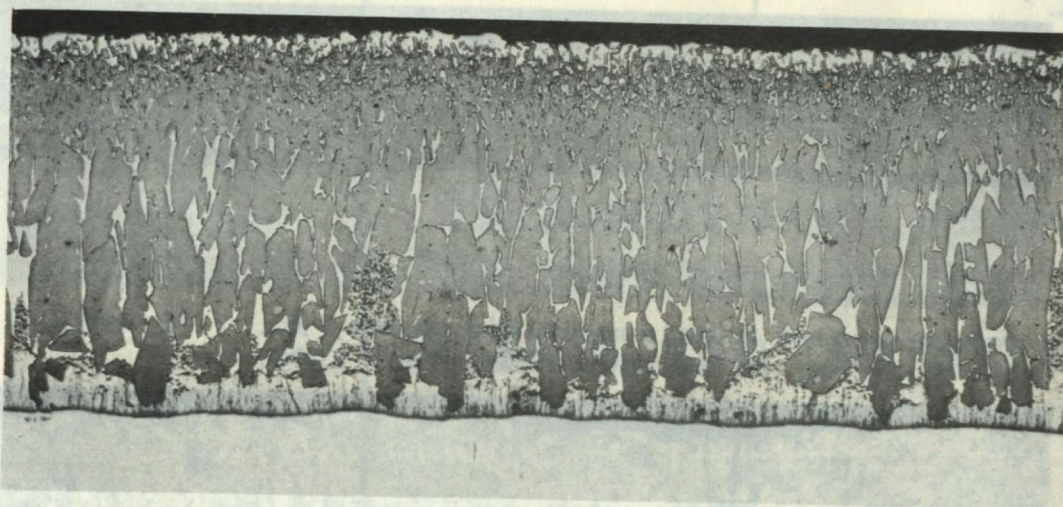


(b) As-received full hard steel, No. 10 (1.0% Pb, 4 minutes immersion) X300.



(c) As-received aluminum-killed steel, No. 6 (0.3% Pb, 10 seconds immersion) X500.

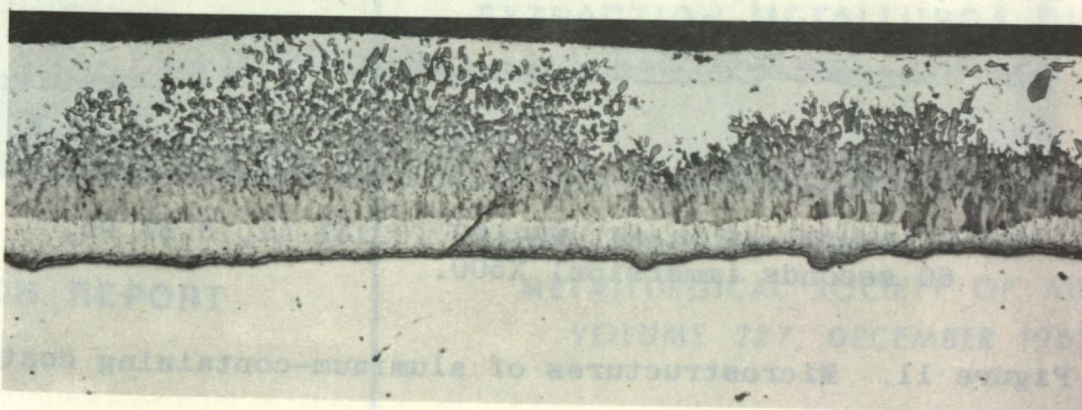
Figure 9. Microstructures of aluminum-free coatings on mild steels.



(a) High-silicon steel, No. 13 (0.3% Pb, 4 minutes immersion) X300.

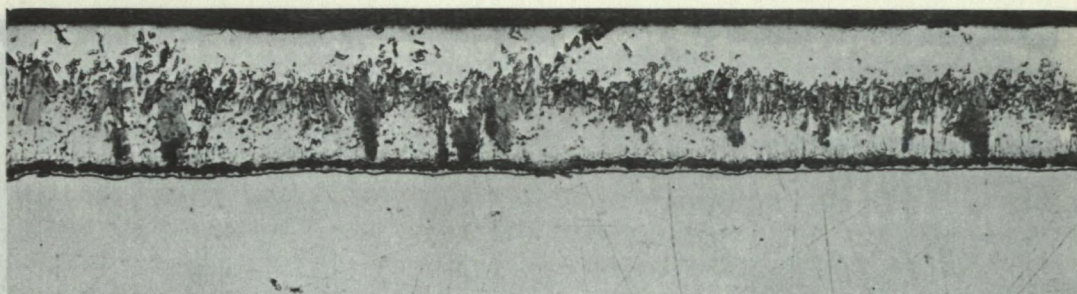


(b) High-silicon high-phosphorus steel, No. 15 (1.0% Pb, 4 minutes immersion) X300.

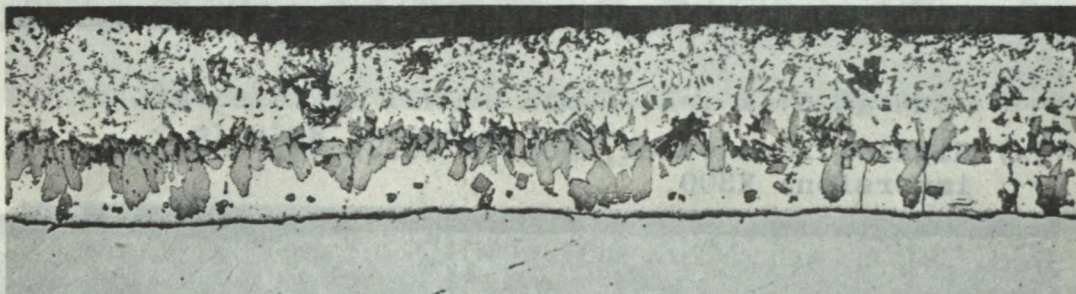


(c) High-manganese steel, No. 14 (0.3% Pb, 4 minutes immersion) X300.

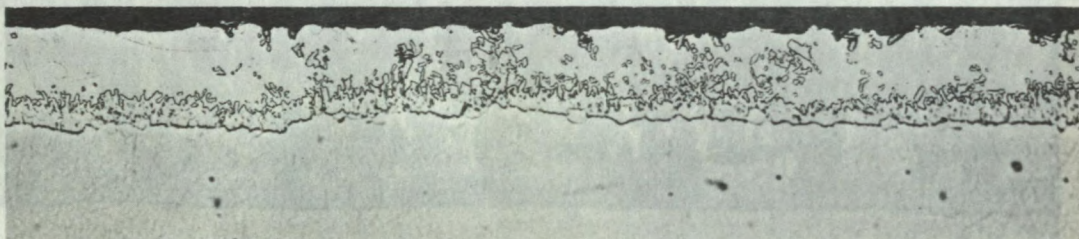
Figure 10. Microstructures of aluminum-free coatings on alloy grade steels.



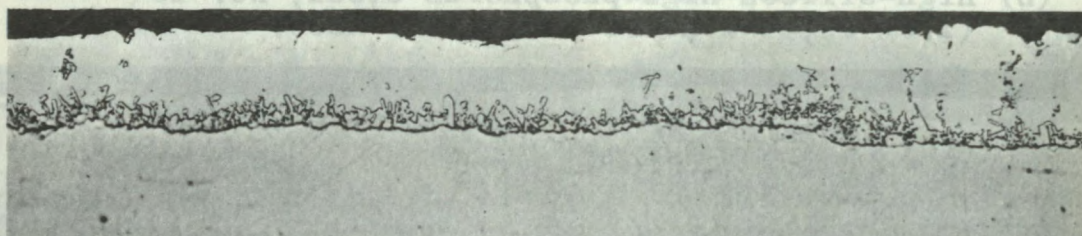
(a) Re-rolled aluminum-killed steel, No. 7 (0.075% Al, 0.3% Pb, 60 seconds immersion) X500.



(b) High-silicon high-phosphorus steel, No. 15 (0.075% Al, 0.3% Pb, 10 seconds immersion) X500.



(c) High-silicon steel, No. 13 (0.075% Al, 0.3% Pb, 60 seconds immersion) X500.



(d) High-silicon steel, No. 13 (0.15% Al, 0.3% Pb, 60 seconds immersion) X500.

Figure 11. Microstructures of aluminum-containing coatings.

Figure 10. Microstructures of aluminum-free coatings on alloy grade steels.