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*GALVANIZING OF LOW-ALLOY  
HIGH-STRENGTH STEELS*

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PHYSICAL METALLURGY DIVISION

GALVANIZING OF LOW-ALLOY HIGH-STRENGTH STEELS

by

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ABSTRACT

Laboratory studies have been made on the galvanizing behaviour of several grades of low-alloy high-strength steel sheet in iron-saturated lead-containing zinc baths otherwise alloyed with chromium, manganese, nickel and vanadium. Beneficial modifications in coating formation and structure revealed were primarily related to suppression of the iron-zinc reaction rate. This was reflected in levelling out of iron-zinc alloy irregularities in coatings on normal activity steels and, at the opposite extreme, the characteristic linear attack of silicon-containing materials was drastically altered to a parabolic form. The bath addition of 0.1% V was found to be most effective and 0.2% Cr, 0.2% Ni and 0.5% Mn followed in that order. Within limits defined by the tests, use of such additions appears to offer improved control of the coating process in galvanizing of this class of steels.

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## INTRODUCTION

In a prior investigation on galvanizing bath additions (1), it was established that several elements effectively modified the coating formation on a plain carbon rimming-grade steel. Suppression of iron-zinc alloy growth and reduction in the total coating thickness were the principal effects observed. This behaviour appeared to have potential application in galvanizing low-alloy high-strength structural steels which, particularly in the case of high silicon grades, can be expected to exhibit high reactivity in galvanizing baths of conventional composition. These materials are of increasing galvanizing interest since they combine a variety of improved engineering properties and offer attractive savings in weight, cost and design flexibility in structural steel applications.

The high reaction rate of silicon-containing steels in molten zinc is well known and has been extensively investigated (2-6). However, the mechanism of this phenomenon remains unexplained and methods of controlling the excessive coating development in commercial galvanizing practice are also limited. The usual precautions include minimizing pickling and galvanizing immersion time combined with quenching after withdrawal. These are partly effective where product size, shape and thickness are favourable, but much less so in the treatment of heavy sections and mixed steel assemblies. A possible alternative control on the iron-zinc



reaction rate was offered by bath alloying, and this approach was explored in the present laboratory investigation. The experiments covered a series of proprietary low-alloy high-strength steels with variable silicon content that were galvanized over a range of time-temperature conditions in baths alloyed with chromium, manganese, nickel and vanadium. These were the elements showing maximum iron-zinc alloy inhibition effects in the previous study.

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

## PROCEDURE

### Steel Materials

The galvanizing tests were made with eight typical low-alloy high-strength steel sheet materials of Canadian and U.S. manufacture. The selection was largely determined by material availability and, fortunately, the alloy steels represented a desired range in galvanizing activity that was further extended by including a plain carbon steel (No. 8).

Table 1 gives chemical compositions and other properties, and shows that four of the alloy steels (No. 19, 20, 16 and 18) were semi-killed with carbon content from 0.13 to 0.19%, and contained up to 0.08% Si. Two of these were niobium-bearing, one contained vanadium, and the fourth

was characterized by a high phosphorus content combined with appreciable alloying additions of copper, nickel and molybdenum. The remaining four alloy steels (No. 21, 17, 15 and 13) were essentially silicon-killed grades with generally lower carbon content around 0.11% and silicon between 0.21 - 0.39%, but otherwise differing significantly in manganese and phosphorus, and to a lesser extent in copper, chromium and nickel content. Steel 17 in this group also contained vanadium. For galvanizing purposes, Steels 15 and 13 could be classified as silicon-phosphorus steels and the former was also distinct in being the only cold-rolled material tested.

Figure 1 shows the typically fine-grained microstructures of the various alloy steels which corresponded to ASTM grain size numbers from 8 to 10 (2000-8000 grains/mm<sup>2</sup>). Ferrite-pearlite structures, varying in the amount and fineness of the pearlite constituent, were evident in all cases except with the cold-rolled Steel 15 which showed a fine spheroidized cementite distribution. In mechanical properties also, the alloy steels differed significantly and Table 1 shows a UTS range from 67.9 - 96.5 kpsi (47.7 - 67.8 kg/mm<sup>2</sup>), YS from 50.4 - 72.6 kpsi (35.4 - 51.0 kg/mm<sup>2</sup>), and elongation from 21.9 - 30.6%. Steel surface roughness disparities (after pickling) were less pronounced, as indicated in Table 1, with the single exception of Steel 16 which had a particularly rough finish. The opposite extreme was represented by the cold finished Steel 15. To what degree these differences in microstructure, mechanical properties and

surface finish were related to alloy steel composition and/or mill finishing conditions is not known since information on the latter could not be obtained.

### Test Programme

The consolidated galvanizing test programme, which was done in separate stages, is outlined in Table 2. All baths were made with SH Grade (9999) zinc to which 0.03% Fe and 1.0% Pb were added. This basic composition was alloyed as indicated with individual additions of 0.2% Cr, 0.5% Mn, 0.2% Ni, 0.1% and 0.2% V. These were introduced as zinc-base master alloys <sup>(1)</sup>. To the manganese- and vanadium-containing baths, 0.005% Al was also added to suppress bath oxidation which interfered with the production of smooth coatings.

The galvanizing procedure duplicated laboratory practice <sup>(1)</sup> and involved the usual steps of degreasing in trichlorethylene, pickling in inhibited sulphuric acid solution, scrubbing and rinsing, and pre-fluxing in aqueous zinc-ammonium-chloride solution. Three or more 4 in. x 6 in. (10 cm x 15 cm) panels of each steel were galvanized at 450°C (840°F), and at 430°C (805°F) for the more active steels, for 1, 2, 5 and 10 minutes in each of the baths indicated in Table 2. The rate of immersion and withdrawal was controlled and the coated panels were air-cooled. A total of forty galvanizing melts was required.

Bath sampling before, during and after galvanizing, as well as spot sampling of selected baths at different levels from the surface, revealed no significant depletion or segregation of the principal bath alloying elements, inclusive of lead. The nominal and actual compositions were invariably in good agreement, and bath instability due to alloying element loss by take-up in the zinc and alloy layers, by flux reaction, as well as by oxidation, drossing, etc., was not encountered. In this connection, the laboratory scale of the experiments is to be emphasized and extrapolation of the observed composition stability to a larger scale galvanizing operation must be treated with caution. The only composition variation found was a progressive increase in iron content, generally of the order of 30% and, in the maximum case, 60%, of the original saturation value of 0.03% Fe.

Evaluation of the galvanizing behaviour of the various steels and of the influence of the bath alloying additions was principally confined to coating weight tests, surface inspection and metallographic examination. Steel weight loss tests could not be included because of material availability and other considerations, and determination of the iron content of the coatings was substituted instead. The iron titrations were made in conjunction with the coating weight stripping tests.



## OBSERVATIONS AND RESULTS

To facilitate description, the designations, "alloyed baths" and "alloyed coatings", are used specifically for the baths and coatings containing chromium, manganese, nickel and vanadium.

### Surface Appearance of Coatings

The surface appearance features of the experimental coatings are described in Table 3. In studying the table, it should be recalled that withdrawal of the panels from the bath was controlled at a uniform rate and the influence of this factor was therefore constant.

With the plain carbon (No. 8) and semi-killed steels (No. 19, 20, 16 and 18), a distinct improvement in brightness and reflectivity was apparent on the alloyed coatings. The surface appearance was further enhanced by spangle formation with vanadium and manganese additions. Grain boundary depression was encountered with nickel and chromium, but was generally slight and only sufficient to delineate the grain structure more clearly. A distinct beneficial effect with all four additions was the elimination of the very rough finish which distinguished the control coatings on Steel 16. As discussed later, this was related to inhibition of the irregularities in iron-zinc alloy growth which otherwise developed on this rough textured steel.

Evidence of the more aggressive attack on two of the silicon-killed steels (No. 21 and 17) with prolonged immersion in the control bath at 450°C (840°F) was apparent from the formation of a broadened, grey network pattern on the surface. This was altered to a thin, line network with manganese in the bath and was eliminated by the other additions at this temperature. To the degree indicated in Table 3, there was a corresponding sacrifice in surface smoothness because of projecting iron-zinc alloy outbursts of varying size and distribution. This type of deterioration was notably severe with the 10-minute nickel-containing coatings on Steel 17 at 450°C (840°F), but, as applicable for all of the other tests listed, a significant improvement was obtained on lowering the bath temperature to 430°C (805°F).

The extent of grey coating formation on the two silicon-phosphorus steels (No. 15 and 13) represented a still higher level of galvanizing activity in the control bath. With Steel 15, this defect was absent on the alloyed coatings at 450°C (840°F), but this overall improvement was again associated with the development of large to gross pimple outbursts at lengthy immersion times. Vanadium produced a scattered distribution of individual mounds whereas, with the other additions, the outbursts were much more numerous and, in combination with incomplete filling in by zinc, resulted in rough unattractive surface areas. Reducing the bath temperature to 430°C (805°F) once more restored a moderately smooth surface free of grey coating on Steel 15, marred only by small outbursts.

Table 3 indicates that Steel 13 was much less responsive to elimination of grey coating in the baths alloyed with chromium, nickel and manganese. The related absence of outburst roughening was also indicative of a minimum influence on the galvanizing reaction rate and is discussed later. In contrast, the effect of vanadium was particularly noteworthy since both defects were eliminated with extended immersion times at 450°C (840°F). Furthermore, the bright coatings in this case had a unique hammered appearance formed by spherical-shaped indentations which increased in size with time. At 430°C (805°F), all of the alloyed coatings on Steel 13 were free of grey coating. A variable scattering of small to large outbursts detracted somewhat from coating smoothness, but the otherwise bright appearance, showing spangle development in some cases, represented a distinct improvement over the corresponding control coatings.

#### Stripping Tests and Metallography

The averaged results of triplicate coating weight and iron content measurements (both sides of sheet) are graphically presented in Figures 2-10, and typical microstructures are reproduced in Figures 11-16. For convenience in plotting and discussion, the plain carbon and semi-killed steels which behaved similarly were grouped together.

##### (a) Steels 8, 19, 20 and 16

Figure 3 indicates that steel base reactivity in the control bath, as represented by the iron content measurements, was a minimum and

approximately similar for the plain carbon steel (No. 8) and three of the low-alloy steels (No. 19, 20 and 16). The coating weight build-up with time (Figure 2) was more variable, being slightly greater on Steel 20 and still more so on Steel 16. The increase in the latter case was found to be directly related to the rougher steel finish which promoted irregular iron-zinc alloy growth and consequently heavier zinc drag-out.

In the alloyed baths, the activity of this group of steels was apparently reduced only slightly (Figure 3), but this was accompanied by appreciable reductions in coating weight (Figure 2) with the single exception of 0.2% Ni as discussed later. The reductions were to some extent time dependent, being more effective at longer immersion times, and of the order of 25% at 10 minutes for Steels 8, 19 and 20 in the baths containing 0.1% and 0.2% V, and 0.5% Mn. These additions were approximately equally effective. Still larger reductions were obtained with Steel 16 in the baths alloyed with 0.1% V and 0.2% Cr.

The anomalous variations in coating weight and iron content were found to be related to well-defined modifications in coating microstructure and the representative coatings for Steel 16 in Figure 11 highlight the principal features. The control coating on this rough surfaced material exhibited typically irregular formation of the iron-zinc alloy phases and the outer zinc layer. Zeta phase outbursts were particularly prominent at lengthier immersion times as shown in Figure 11(a) and were reflected in the rough coating finish referred to earlier.



The contrasting alloyed coatings, on the other hand, were distinguished by appreciable thinning of the zeta layer, thicker delta prime formation, and by significant improvement in uniformity of all the individual layers. The latter effect was a direct result of the suppression of the local reaction irregularities of the type shown in Figure 11(a). The uniformity and compactness of the zeta layer varied with the different bath additions as illustrated by Figures 11(b)-(e) and particular attention is drawn to the unusually thin zeta band in the nickel-containing coating. Variable contamination of the outer zinc layer by intermetallic compounds, except with manganese, can also be seen. The compounds were generally very small with chromium and vanadium present whereas, in the nickel-containing coatings, a characteristic dispersion of gross hexagonal-shaped crystals was formed as in Figure 11(b). The rate of nucleation and growth of the particles was accelerated at longer immersion times, thereby progressively increasing zinc drag-out in direct proportion. The increased drag-out compensated for, and in fact tended to exceed (Steels 8, 19 and 20), the thickness reduction otherwise achieved in the iron-zinc alloy layers, and thus accounted for the apparently lesser and variable effect of nickel on coating weight (Figure 2).

(b) Steels 18, 21 and 17

The control coating results at 450°C (840°F) plotted in Figures 4-6 suggest that this group of materials could be classified as representing a low, to relatively high, level of intermediate galvanizing activity. The latter was represented by the silicon-killed grades (No. 21 and 17) which yielded near linear relationships of coating weight and iron content with immersion time. The semi-killed steel (No. 18) was at the opposite extreme. Compared to the other semi-killed steels just discussed, Steel 18 was more aggressively attacked, presumably because of its higher silicon content of 0.08% combined with high phosphorus at 0.07%. To what extent the steel surface chemistry and activity in this case were also influenced by the high levels of copper, nickel and molybdenum present is not known. Lowering the control bath temperature to 430°C (805°F) was moderately effective in reducing the activity of Steel 17 but the change with Steels 18 and 21 was relatively small.

In striking contrast, Figures 4-6 show that the influence of the bath alloying additions in the same direction was much more pronounced with all three materials. Vanadium and chromium behaved similarly and were most effective as emphasized by the marked change in the trend of the curves to a typical parabolic form for the high activity Steels 21 and 17. At the maximum immersion time of 10 minutes, the coating weight and iron content were reduced in excess of 50%. In effect, the behaviour of these steels, and also Steel 18, was modified to a close approximation of

the plain carbon steel (No. 8) in the control bath. Of further note is the fact that the vanadium and chromium additions were relatively insensitive to temperature, and near equivalent effects were produced at 450°C (840°F) and 430°C (805°F). The same order of effectiveness was also achieved with nickel and manganese, but only at the lower bath temperature.

At 450°C (840°F), the reductions in coating weight and iron content were still substantial, although variable between the three steels and significantly less than obtained with vanadium and chromium. Maximum effects with nickel and manganese thus appeared to be coincident with a minimum galvanizing temperature.

A typical, long-immersion control coating microstructure, which was more or less representative for this group of steels at both temperatures, is illustrated in Figure 12(a). Evidence of aggravated steel attack was well defined by the predominant mass of angular, ideomorphic zeta phase crystals embedded in a zinc matrix. Other related features included a generally thin covering layer of zinc, and limited delta prime growth. In the thinner coatings formed at short immersion times, the zeta phase was more densely compacted and lacked individual crystalline definition, but remained as the major coating layer.

The superior iron-zinc alloy inhibition characteristics of vanadium (and chromium), as earlier revealed by the iron content measurements, are further defined by the representative microstructure in Figure 12(c).

This shows that the otherwise high reaction activity of all three steels, and notably of Steels 17 and 21, was effectively suppressed. For immersion times of up to 10 minutes at both 450°C (840°F) and 430°C (805°F), the coating structures obtained were not greatly dissimilar from conventional coatings on a plain carbon steel. The heavily serrated zeta phase boundary was a typical feature, but local outbursts of sufficient size to project through the surface were relatively infrequent. Intermetallic compound particles, which were identifiable from the floating zeta crystals, were also generally small with either vanadium or chromium present.

The variable inhibition by nickel (and manganese) at 450°C (840°F) was also confirmed in the coating microstructures. On Steel 21, the reduction in thickness of the zeta band was very irregular as in Figure 12(b). Much more effective inhibition was evident over extensive areas of the surface on Steel 17, but numerous zeta outbursts as in Figure 13 indicated local breakdown and a reversion to aggravated steel base attack. Coating surface smoothness was accordingly affected as already noted. With the less active semi-killed steel (No. 18), isolated alloy high spots only were apparent, and good uniformity was retained in the thin zeta layer formed. As illustrated, the outer zinc layer in the nickel-containing coatings was again heavily interspersed with large interaction compounds and contrasted with the relative absence of particles in the coatings prepared with manganese in the bath.



At 430°C (805°F), the improved effectiveness of nickel and manganese noted earlier was seen to be microstructurally related to the greatly reduced incidence of local inhibition breakdown. However, the zeta outbursts were not entirely eliminated, except with Steel 18 which exhibited uniformly thin zeta and delta prime layers representing about 45% of the total coating thickness at 10 minutes immersion.

This particular group of experiments suggests that low-alloy high-strength steels containing appreciable silicon, and which are prone to aggressive attack in conventional galvanizing baths, are amenable to effective control of coating structure, uniformity and thickness by bath alloying. For the conditions tried, vanadium and chromium were found to be particularly strong inhibitors of iron-zinc alloy growth and were significantly and more consistently effective than nickel and manganese.

(c) Steels 15 and 13

For ease of description in this section, the stripping tests results and metallographic observations are discussed together.

The control coating surface characteristics described previously and the distinctly linear relationships of coating weight and iron content with immersion time shown in Figures 7-10 clearly distinguished the extreme galvanizing reactivity of these two silicon-phosphorus steels at 450°C (840°F). Figure 14(a) exemplifies the gross coating development, consisting mostly of zeta crystals in a zinc matrix, that was formed on both materials at 10

minutes immersion. The superficially thin outer zinc layer associated with grey coating formation can also be seen. In this connection, the porosity evident in the zeta crystal mass is of interest since in many cases it appeared to be directly related to the grey network defect. This open structure, representing absence of the zinc matrix, was invariably found beneath a grey area on the surface. In Figures 7-10, the appreciable effect of reducing the control bath temperature to 430°C (805°F) is also defined. A corresponding microstructure is illustrated in Figure 15(a).

Figures 7-8 indicate that the apparent inhibition of Steel 15 reactivity by vanadium in the bath was relatively much greater than found with the other steels discussed earlier. A drastic change from linear to parabolic coating build-up was well defined. A negligible temperature dependence was again shown and the very large reductions in coating weight and iron content with 10 minutes immersion were of the order of 400%. Chromium was slightly less effective in the single series of tests made at 450°C (840°F), whereas nickel and manganese were still less so, particularly with respect to coating weight. However, at 430°C (805°F), the influence of the latter two additions was approximately equivalent to that of vanadium.

The coating microstructure modifications on this cold-rolled steel were equally striking and the gross iron-zinc alloy development of Figures 14(a) and 15(a) was altered over large areas of the surface to thin, uniform, compact layers of zeta and delta prime phases. Figures 14(c) and 15(b), as well as pertinent areas of Figures 14(b) and (d), reflect the typical

pronounced changes at both temperatures. The latter figures also illustrate the characteristic local reversion to aggravated attack and the prominent zeta outbursts formed at these sites of inhibition breakdown. The resultant deterioration in coating appearance discussed previously, varied with the different bath additions and was minimal with the vanadium-containing coatings. It is emphasized that the outbursts assumed massive proportions as in Figure 14(b) only with prolonged immersion at 450°C (840°F). Under all other test conditions, the localized bursts were generally small and/or widely scattered and were thereby much less detrimental to iron-zinc alloy and total coating uniformity. The usual intermetallic compound dispersion observed in the nickel-containing coatings can again be seen in Figure 14(b).

It will be recalled that Steel 13 differed significantly from Steel 15 with respect to composition, structure and mill finished condition. For one or more of these reasons, its behaviour in the alloyed baths at 450°C (840°F) was likewise different and Figures 9-10 show that the inhibition effect of chromium, manganese and nickel was negligible in this case. The basic microstructure of Figure 14(a) was largely reproduced and the only change of note was a tendency to increased zinc drag-out because of intermetallic compound formation in the nickel-containing coatings as in Figure 16(a).

Vanadium remained as the only effective addition at this higher temperature and, unusually so, the inhibition achieved was apparent only with prolonged immersion. Although not indicated in the graphs, this addition was equally effective with 20 minutes immersion of Steel 13. Extrapolation from the pertinent curves in Figure 10 reveals the remarkable inhibition thereby represented. Figure 16(b) illustrates the characteristic microstructure change to a thinner, columnar-structured zeta phase layer and well-defined uniform growth in the delta prime phase. The finely serrated zeta boundary, which followed a shallow wave-like contour because of uneven growth in this layer, was another distinctive feature. The zinc layer was correspondingly uneven and, by reproducing the zeta contour, accounted for the peculiar hammered appearance described previously. Intermetallic compound formation in the zinc layer was confined to a grain boundary dispersion of fine particles, and some eutectic was also evident.

Figures 9-10 show that all four bath additions were once more markedly effective in reducing coating weight and iron content at 430°C (805°F). Even in the extreme case of Steel 13, therefore, it was confirmed that pronounced inhibition of steel base attack was possible, but only at this lower galvanizing temperature with additions other than vanadium. The respective alloyed coating microstructures were much similar to those on Steel 15 for corresponding conditions, and a representative coating produced with manganese in the bath is illustrated in Figure 16(c).



The pronounced change from the comparable control coating, which was similar to that shown in Figure 15(a), is clearly evident.

### SUMMARY AND DISCUSSION

From the laboratory investigations made, it was established that alloying of an iron-saturated lead-containing zinc bath with individual additions of 0.2% Cr, 0.5% Mn, 0.2% Ni and 0.1% V was variably beneficial in modifying galvanized coating formation and structure on a wide range of low-alloy high-strength steels. The results may be summarized as follows:

With so-called normal activity semi-killed steels containing low silicon and phosphorus, all of the alloyed coatings exhibited moderate improvements in surface appearance. Superior uniformity in the integral coating layers was also achieved by elimination of irregularities in iron-zinc alloy growth which are frequently apparent in conventional coatings. Such inhibition was particularly well-defined with a rough surfaced steel in this group and the improvement in coating uniformity and smoothness was accordingly marked.

Much more pronounced inhibition effects in the alloyed baths were realized with two silicon-killed steels, and to a lesser extent with a high phosphorus semi-killed steel. The characteristic linear reaction rate and the coating build-up on the former were drastically altered to a parabolic form

not greatly dissimilar from that of plain carbon steel. The bath additions of 0.1% V and 0.2% Cr were equally effective and superior to 0.2% Ni and 0.5% Mn at a galvanizing temperature of 450°C (840°F). The beneficial influence of nickel and manganese were, however, apparent at 430°C (805°F) and more nearly reproduced the strong inhibition effects of the other two additions. The alloyed coatings on these steels were largely free of grey coating formation, but the surface appearance was otherwise marred by projecting pimples which developed with lengthy immersion times at the higher bath temperature. These represented sites of local inhibition breakdown at which the iron-zinc reaction velocity returned to normal. Vanadium- and chromium-containing coatings were less prone to this defect as were all of the alloyed coatings at the lower bath temperature. It will be appreciated that coating uniformity was less than desirable in the vicinity of such outbursts. However, any consideration of the detrimental nature of such imperfections would have to be balanced against the major advantages of large reduction in the average coating thickness and much greater latitude in immersion time control provided by bath alloying.

The response of two extremely active silicon-phosphorus steels was variable. In the case of a cold-rolled product, inhibition by 0.1% V was particularly pronounced irrespective of bath temperature. Substantial effects were also apparent with the other bath additions at 450°C (840°F), but, despite elimination of the grey coating defect, the incidence of large pimple outbursts at long immersion times resulted in rough unattractive

coatings. On this account, the usefulness of chromium, manganese and nickel was limited to short immersion times at this temperature. However, at 430°C (805°F) all addition elements were effective. Somewhat similar limitations were also apparent with a second silicon-phosphorus steel tested. In this case, the beneficial effects of bath alloying were largely confined to this lower temperature and the only significantly useful addition at 450°C (840°F) was 0.1% V. The unique influence of vanadium in this case is still more noteworthy since it remained strongly inhibitive even with 20 minutes immersion of this highly active steel.

The mechanism of iron-zinc alloy inhibition that was achieved by bath alloying in this investigation is a matter for speculation at this stage. Inhibition was principally manifested by modification in the growth characteristics of the zeta iron-zinc phase and, in this connection, the nickel-containing coatings are of special interest. In this case, there was a direct relationship between zeta thickness and the formation of gross intermetallic compounds in the outer zinc layer. Although it was not uncommon to see individual compound particles in intimate contact with the zeta phase layer, the particle size, shape and distribution suggest that they were nucleated from the melt at or near the zinc-zeta interface. Bath samples examined contained a scattering of similar intermetallics, but the degree of contamination did not remotely resemble that in the coatings.

The regularity of the iron-zinc alloy layers generally apparent in the alloyed coatings is also of note since it duplicated the effect obtained

by Haughton (7) in galvanizing mild steel in an iron-free bath. He refers to the formation of thinner zeta layers with agitated specimens dipped for 5 minutes at 450°C (840°F), but concludes that variation in iron content of an otherwise pure zinc bath had no observable effect on coating structure or attack of the steel base. However, in conjunction with the results of the present investigation, the effects illustrated in his photomicrographs of low-iron coatings do appear to be significant. In any event these various observations, collectively, suggest that the presence of nickel in the bath (and presumably of chromium, manganese and vanadium also) was instrumental in modifying the equilibrium state at the zeta-melt interface. To what extent this resulted in direct reduction in the velocity of zeta phase formation, separately or in combination with the alternative possibility of melt dissolution of the zeta layer, remains to be determined. In one sense, the former mechanism is favoured in view of the prominently thick and uniform delta prime phase formation usually evident in the alloyed coatings. On the other hand, the very thin zeta layer formation in the nickel-containing coatings, which was combined with increasing size of compound particles with time, clearly suggests a dissolution mechanism.

In consequence of the practical importance of the findings in this investigation, patent applications pertinent thereto have been filed. At the same time, a large scale pilot study was undertaken by an independent laboratory under ILZRO sponsorship to more fully evaluate the commercial potential of the alloyed bath process. The objectives of this study, which



is well advanced, are (a) to assess the practical feasibility of the process for alloyed coating production by the wet and dry galvanizing techniques and (b) to evaluate the formation and properties (including corrosion behaviour and adherence) of coatings formed on various low-alloy and unalloyed steel compositions and products.

### CONCLUSIONS

Galvanized coating formation and structure on a group of low-alloy high-strength steels of variable silicon content were beneficially altered, in some cases to a marked degree, by selective alloying of a zinc bath of conventional composition. For the conditions studied, a bath addition of 0.1% V was most consistently effective and 0.2% Cr, 0.2% Ni and 0.5% Mn followed in that order. The usefulness of the alloyed baths was restricted at a normal galvanizing temperature of 450°C (840°F) with steels having particularly high galvanizing activity, but remained effective at a lower temperature of 430°C (805°F).

The tests made defined a promising method for controlling the excessive reaction behaviour of steels which, for galvanizing purposes, have a high silicon content. Useful improvements in coating formation on lower and normal activity steels were also indicated, particularly in the case of materials with a rough, hot-rolled mill finish. These effects in combination should be materially beneficial in reducing coating thickness differential in galvanizing of mixed steel assemblies.

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TABLE 1

Steel Composition and Properties \*

| Steel No. | Gauge | %    |       |       |      |       |        |      |      |      |      |      |      |       | UTS<br>(kpsi) | YS<br>0.2% offset<br>(kpsi) | El.<br>% in 2 in. | C.L.A.<br>Roughness<br>(micro in.) |
|-----------|-------|------|-------|-------|------|-------|--------|------|------|------|------|------|------|-------|---------------|-----------------------------|-------------------|------------------------------------|
|           |       | C    | P     | S     | Mn   | Si    | Al     | Cu   | Cr   | Ni   | Mo   | Nb   | V    | N     |               |                             |                   |                                    |
| 8         | 14    | 0.13 | 0.007 | 0.038 | 0.34 | <0.01 | <0.01  | -    | -    | -    | -    | -    | -    | 0.005 | 51.6          | 44.7                        | 36.2              | 69                                 |
| 19        | 14    | 0.15 | 0.012 | 0.038 | 0.82 | 0.01  | <0.01  | -    | -    | -    | -    | -    | 0.06 | 0.003 | 71.9          | 50.4                        | 28.9              | 60                                 |
| 20        | 14    | 0.19 | 0.012 | 0.017 | 0.75 | 0.04  | <0.01  | 0.05 | 0.02 | -    | -    | 0.02 | -    | 0.005 | 84.5          | 66.0                        | 21.9              | 78                                 |
| 16        | 14    | 0.18 | 0.006 | 0.022 | 0.87 | 0.03  | <0.005 | 0.26 | 0.02 | 0.01 | -    | 0.02 | -    | 0.008 | 70.7          | 60.8                        | 25.4              | 120                                |
| 18        | 12    | 0.13 | 0.070 | 0.025 | 0.72 | 0.08  | <0.01  | 1.11 | -    | 0.69 | 0.13 | -    | -    | 0.006 | 96.5          | 72.6                        | 23.8              | 58                                 |
| 21        | 12    | 0.12 | 0.010 | 0.025 | 0.72 | 0.21  | <0.01  | 0.55 | 0.15 | 0.54 | 0.05 | -    | -    | 0.005 | 78.6          | 63.6                        | 27.0              | 65                                 |
| 17        | 14    | 0.17 | 0.010 | 0.030 | 1.26 | 0.22  | 0.06   | 0.25 | 0.44 | 0.40 | -    | -    | 0.02 | 0.005 | 85.0          | 60.9                        | 24.3              | 75                                 |
| 13        | 14    | 0.09 | 0.032 | 0.030 | 0.37 | 0.23  | 0.01   | 0.30 | 0.23 | 0.35 | -    | -    | -    | 0.005 | 72.4          | 55.9                        | 30.6              | 60                                 |
| 15**      | 16    | 0.10 | 0.065 | 0.026 | 0.41 | 0.39  | <0.01  | 0.30 | 0.66 | 0.32 | -    | -    | -    | 0.002 | 67.9          | 53.8                        | 29.7              | 45                                 |

\* Chemical composition by wet analysis.  
Tensile properties - average of six tests.

\*\* Cold rolled (all others hot rolled).

TABLE 2  
Galvanizing Programme

| Bath<br>Temp.<br>Comp. | Steel No.              |                    | Immersion<br>Time<br>(min.) |
|------------------------|------------------------|--------------------|-----------------------------|
|                        | 450°C (840°F)          | 430°C (805°F)      |                             |
| Control *              | all                    |                    | 1, 2, 5, 10                 |
| "                      |                        | 18, 21, 17, 15, 13 | "                           |
| Control + 0.2% Cr      | 16, 18, 21, 17, 13, 15 |                    | "                           |
| " "                    |                        | 18, 21, 13         | "                           |
| " + 0.5% Mn            | all                    |                    | "                           |
| " "                    |                        | 18, 21, 17, 15, 13 | "                           |
| " + 0.2% Ni            | all                    |                    | "                           |
| " "                    |                        | 18, 21, 17, 15, 13 | "                           |
| " + 0.1% V             | all                    |                    | "                           |
| " "                    |                        | 18, 21, 17, 15, 13 | "                           |
| " + 0.2% V             | 8, 19, 20              |                    | "                           |

\* Basic composition: Zn + 0.03% Fe + 1.0% Pb (+ 0.005% Al with Mn and V additions).

TABLE 3  
Surface Appearance \*

| Steel No. | Bath Temp.    | Immersion Time (min) | Bath Composition                                      |   |   |   |  |
|-----------|---------------|----------------------|---|---|---|---|--|
|           |               |                      | Control   | + 0.2% Cr   | + 0.5% Mn                                 | + 0.2% Ni   | +0.1% V  |
| 8, 19, 20 | 450°C (840°F) | 1, 2, 5, 10          | dull, large grains, low contrast.                     | -   | medium spangles, good contrast.           | medium grains, boundary depressions varying with time.    | medium spangles, high contrast.                          |
| 16        | 450°C (840°F) | 1, 2, 5, 10          | fine to very coarse texture with time, medium grains. | medium grains.  | as for 8, 19, 20.                         | as for 8, 19, 20.   | as for 8, 19, 20.  |
| 18        | 450°C (840°F) | 1, 2                 | dull, medium grains.                                  | medium grains.  | small grains.                             | medium grains, depressed boundaries.                      | medium spangles, high contrast.                          |
|           |               | 5, 10                | dull, large grains, depressed boundaries.             | dendritic pattern in large grains, depressed boundaries.              | large grains.                             | dendritic pattern in medium grains, depressed boundaries. | large spangles, high contrast.                           |
|           | 430°C (805°F) | 1, 2                 | as at 450°C.  | as at 450°C.  | small spangles, good contrast.            | as at 450°C.  | small spangles, high contrast.                           |
|           |               | 5, 10                | as at 450°C.  | large grains, depressed boundaries.                                   | medium spangles, good contrast.           | as at 450°C.  | as at 450°C.   |
| 21        | 450°C (840°F) | 1, 2                 | as for 18.  | as for 18.  | as for 18.                                | as for 18.  | as for 18.   |
|           |               | 5, 10                | dull, broadened grey network, large grains.           | rough (small outbursts), medium grains.                               | grey (line) network, medium grains.       | as for 18.  | rough (small outbursts), medium spangles, high contrast. |
|           | 430°C (805°F) | 1, 2                 | as for 18.  | as for 18.  | as for 18.                                | as for 18.  | as for 18.   |
|           |               | 5, 10                | dull, large grains.                                   | as for 18.  | as for 18.                                | rough (small outbursts), medium grains.                   | very small outbursts, medium spangles, high contrast.    |
| 17        | 450°C (840°F) | 1, 2                 | dull, large grains.                                   | as for 21.  | small spangles, low contrast.             | as for 21.  | as for 21.   |
|           |               | 5                    | as for 21.  | rough (small outbursts), colonies and line formations), large grains. | rough (small outbursts), medium spangles. | rough (large outbursts), medium grains.                   | as for 21.   |
|           |               | 10                   | "   | "   | "   | very rough (closely-packed gross outbursts).              | "  |
|           | 430°C (805°F) | 1, 2                 | dull, medium grains.                                  | -   | as at 450°C.                              | as at 450°C.  | small spangles, high contrast.                           |
|           |               | 5, 10                | dull, large grains.                                   | -   | medium spangles, good contrast.           | as for 21.  | very small outbursts, medium spangles.                   |
|           |               |                      |   |   |   |   |  |

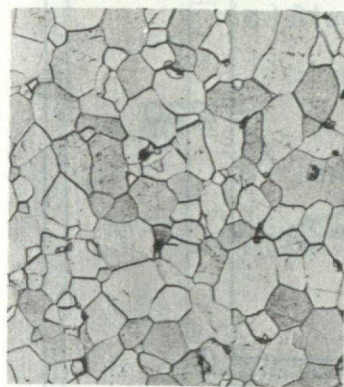


TABLE 3 (Cont'd.)  
Surface Appearance \*

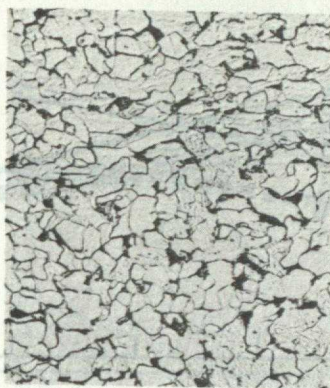
| Steel No. | Bath Temp.       | Immersion Time (min) | Bath Composition  |   |  |   |  |
|-----------|------------------|----------------------|---|---|--|---|--|
|           |                  |                      | Control   | + 0.2% Cr   | + 0.5% Mn  | + 0.2% Ni   | + 0.1% V   |
| 15        | 450°C<br>(840°F) | 1, 2                 | as for 17.  | very small outbursts, large grains, depressed boundaries.                                     | very small outbursts, small spangles, low contrast.      | very small outbursts, medium grains.              | very small outbursts, small spangles, high contrast.   |
|           |                  | 5                    | dull, broadened grey network, large grains.                                       | rough (colonies of large outbursts), dendritic pattern in large grains, depressed boundaries. | very rough (closely-packed gross outbursts).             | rough (scattered gross outbursts), medium grains. | rough (scattered large outbursts), large spangles, high contrast.                                  |
|           |                  | 10                   | dull, very broad grey network (50% of surface), large grains.                     | very rough (closely-packed gross outbursts).  | "  | very rough (closely-packed gross outbursts).      | rough (scattered gross outbursts), large spangles, high contrast.                                  |
|           | 430°C<br>(805°F) | 1, 2                 | as for 17.  | -   | dull, small spangles.                                    | medium grains.                                    | small spangles, high contrast.   |
|           |                  | 5                    | dull, dendritic pattern in medium grains, as for 5 min, plus grey (line) network. | -   | dull, medium spangles, good contrast.                    | rough (small outbursts), medium grains.           | medium spangles, high contrast.  |
|           |                  | 10                   |   | -   | "  | "   | rough (small outbursts), medium spangles, high contrast.   |
| 13        | 450°C<br>(840°F) | 1, 2                 | as for 15.  | dull, large grey patches, large grains.   | dull, small grains.                                      | dull, small grey patches, medium grains.          | dull, grey (line) network and patches, small surface indentations, small grains.                   |
|           |                  | 5                    | as for 15.  | dull grey (line) network, large grains.   | dull, grey (line) network, medium grains.                | dull, grey (line) network, medium grains.         | dull, more extensive grey network and patches, numerous large rounded indentations, medium grains. |
|           |                  | 10                   | as for 15.  | dull, grey coating (75% of surface), grains not defined.                                      | dull, grey coating (75% of surface), grains not defined. | "   | hammered appearance, large grains.   |
|           | 430°C<br>(805°F) | 1, 2                 | as for 15.  | medium grains.  | small spangles, high contrast.                           | medium grains.                                    | small spangles, high contrast.   |
|           |                  | 5                    | as for 15.  | dendritic pattern in medium grains, depressed boundaries.                                     | medium spangles, high contrast.                          | rough (small outbursts), medium grains.           | rough (small outbursts), medium spangles, high contrast.   |
|           |                  | 10                   | as for 15.  | rough (scattered large outbursts), medium grains.   | large spangles, high contrast.                           | rough (scattered large outbursts), medium grains. | rough (scattered large outbursts), medium spangles, high contrast.                                 |

\* Unless otherwise noted, coatings were smooth and bright and degree of grain boundary depression was slight.

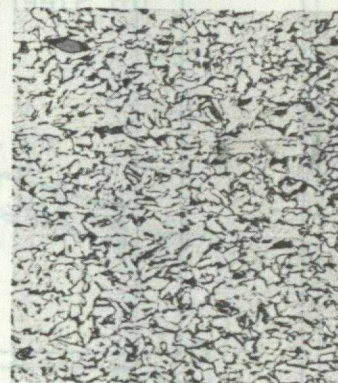




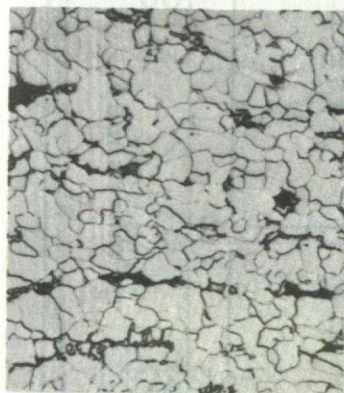
(a) Steel 8 (8)



(b) Steel 19 (9)



(c) Steel 20 (10)



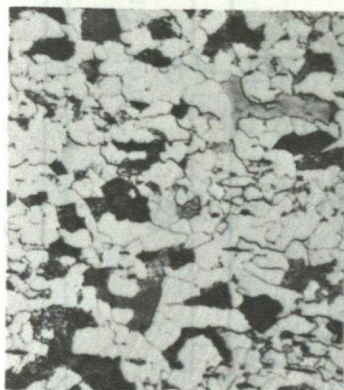
(d) Steel 16 (9)



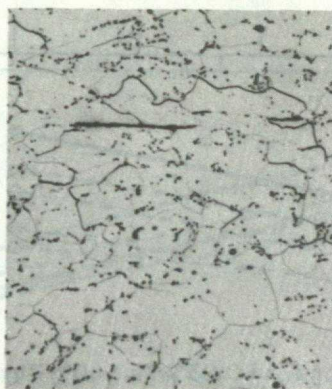
(e) Steel 18 (9)



(f) Steel 21 (9-10)



(g) Steel 17 (9)



(h) Steel 15 (8-9)



(i) Steel 13 (9)

Figure 1. Steel microstructures with ASTM grain size number in brackets.  
Nital etch, X500.



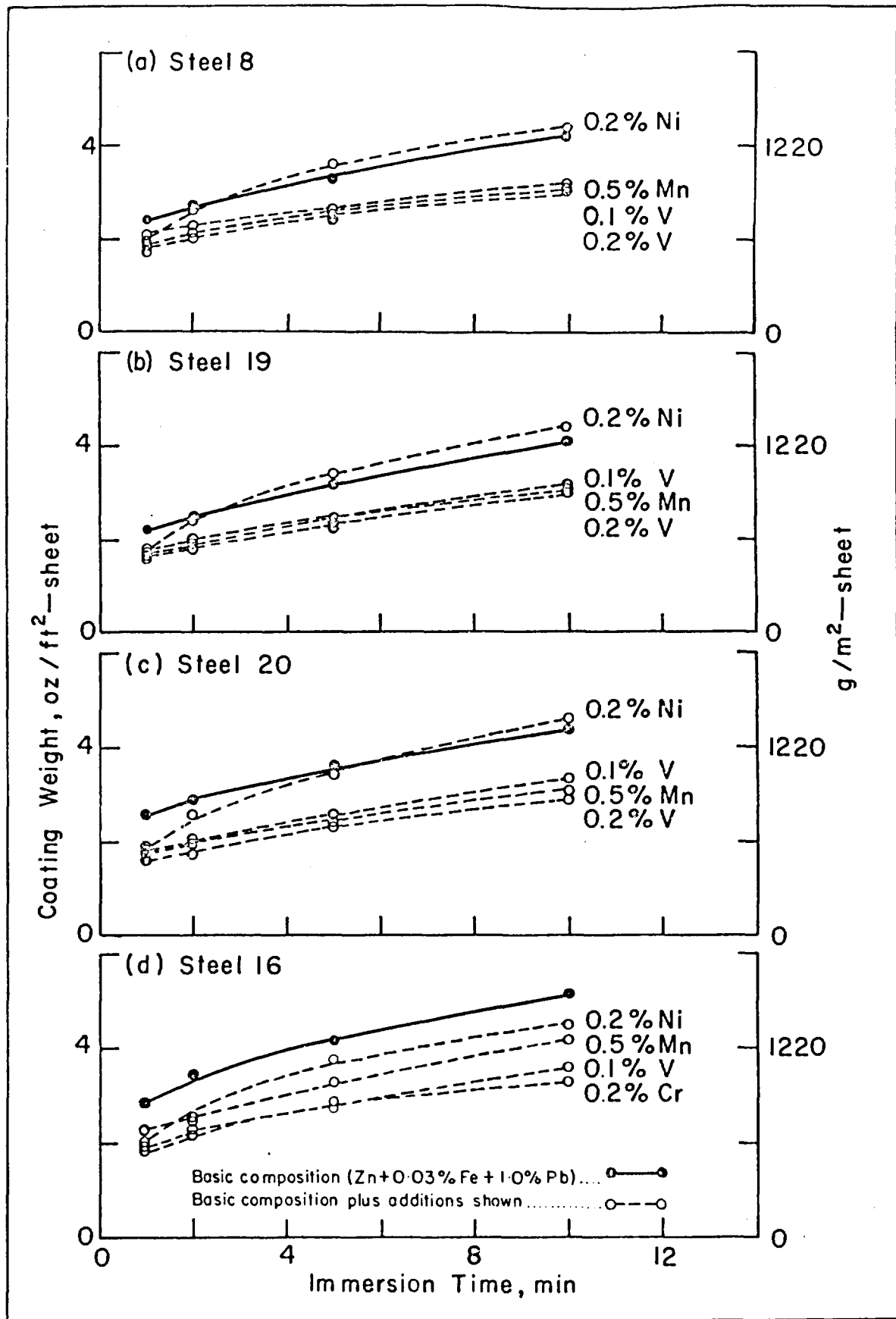


Figure 2. Coating weight vs immersion time for Steels 8, 19, 20 and 16 galvanized at 450°C (840°F).

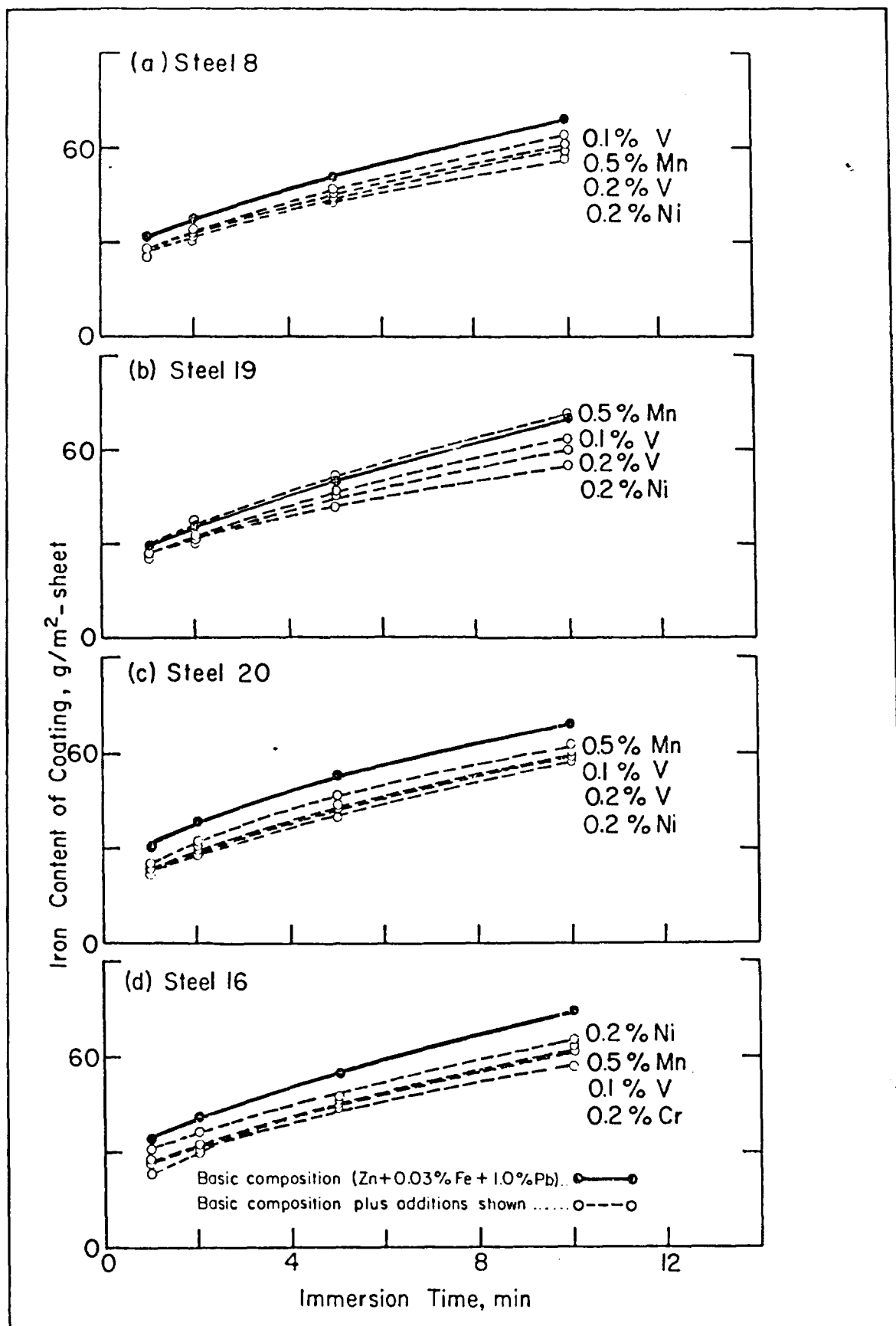


Figure 3. Iron content of coating vs immersion time for Steels 8, 19, 20 and 16 galvanized at 450°C (840°F).

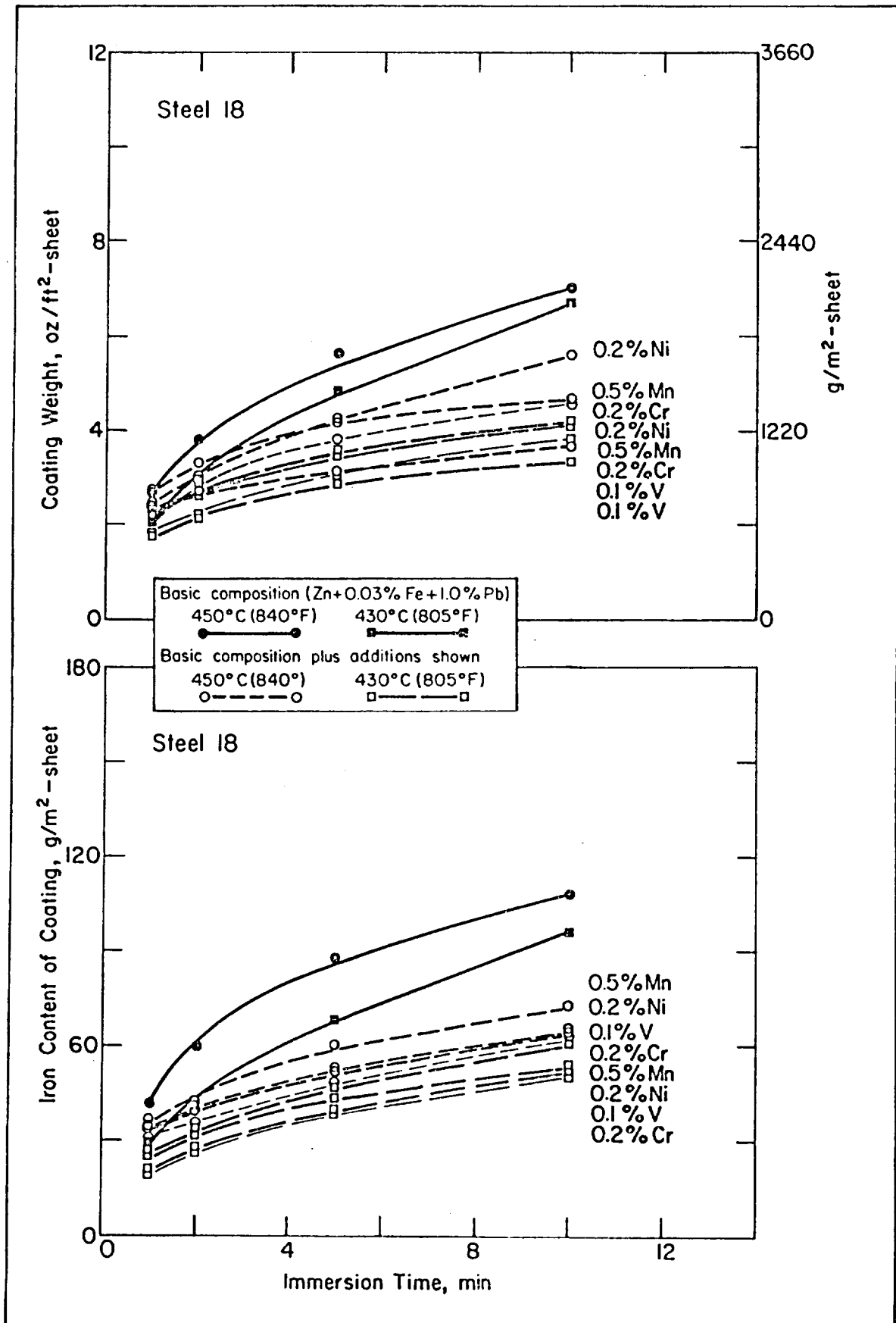


Figure 4. Coating weight and iron content of coating vs immersion time for Steel 18.

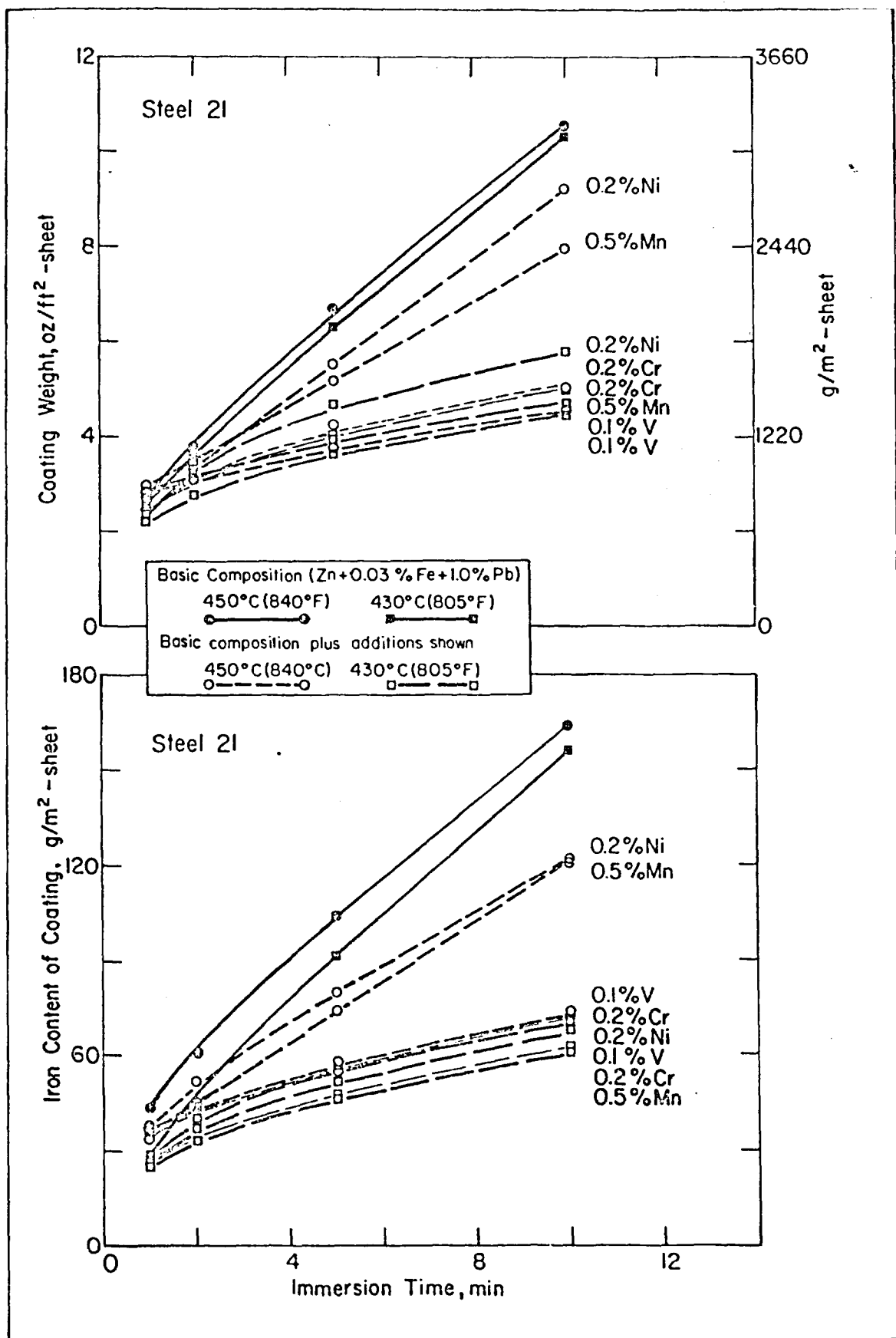


Figure 5. Coating weight and iron content of coating vs immersion time for Steel 21.

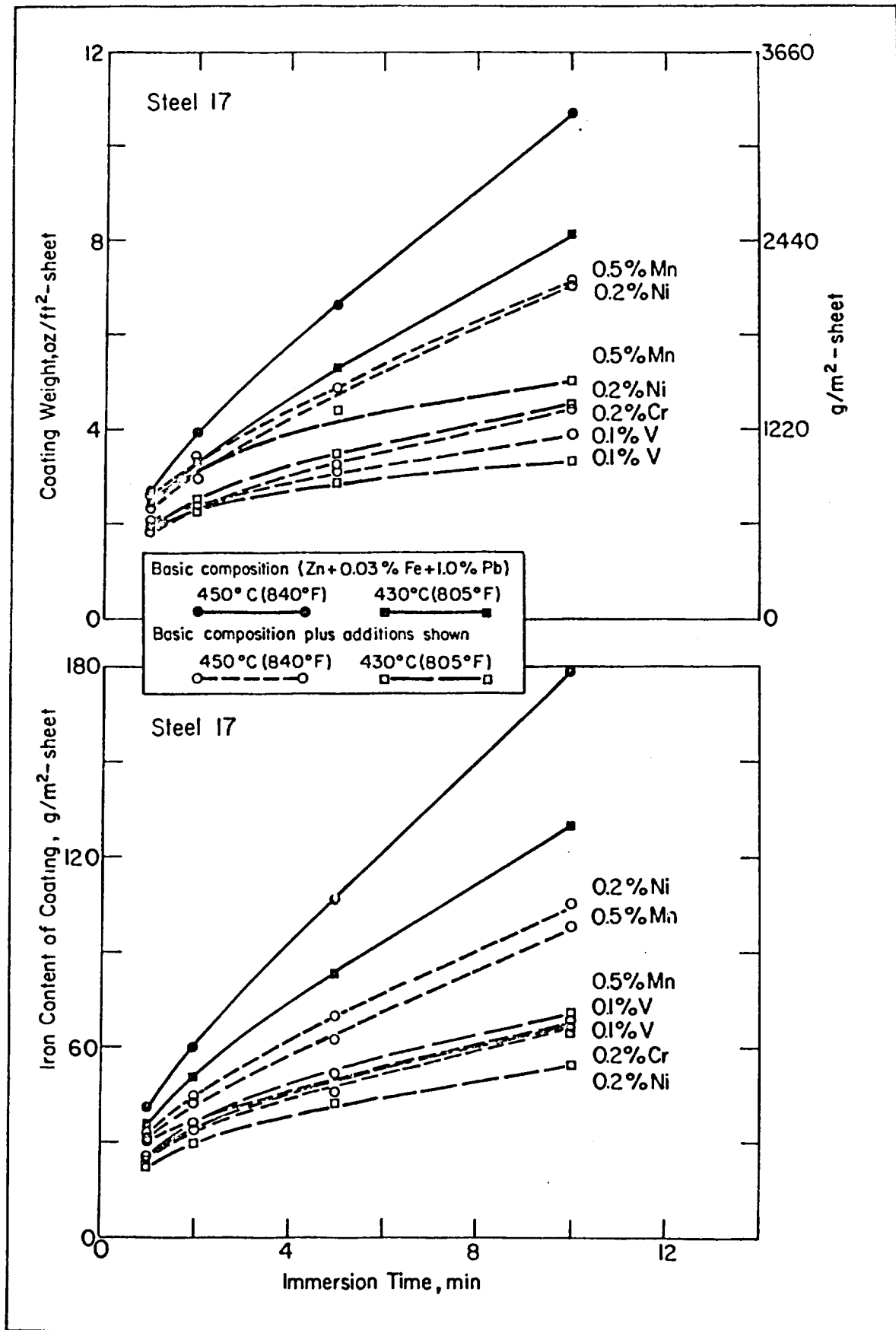


Figure 6. Coating weight and iron content of coating vs immersion time for Steel 17.

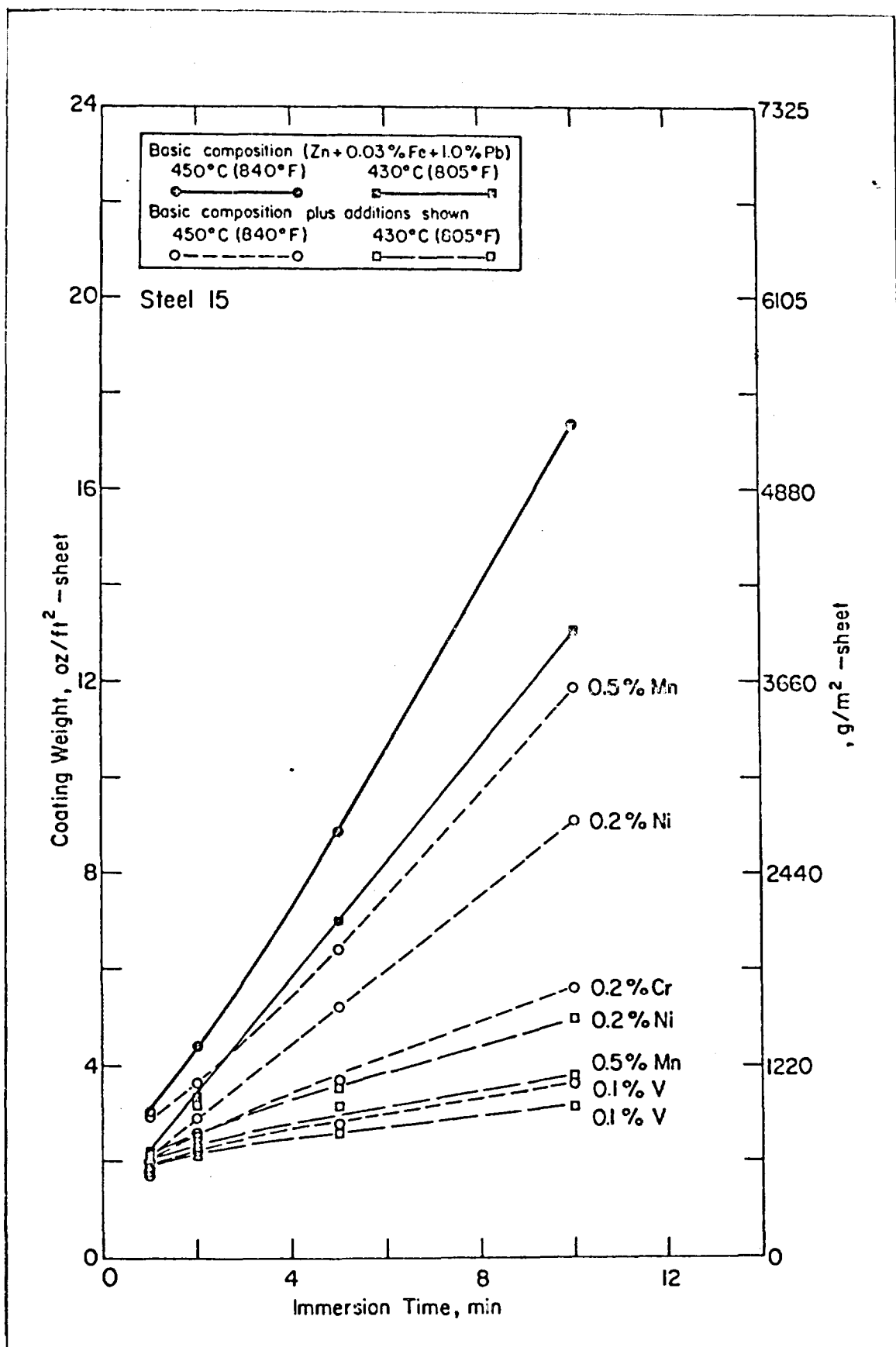


Figure 7. Coating weight vs immersion time for Steel 15.



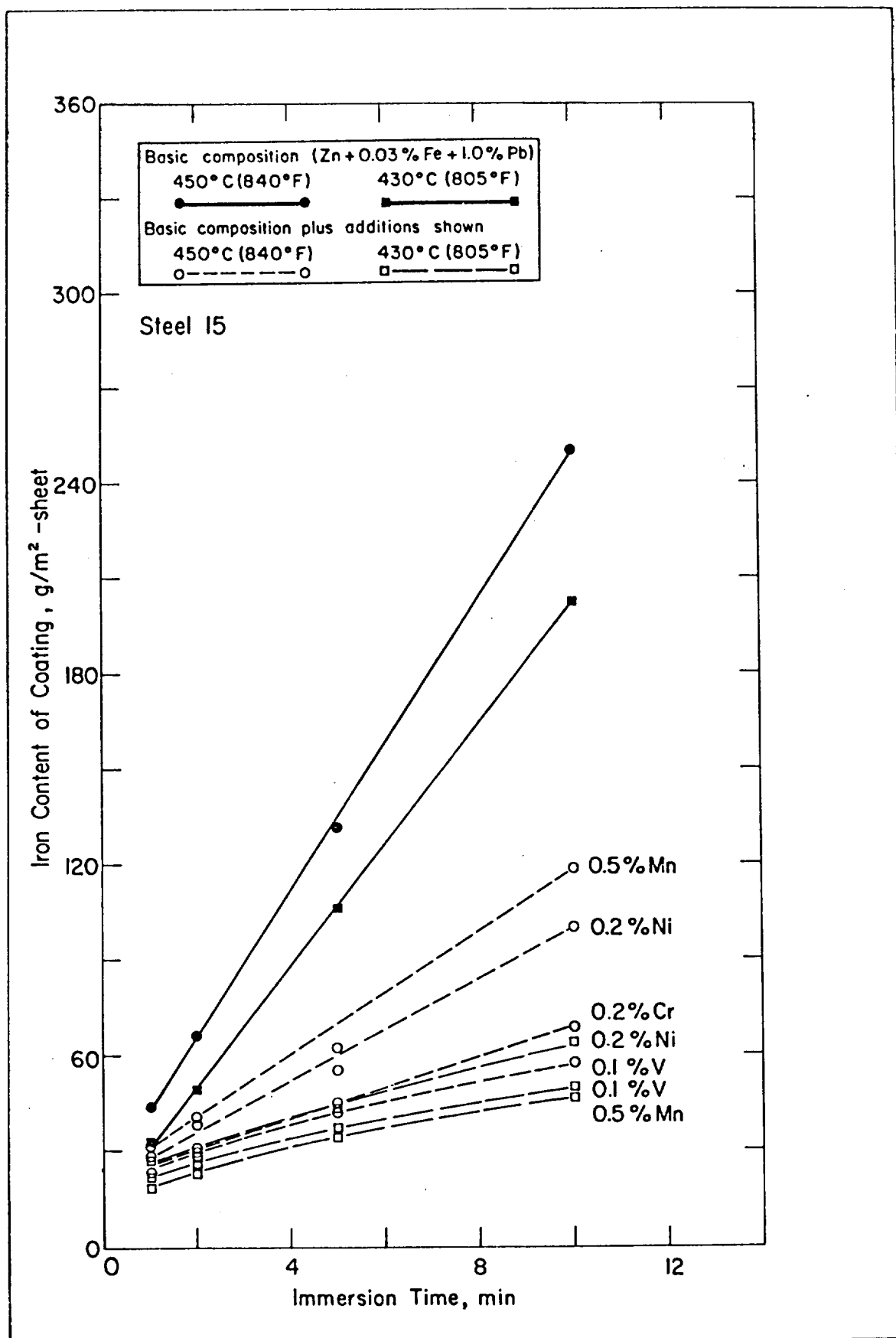


Figure 8. Iron content of coating vs immersion time for Steel 15.

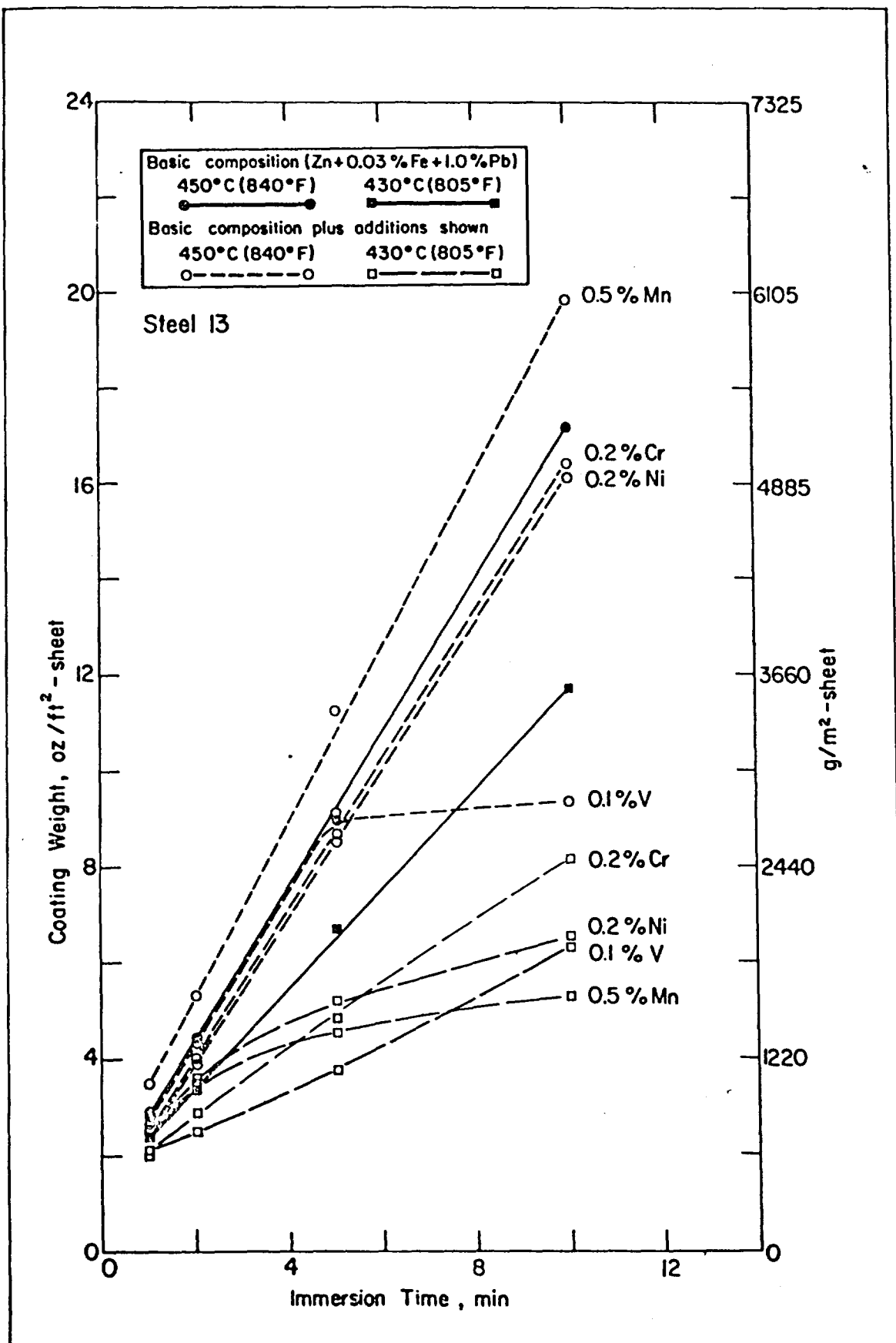


Figure 9. Coating weight vs immersion time for Steel 13.

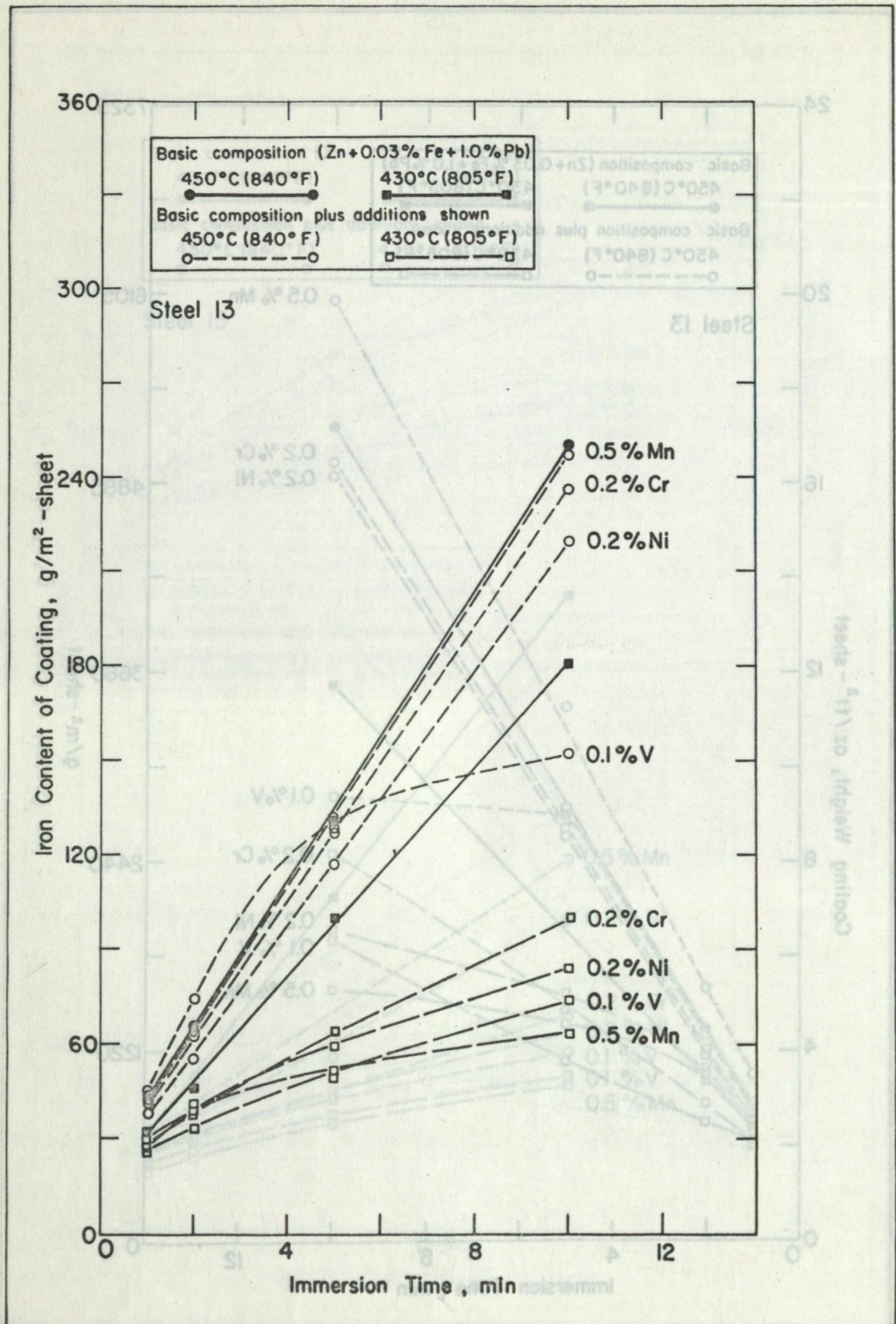
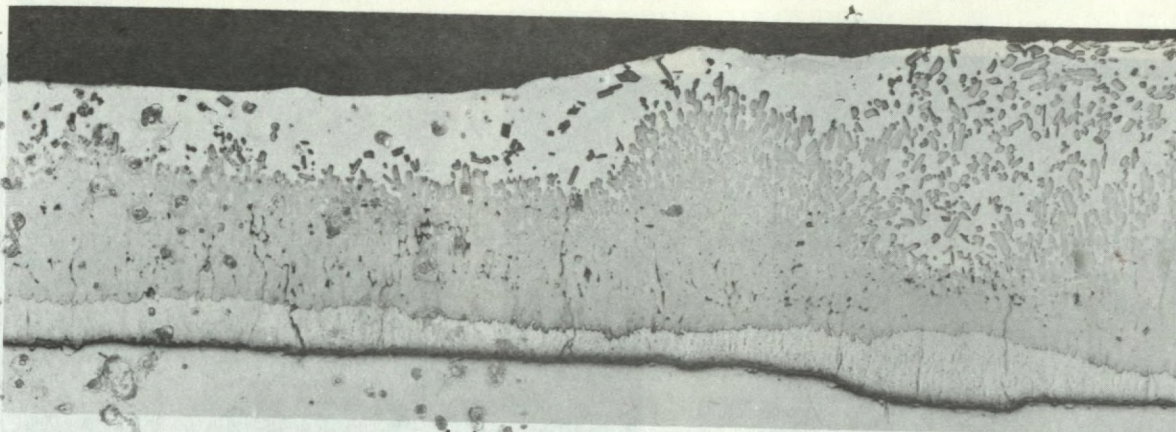
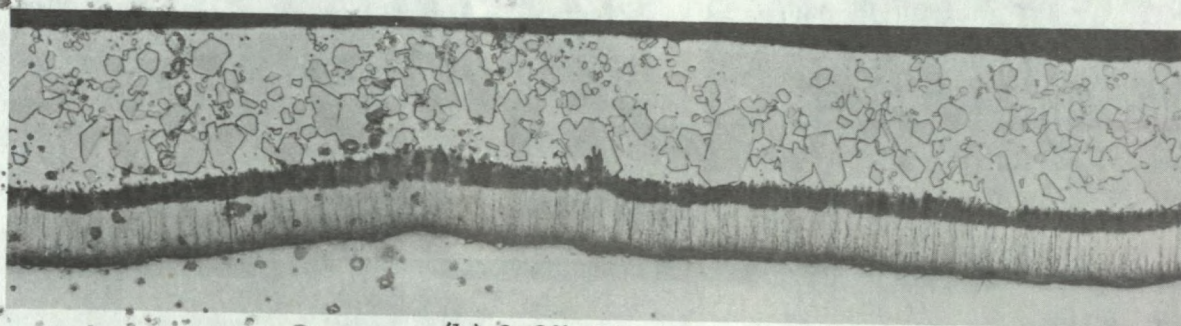


Figure 10. Iron content of coating vs immersion time for Steel 13.

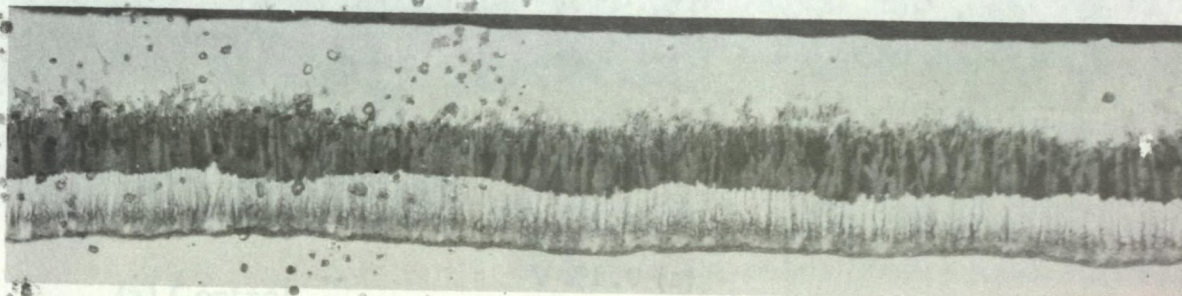




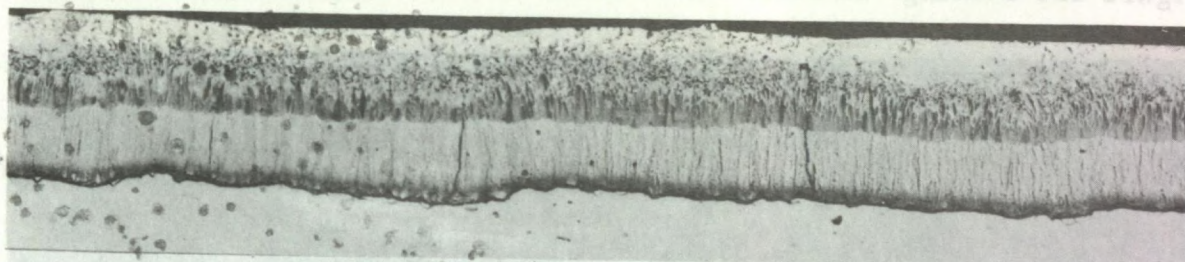
(a) Control



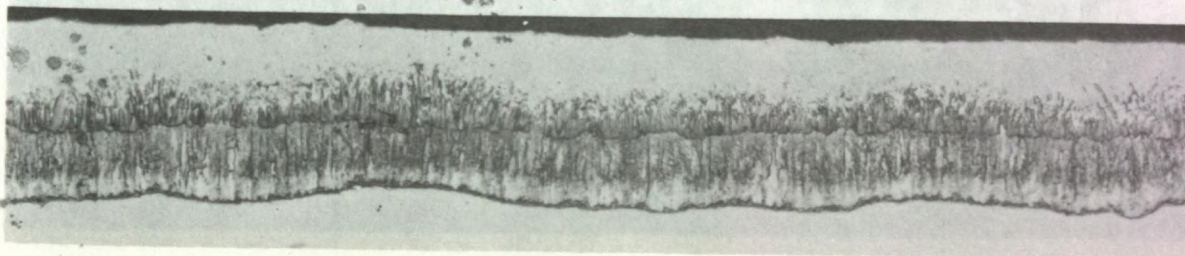
(b) 0.2% Ni



(c) 0.5% Mn



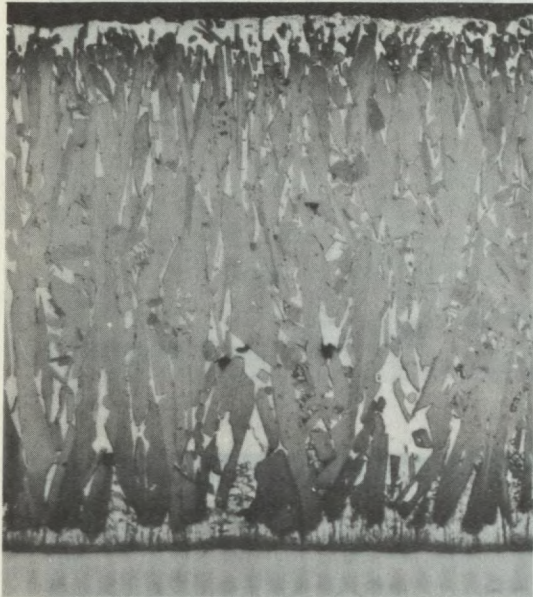
(d) 0.2% Cr



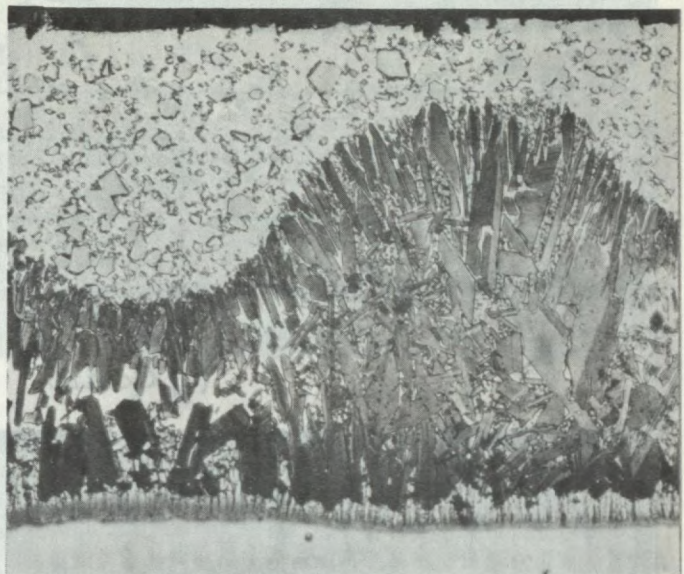
(e) 0.1% V

Figure 11. Coatings on Steel 16: 10 minutes immersion at 450°C (840°F), X 300.

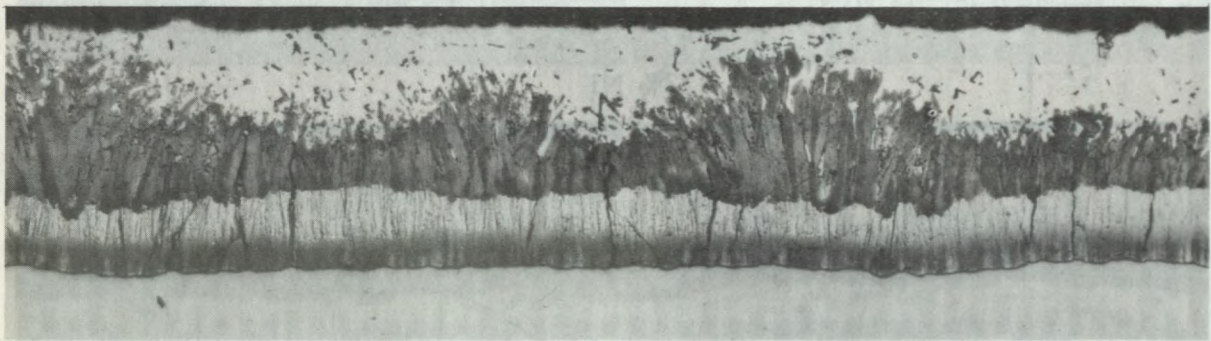




(a) Control



(b) 0.2% Ni



(c) 0.1% V

Figure 12. Coatings on Steel 21: 10 minutes immersion at 450°C (840°F), X300.

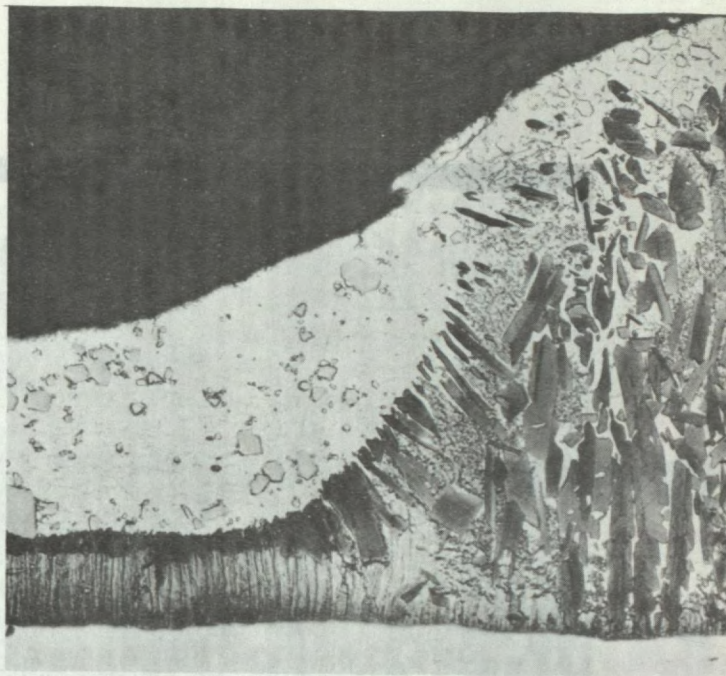


Figure 13. Nickel-containing (0.2%) coating on Steel 21: 10 minutes immersion at 450°C (840°F), X300.

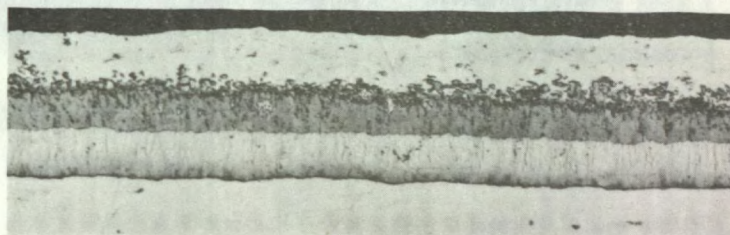




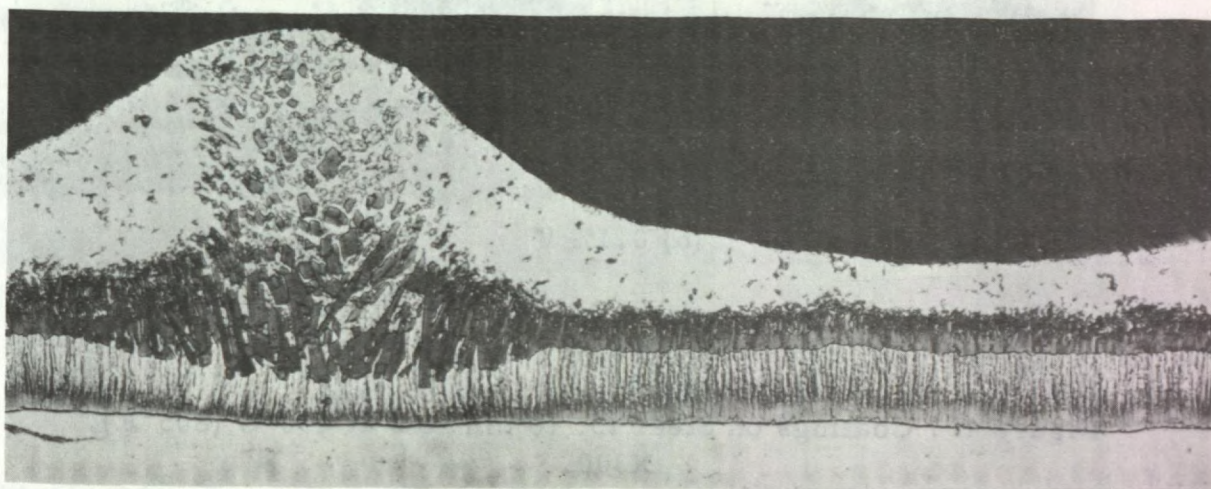
(a) Control



(b) 0.2% Ni



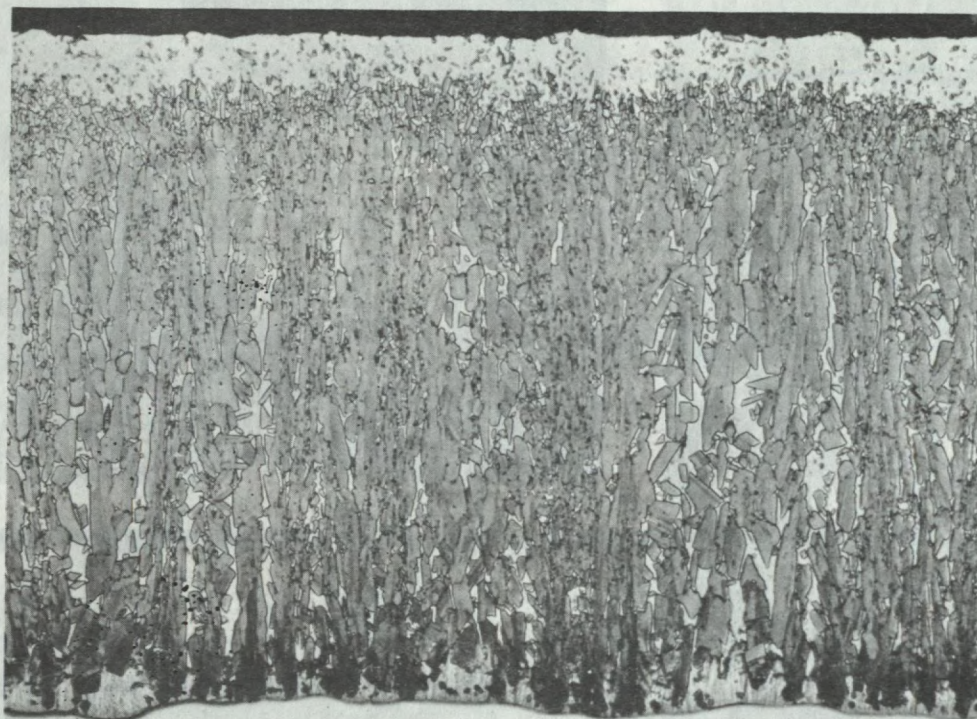
(c) 0.1% V (5 minutes immersion)



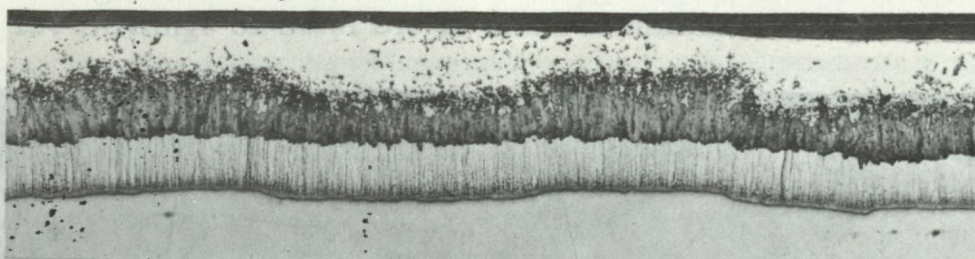
(d) 0.1% V

Figure 14. Coatings on Steel 15: 10 minutes immersion (except as indicated) at 450°C (840°F), X300.





(a) Control



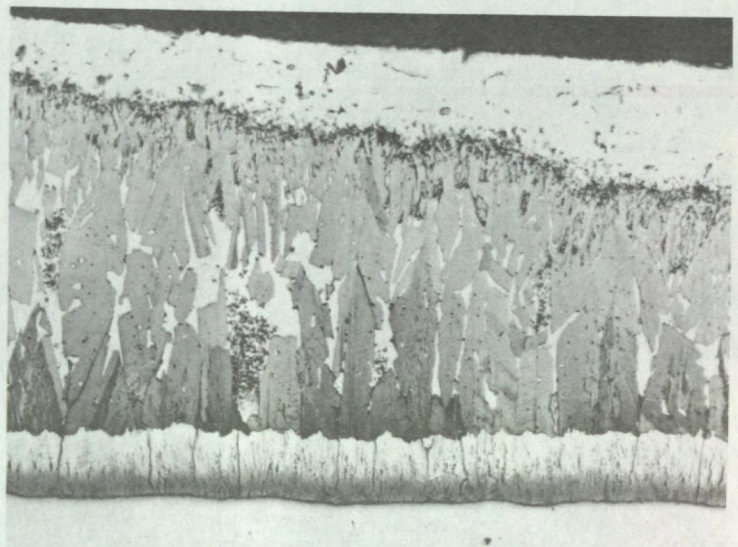
(b) 0.1% V

Figure 15. Coatings on Steel 15: 10 minutes at 430°C (805°F), X300.

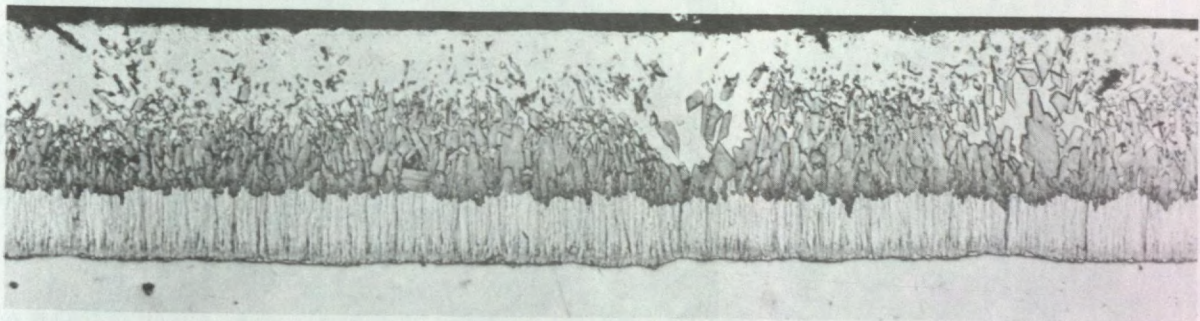




(a) 0.2% Ni, 450°C (840°F)



(b) 0.1% V, 450°C (840°F)



(c) 0.5% Mn, 430°C (805°F)

Figure 16. Coatings on Steel 13: 10 minutes immersion at temperatures indicated, X300.