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CONTINUOUS-STRIP GALVANIZED COATINGS AT ELEVATED TEMPERATURES

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PHYSICAL METALLURGY DIVISION

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The elevated-temperature deterioration of a continuous-strip galvanized product has been investigated by air-atmosphere heating in the temperature range 150°-400°C (300°-750°F) for periods up to 20 weeks. Various forms and degrees of deterioration were revealed which were dependent on the conditions of exposure. The principal mechanism of failure involved the development of local iron-zinc reaction outbursts which caused breakup and separation of the zinc layer and, in more advanced stages, intergranular penetration and embrittlement of the steel substrate. The significance of the experimental findings to elevated-temperature use of the strip material tested is discussed.

Elevated-temperature heating of hot-dip galvanized coatings is generally considered to result in rapid failure by peeling or spalling of the coating. This view makes no distinction between different types of coating—the same deterioration mechanism being assumed in all cases, even though coating microstructure can vary widely depending on the conditions of formation.

The best-known form of peeling deterioration is encountered with conventional hot-dip coatings of the type applied in general galvanizing practice. The typical microstructure consists of iron-zinc reaction phases in characteristic layer formation, with an outer cover of pure zinc. When such coatings are heated to moderately elevated temperatures, or under certain conditions of cooling after galvanizing, rapid destruction of the zinc-zeta interface bond takes place and the outer zinc layer can be readily peeled away.

Galvanized coatings formed on high-speed continuous-strip processing lines represent an entirely different product, microstructurally and in other respects. In the most widely produced class are coatings consisting essentially of pure zinc bonded to the steel by a thin reaction layer of iron-zinc alloy crystals. This modification would be expected to have a significant effect on the rate and mode of elevated-temperature deterioration and, in fact, improved performance is claimed, based on industry recommendations (1) of a maximum service temperature of about 290°C (550°F). For conventional coatings, the limiting temperature is considered to be about 200°C (390°F).

Apart from such recommendations, the only available information on the elevated-temperature performance of continuous-strip coatings is that due to Pipe (2), who attempted short-term tests on continuous strip of two different gauges. He reported no marked changes in the coating after 5 weeks at 200°C (390°F). In the range 250°-350°C (480°-660°F), coating deterioration was a time-temperature function, being manifested, first, by the formation of massive local iron-zinc alloy outbursts which broke through the outer zinc layer, and, second, by oxidation effects at and below the zinc surface. In connection with a study on the mechanism of iron-zinc alloy suppression by aluminum, Hughes (3) also refers to the formation of alloy nodules in high-aluminum (0.3%) coatings heated at 350°C (660°F) and 375°C (705°F) for 1 and ½ hr, respectively. These were explained as being more reactive areas on the steel base, where iron-zinc alloy growth was more rapid when once initiated.

This lack of experimental or "case history" data, especially with respect to long-term performance, prompted the present investigation. It involved laboratory heating experiments on commercial strip over a wide range of time-temperature conditions. Material behavior was principally evaluated by study of the rate and mode of coating and steel base deterioration. The investigation was carried out with the active cooperation and assistance of the Canadian Zinc and Lead Research Organization and the International Lead Zinc Research Organization, Inc.

Experimental Materials and Procedure

The 24-gauge (0.025-in.) strip tested was standard commercial stock with a 1.4-oz/ft² coating made on an "out-of-line" anneal system. The coating contained 0.25% Al, 0.23% Pb, and 0.34% Fe (75 mg/ft² surface). The steel substrate composition was: 0.032% C, 0.01% P, 0.027% S, 0.33% Mn, and 0.002% Si. A representative cross section illustrated in Fig. 1 shows that the coating was composed substantially of zinc, bonded to the steel by a thin interface layer of iron-zinc alloy. The surface appearance was also characteristic and showed a uniform pattern of small, polygonal, spangle grains varying in reflectivity in the usual manner.

Following preliminary tests at 150°C (300°F) which yielded no significant effects, the heat-treatment program detailed in Table I was carried out. As indicated, panels (4 × 6 in.) were subjected to air-atmosphere heating for varying periods at six temperatures in the range 200°-400°C (390°-750°F). The panels were degreased and racked vertically about ½ in. apart in forced-air convection ovens. Duplicate panels were removed for inspection and testing at the scheduled intervals shown, giving maximum exposures of 20, 12, and 4 weeks, respectively, at the two low, two intermediate, and two high temperatures.

The continuous-exposure program was supplemented by thermal cycling tests at 200°, 250°, and 300°C (390°, 480°, 570°F). This involved removal of racked panels from the oven for air cooling to room temperature three times per working day. Time and oven capacity limitations prevented extension of this series to other temperatures.

The influence of heating was evaluated by surface inspection, coating-weight and iron-content determinations, metallographic examination, and by tensile

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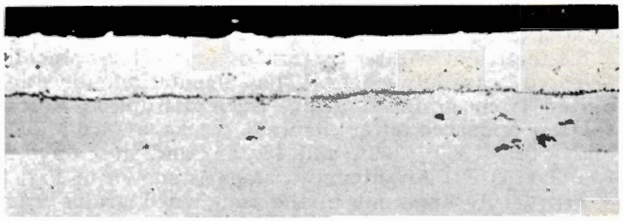

Fig. 1. Microstructure of as-galvanized strip. X250

Table I. Experimental program

exposure	Exposure temp °C	°F	Maximum exposure, weeks	Sampling, *etc.*
Continuous	200	390	20	2 panels removed for testing every 2 weeks.
Cycled	200	390	20	Panels air cooled to ambient 3 times per working day. Sampling as for cont. exposure.
Continuous	250	480	20	2 panels removed for testing every 2 weeks.
Cycled	250	480	20	Panels air cooled to ambient 3 times per working day. Sampling as for cont. exposure.
Continuous	300	570	12	2 panels removed for testing daily in 1st week, weekly to 8 weeks, and every 2 weeks thereafter.
Cycled	300	570	12	Panels air cooled to ambient 3 times per working day. Sampling as for cont. exposure.
Continuous	335	635	12	2 panels removed for testing daily in 1st week, weekly to 8 weeks, and every 2 weeks thereafter.
Continuous	365	690	4	2 panels removed for testing at 2, 4, 6, 8, 10, and 16 hr, daily in 1st week, and every 2 or 3 days thereafter.
Continuous	400	750	4	2 panels removed for testing at 1, 2, 4, 8, 12, and 16 hr, daily in 1st week, and every 2 or 3 days thereafter.

tests on the steel base. For the stripping measurements, uninhibited 20% HCl acid solution was used, thereby simplifying the titration for iron. One surface only was stripped so as to reduce the effect of inherent coating-thickness variations found on opposite sides of the strip. The same surface was treated as far as identification of the original stock would permit. Tensile pieces were cut parallel to the strip-rolling direction and, just prior to testing, the coating was stripped in standard $SbCl_3$-inhibited HCl acid solution. Metallographic etchants based on those developed by Rowland (4) were used to reproduce microstructural effects.

Results

Typical surface and microstructural effects are reproduced in Fig. 2-7. Least-square fits for the iron-content determinations and the tensile tests were computed and are plotted in Fig. 8-11. Coating-weight measurements were not similarly treated because consistent trends were not defined. This was not unexpected in view of the nature and mode of coating deterioration, and which also accounts in large measure for the scatter in some of the plotted results. It is to be noted that the fitted curves combine the results for both continuous and thermal cycling tests. This treatment was justified for the reason given below.

Surface Effects Due to Thermal Cycling.—The thermal cycling tests defined in Table I indicate that the cycling treatment was applicable for less than ¼ of the total exposure time. This limitation was reflected in the similar response of continuous and cycled samples, except for the surface phenomena described below. These represent the only distinction made between the continuous and thermal cycling results.

An early surface change was a well-defined brightening of random grains contained within, or separate from, spangle formations. The increased reflectivity was related to a heavily roughened texture which showed a distinctive wavelike pattern of crystallographically oriented parallel ridges. The orientation direction varied from grain to grain. Such disruption of the surface appeared after about 2 weeks at 150°, 200°, and 250°C (300°, 390°, and 480°F), and in 2 days at 300°C (750°F). An advanced stage is shown in Fig. 2.

Frequently apparent in the roughened grains were parallel cleavage cracks which were always aligned with the ridges and defined the crystallographic orientation more precisely. In cross section, these appeared as sharp V-shaped breaks penetrating through the zinc layer to the steel base. An associated effect was

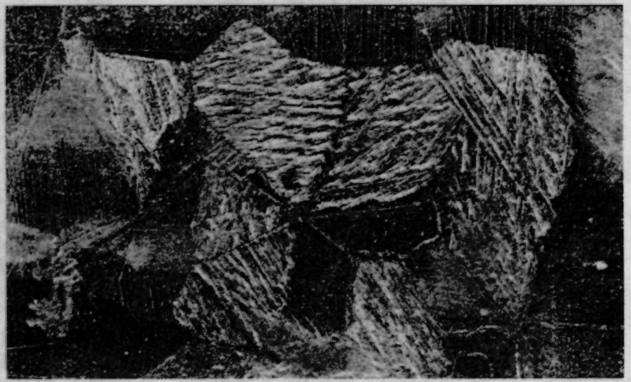

Fig. 2. Crystallographically oriented wrinkling deformation, cleavage cracking and slip lines, and grain boundary separation produced by thermal cycling for 20 weeks at 250°C (480°F). X30.

the development of pronounced gaps around the grain boundaries (Fig. 2). Also observed on the surface of otherwise unaffected grains were fine parallel striations, indicative of crystallographic slip. Of significance is that the slip lines continued across the grains to the grain boundaries.

It is well known that zinc exhibits marked anisotropy in thermal expansion and other physical properties because of its hexagonal crystal structure. Boas and Honeycombe (5) have shown that this inherent property also accounts for plastic deformation by slip, twinning, and surface rumpling which they observed in thermal cycling tests on bulk samples of pure zinc. The same phenomena would appear to be confirmed in the present case with, however, more advanced deformation being indicated by the cleavage cracking and the grain-boundary separation found. These were presumably partly affected by the thin nature of the zinc coating. Also, the restraint imposed by the attachment to the steel base, with its different expansion characteristics, would have to be involved. Detailed study of the above phenomena was beyond the scope of this investigation. However, there was no evidence that they were detrimental as far as flaking and separation of the outer zinc layer, or of the coating as a whole, were concerned.

Exposure at 200°C (390°F).—The original spangled appearance of the galvanized coating was retained throughout the full 20-week exposure period at 200°C (390°F), although with some loss in reflectivity because of oxidation. A more obvious reaction effect, confirmed by touch and low-power macroexamination, was the occurrence of scattered small protrusions, better described as pimples, after 6-week exposure. The number formed increased with time but, even at 20 weeks, they were barely discernible with the naked eye. As described and illustrated in exaggerated form later, the pimples represented sites of locally-developed mounds of iron-zinc alloy which eventually punctured through the zinc layer.

Metallographically, the coatings in this series were unaffected except for the local growths which were hard to find, being widely scattered and of a small size. The good performance of the strip at this temperature was further defined by the negligible changes in both the iron content of the coating (Fig. 8) and the tensile properties of the steel base (Fig. 9-11).

It should be noted that at all temperatures, one and sometimes both sides of random panels showed haphazard development of local disruptions, frequently much larger than the characteristic pimples. These occurred in irregular colonies or in string-of-beads formation, and occasionally in bands of variable width densely covered by pimples. This abnormal iron-zinc alloying activity was related to imperfections such as inclusions, seams, and laminations at the steel surface, or to scraping abuse of the surface, before galvanizing. These were assumed to be peculiar to the particular batch of material tested and were avoided as far as possible in sampling and evaluation.

Exposure at 250°C (480°F).—Pimple growths were distinctly visible after 2 weeks at 250°C (480°F), but even at 20 weeks the growths were still small and the closest spacing was about ¼ in. Most of the surface was thus unaffected except for slight oxidation.

The coating microstructures reflected the increased incidence of local pimple disruption, but the fringe layer of iron-zinc alloy between the growths was unchanged. The coating as a whole remained firmly adherent for the full 20-week period. Also, as indicated in Fig. 8-11, neither the measurement of iron-zinc alloying activity nor the tensile properties of the steel base were significantly altered.

Exposure at 300°C (570°F).—Deterioration of the coating was markedly accelerated at 300°C (570°F). Small pimples appeared in the first day and new outbursts formed rapidly with time. At 6 weeks, the disrupted surface had a uniform, frosty texture which obscured the original spangle finish. No undisturbed areas remained at 8 weeks and, because the growths tended to reach a small limiting size, the coating at this stage had a fine sandpaperlike finish. Prolonging the exposure to 12 weeks produced little further change. There was, again, no evidence of adherence deterioration. Indicative of the higher reaction rate at this temperature is the panel in Fig. 3 which was heated for 1 week. The prominent bands of densely packed pimples represent areas of pregalvanizing abuse of the steel surface referred to earlier.

The microstructure in Fig. 4(*a*) shows an early stage in pimple growth, with the surrounding zinc still in contact. In Fig. 4(*b*), the marked growth after heating for 1 week suggests that most of the underlying zinc was initially consumed by reaction and this was followed by sudden and complete separation of the zinc enclosing the expanding alloy mound. In the process, the thin zinc layer at the crown was punctured and the unreacted zinc around the base of each growth was torn out of contact with the steel surface. From the etching behavior and microhardness measurements, the principal constituent of the growths at this stage was indicated to be the zeta phase. The characteristic penetration into the steel base on a convex front can also be noted.

A group of outbursts showing variable development after 2-week exposure is illustrated in Fig. 4(*c*). The zeta phase has now been consumed, and advanced growth of the higher-iron-alloy phases is apparent, as well as initiation of breakup in the pimple crowns. The fragmentation appeared to be related to reaction depletion of zinc in the low-iron-content "palisade" portion of the delta-prime phase (6,7) that formed the outer crown. Such breakup was usually combined with marked gamma-phase growth which suggests a rapid inward diffusion of zinc. With more prolonged heating, the pronounced reaction effects shown in Fig. 4(*d*) were found. At this stage, the growths consisted almost entirely of the gamma phase with fragmented particles of an unidentified phase distributed at and near the steel surface. This unidentified phase also enclosed individual grains from the steel base which had been undermined by the extensive intergranular penetration shown. This phase is of practical interest since it is apparently directly involved in the steel penetration process and, according to electron probe analysis on more massive formations, has an iron content of the order of 30%. This

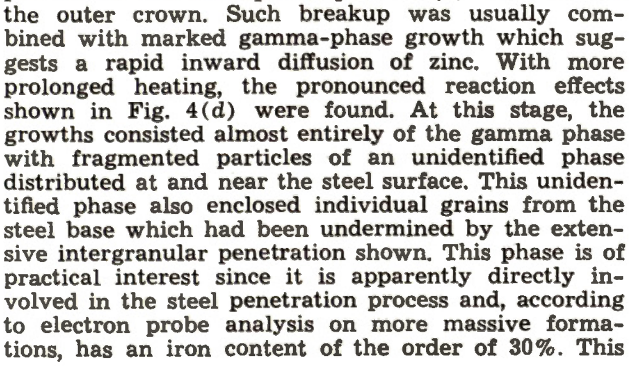

Fig. 3. Surface of panel heated for 1 week at 300°C (570°F). X1

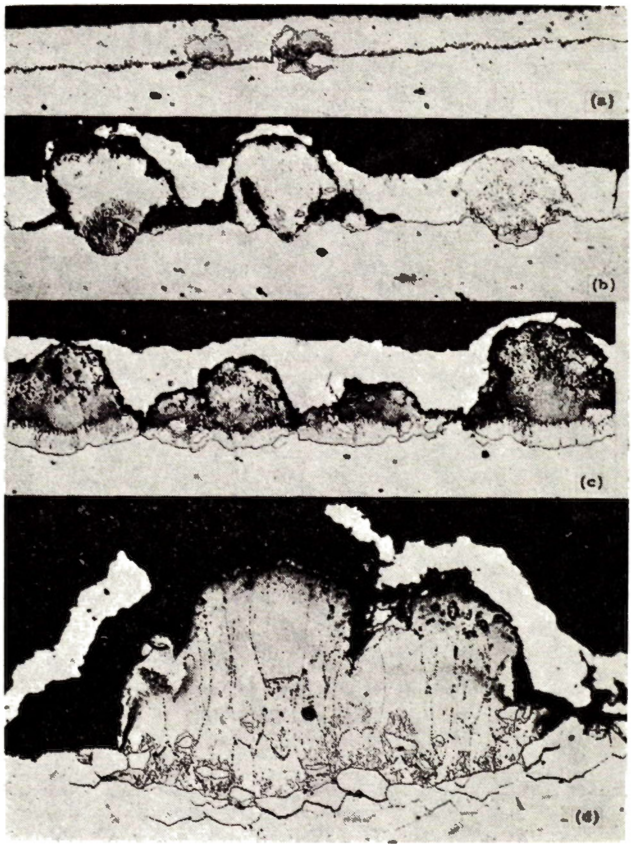

Fig. 4. Typical coating microstructures for periods indicated at 300°C (570°F). X250. (*a*) 2 days, (*b*) 1 week, (*c*) 2 weeks, (*d*) 12 weeks.

exceeds the maximum of 28% Fe for the gamma phase given in the accepted Fe-Zn equilibrium diagram.

Another feature of interest in Fig. 4(*d*) is the beadlike network of particles which shows a correspondence with the steel grain structure. These are most likely inclusions and/or carbides which, being nonreactive with zinc, are fragmented and distributed in the growth according to their prior location in the steel base, and to the rate of dissolution of the steel.

Confirmation of the higher reaction rate at 300°C (570°F) is provided by the relevant iron curve in Fig. 8. The increase with time was very rapid and tapered off in the later stages in a parabolic manner to a final gross value of 3000 mg/ft^2. Significant reductions in the tensile and yield strengths were also apparent, amounting to total drops of about 5000 and 7000 psi, respectively, after 12-week exposure (Fig. 9 and 10). The elongation, on the other hand, remained at a uniform level exceeding the original value (Fig. 11).

Exposure at 335°C (635°F).—General deterioration at 335°C (635°F) followed the pattern developed at 300°C (570°F) but at a considerably more accelerated rate. The coating was extensively covered by small pimples after only 12 hr, and within 5 days the characteristic frosty texture largely masked the spangle pattern. At 2 weeks, the growths retained their individual identity but were so numerous that the surface was completely blanketed. Essentially no further major change was noted through the remainder of the 12-week period. The extent of disruption on a typical panel is evident in Fig. 5(*b*). Particular attention is drawn to the uniform small size and distribution of the growths.

An important observation with exposures longer than 2 weeks was the lack of adherence of the heavily punctured zinc layer. It was mechanically keyed only and could be readily picked or peeled away as in Fig. 5(*a*). The exposed surface had a dark-gray to

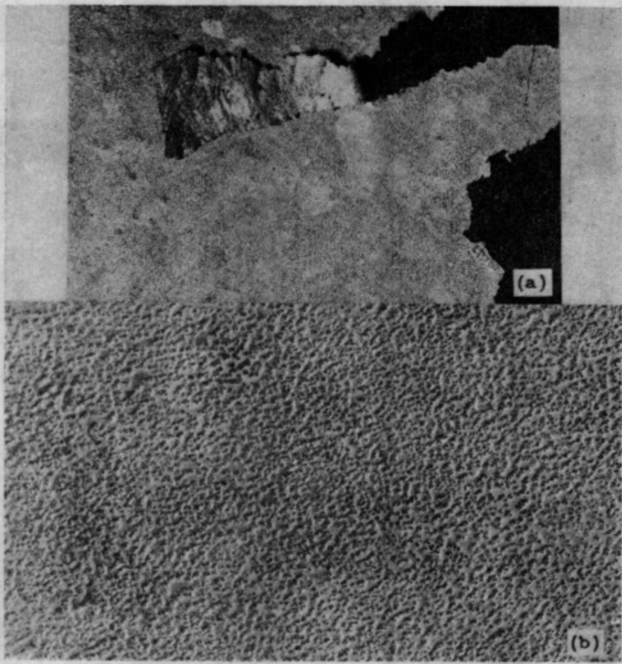

Fig. 5. Poor adherence of zinc layer in (*a*), and coating surface at longer exposure in (*b*), produced by heating at 335°C (635°F): (*a*) 6 weeks, X1; (*b*) 12 weeks, X12.

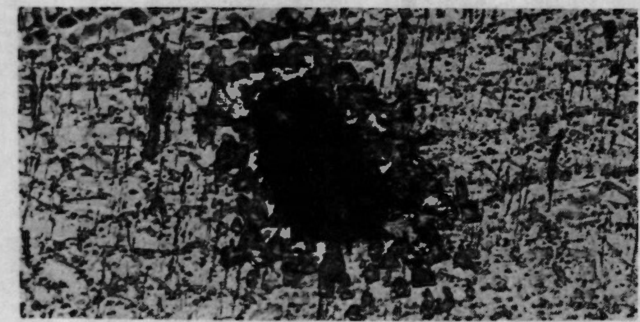

Fig. 6. Pimple growth (dark patch) surrounded by faceted pits on panel heated for 5 weeks at 335°C (635°F). X190.

black appearance, and the mounded growths stood proud of the surface. After acid stripping, shallow depressions at each site indicated the extent of local attack of the steel base.

Another surface feature associated with pimple growth in general was a ring of faceted pits surrounding each site and showing well-defined orientation alignment. A typical formation, and the cross-section angularity of the pits, can be seen in Fig. 6 and 7(*a*), respectively. From evidence in other related studies, the pits cannot be accounted for by oxidation or evaporation effects. The unusual distribution rather suggests that they are diffusion induced, probably by a mechanism involving inward movement of zinc toward the alloy growth and a return migration of crystal lattice vacancies to the surface acting as a sink.

The metallographic effects found at 300°C (570°F) were reproduced at 335°C (635°F), but in much more exaggerated form for equivalent times. The same sequence of coating deterioration was observed, but lateral spreading of the pimples, puncturing, and breakup of the outer zinc layer, and intergranular penetration of the steel base were all much more pronounced, as shown by Fig. 7(*a*). With respect to steel base attack, maximum penetration in this series was generally confined to a layer several grains deep. However, it was not uncommon to find single cracks penetrating to a depth of about 10% of the total sheet thickness with exposures exceeding 6 weeks. Figure 7(*a*) shows particularly good definition of the unidentified high-iron phase (dark etching) involved in pene-

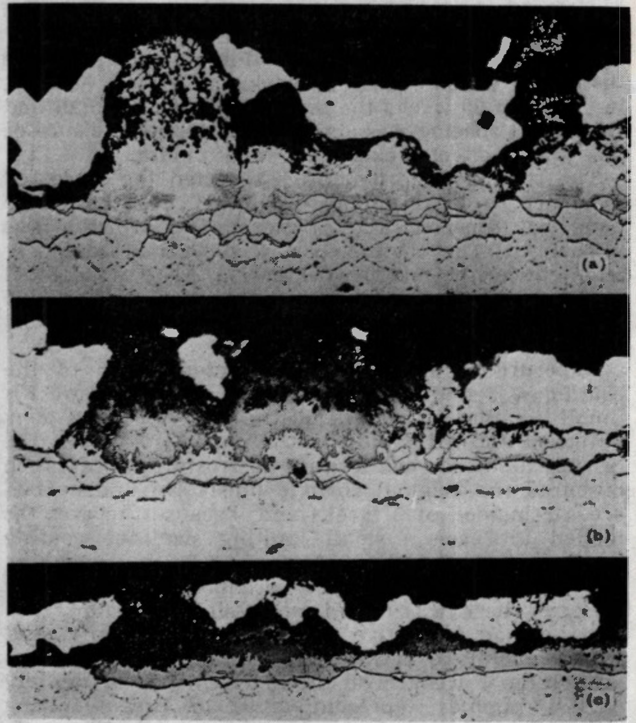

Fig. 7. Typical coating microstructures for time-temperature conditions indicated. X250. (*a*) 12 weeks at 335°C (635°F), (*b*) 3 weeks at 365°C (690°F), (*c*) 1 day at 400°C (750°F).

tration of the steel base, which was referred to in the previous section.

The extent of deterioration at this temperature was further substantiated by a very rapid parabolic buildup of iron in the coatings to a high level (Figure 8), and by marked reductions in tensile properties of the steel base. The yield strength (Fig. 10) was less seriously affected than the ultimate tensile strength (Fig. 9), but the elongation (Fig. 11) was drastically reduced in the later stages of the 12-week test period. Of practical interest is the sudden drop in these latter properties after 4 weeks. This must represent the development of intergranular penetration of the steel base to a critical limit at this temperature.

Exposure at 365°C (690°F) and 400°C (750°F).— Heating at these high temperatures was clearly beyond the practical limit, as suggested by the rapidity and extent of coating deterioration at a very early stage. At 365°C (690°F), small pimples covered the surface within 2 hr and the transition to a disrupted dull-gray oxidized finish was complete in 16 hr. This appearance was retained with little further change for the 4-week test period. The outer zinc layer could be picked away after 3 days.

At 400°C (750°F), the above effects were repeated at a still faster rate, and the final appearance after 4 weeks was much the same as that achieved within 4-5 hr. The zinc layer could be spalled off after 16 hr. At this high temperature, a very small pimple size and a smooth surface finish were retained throughout and were distinguishing features of significance with respect to steel-base deterioration discussed later.

Metallographic examination of the coatings heated at 365°C (690°F) revealed that the localized nature of pimple growth was retained but was combined with considerable lateral spreading and coalescence of the individual bursts. Comparison of the typical area in Fig. 7(*b*) with Fig. 7(*a*) suggests that the deterioration produced was not unlike that found with the lengthier exposure at 335°C (635°F). The pronounced intergranular penetration of the steel base in both cases is well defined.

At 400°C (750°F) on the other hand, the coating microstructures were highlighted by limited vertical

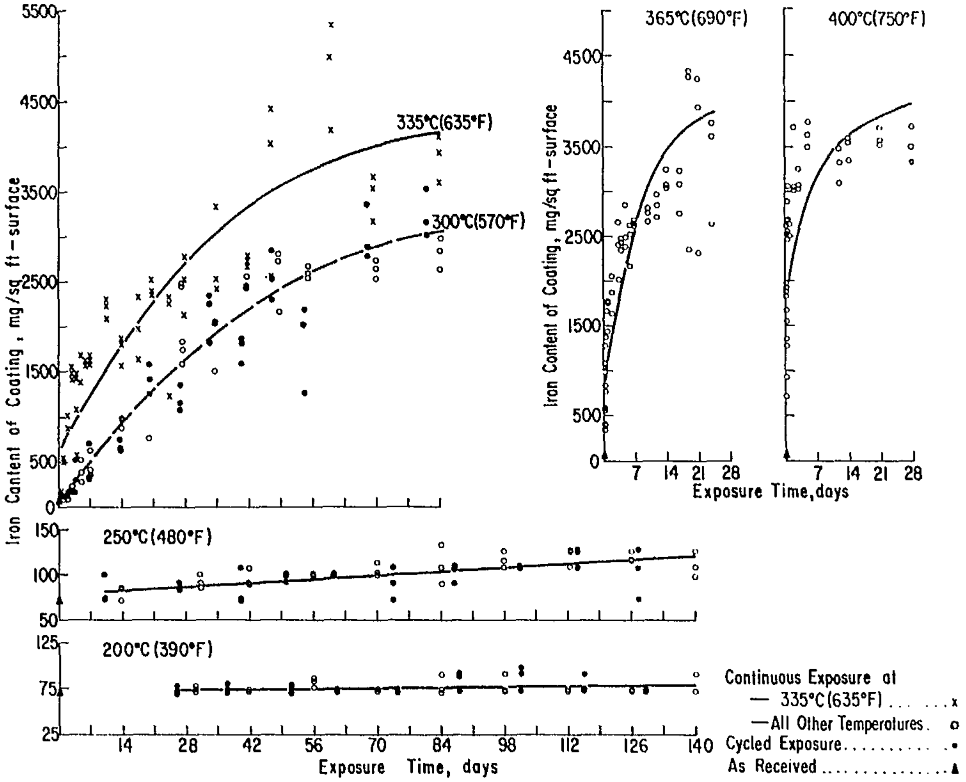

Fig. 8. Iron content of coating vs. exposure time. Note different ordinate scales at and above 300°C (570°F).

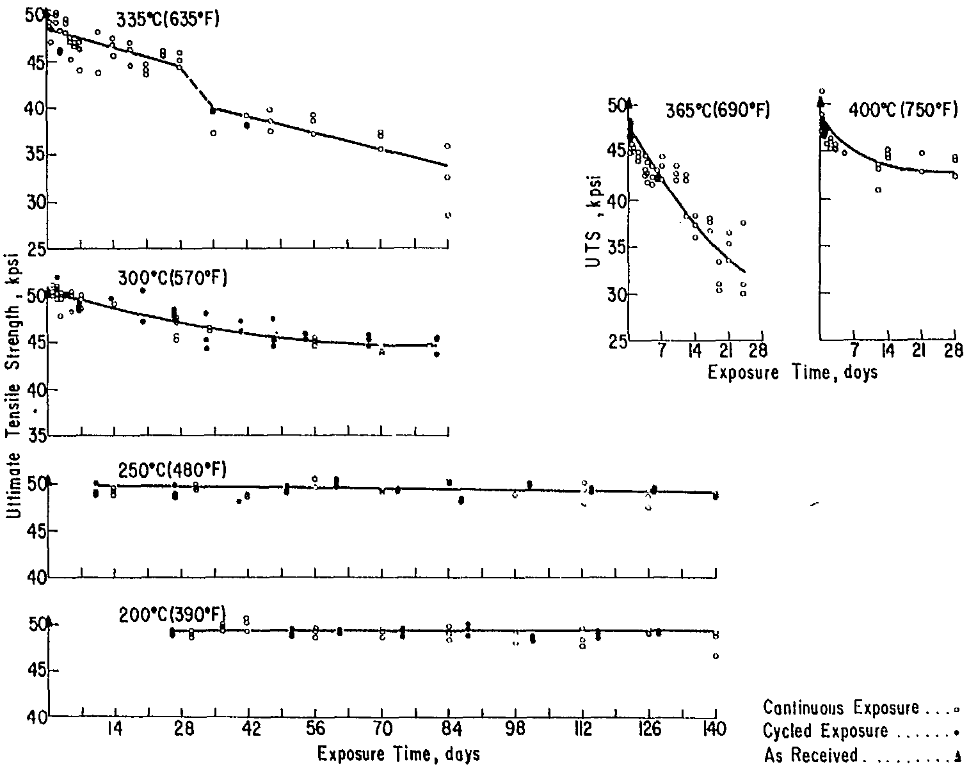

Fig. 9. Ultimate tensile strength of steel base vs. exposure time.

growth of the pimples. Lateral spreading and merging were very rapid and resulted in extensive area coverage of the steel surface. A thick and relatively uniform layer of the gamma iron-zinc phase was continuous over large areas and was the major constituent as illustrated in Fig. 7(*c*). Of particular note is that intergranular penetration of the steel base was conspicuously less pronounced in such reaction areas.

The gross buildup of iron at both temperatures can be seen in Fig. 8. Scatter of the results at longer exposures is again evident but is not unusual in view of the nature of the iron-zinc reaction effects noted above.

With respect to steel base properties, Fig. 9 and 10 show that the ultimate tensile strength and yield strength at 365°C (690°F) were appreciably lowered to approx 2/3 of the original values through the 4-week exposure period. However, the extent of embrittlement damage was more strikingly reflected in the elongation which dropped to a very low value (Fig. 11). Although not defined by the fitted curves, the individual points plotted again indicate a sudden

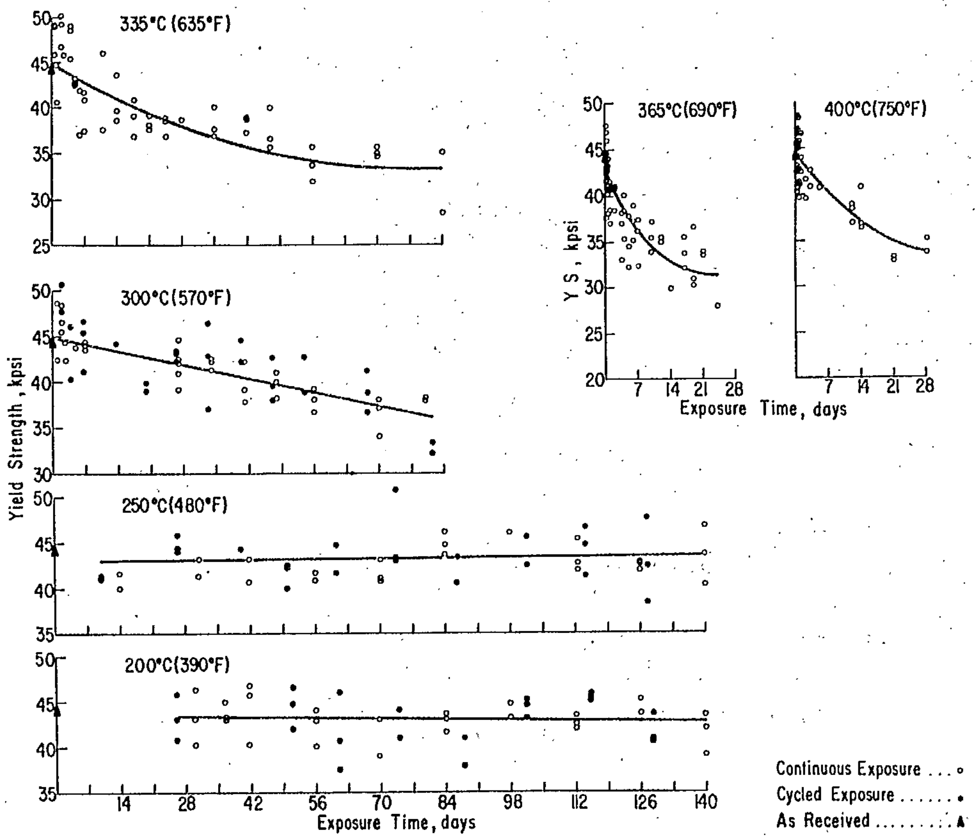

Fig. 10. Yield strength of steel base vs. exposure time.

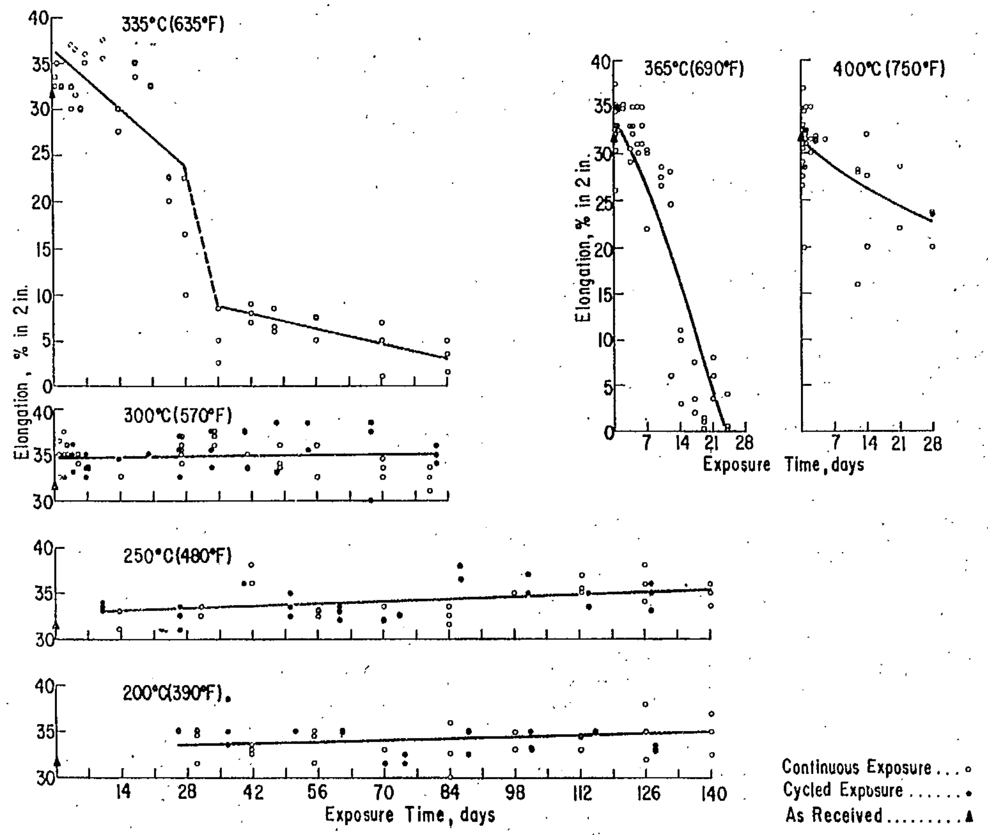

Fig. 11. Elongation of steel base vs. exposure time.

reduction in both the ultimate tensile strength and elongation after 2 weeks, in much the same manner as found at 335°C (635°F).

In marked contrast, the deterioration in properties at 400°C (750°F) was less drastic, particularly with respect to the ultimate tensile strength and elongation. The better resistance to heating embrittlement was apparently related to the development of iron-zinc alloy on a broad front over the surface as described above. It is not known to what extent the formation of a more or less continuous, thick, gamma-phase layer was instrumental in restricting intergranular penetration and consequent embrittlement. However, a well-defined relationship was indicated.

Summary and Conclusions

The foregoing experiments established that continuous-strip galvanized coatings of the type tested undergo various forms and degrees of deterioration in air-atmosphere, elevated-temperature exposure. The nature and mode of deterioration were determined by the conditions of exposure.

Thermal cycling exposure in the range 150°-300°C (300°-570°F) tended to induce plastic deformation mechanisms in the zinc layer which resulted in wrinkling disruption of the surface, failure by cleavage cracking, and loss in grain-boundary cohesion. For the range of conditions investigated, the degree of these forms of damage found was not indicated to be detrimental to the adherence of the zinc layer or of the coating as a whole.

The principal failure mechanism for both continuous and cycling conditions of exposure was by development of locally growing iron-zinc alloy outbursts. Rapid diffusion growth of the mounded forms resulted in puncturing and breakup of the zinc layer. At the same time, penetration into the steel base occurred on a convex front initially, and intergranularly at a later stage. The rate of nucleation and growth of the reaction sites was time- and temperature-dependent and, in advanced stages of development, adherence of the remaining outer zinc layer was destroyed, permitting it to be peeled or picked away. Further deterioration was represented by severe steel base penetration and embrittlement.

The strip product tested showed good resistance to the above deterioration mechanisms on exposure for up to 20 weeks at temperatures at and below 250°C (480°F). The original spangled appearance of the coating was largely unchanged except for small, widely scattered alloy outbursts, the coating remained firmly adherent, and the mechanical properties of the steel base were not detrimentally altered.

At higher temperatures, the material was prone to rapid initiation of numerous reaction growths over the entire surface. The related puncturing and disruption of the zinc layer eventually contributed to complete loss of adherence, permitting the layer to be peeled away. Also, the onset and propagation of steel base intergranular penetration and embrittlement was greatly accelerated at these higher temperatures.

From the results obtained, it is considered that the maximum permissible service temperature for extended use of this particular class of strip is significantly below 300°C (570°F). This is based on the high iron-zinc alloying rate and the change in mechanical properties of the steel base found at this temperature. An actual limiting temperature was not defined but would be above 250°C (480°F). It will be recalled (1) that the industry-recommended maximum for continuous-strip galvanized coatings in general is 290°C (550°F). However, no time limitation is defined.

It is emphasized that the above recommendation is predicated on the experimental performance of the particular batch of material tested. It also involves the acceptability in service use of some degree of local coating disruption after prolonged heating exposure. The extent to which this can be tolerated will depend on coating smoothness requirements and the as-yet unknown influence of such disruptions on the corrosion behavior. The latter was not investigated.

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Any discussion of this paper will appear in a Discussion Section to be published in a forthcoming issue.

REFERENCES

1. K. Oganowski, *Sheet Metal Ind.*, **41**, 675 (1964).
2. C. R. Pipe, Private communication (1960).
3. M. L. Hughes, *J. Iron Steel Inst.*, **166**, 77 (1950).
4. D. H. Rowland, *Trans. Am. Soc. Metals*, **40**, 983 (1948).
5. W. Boas and R. W. K. Honeycombe, *Proc. Roy. Soc.*, **186**, 57 (1946).
6. D. I. Cameron and M. K. Ormay, *Proc. Sixth Intern. Galvanizing Conf. Zinc Development Assoc., London*, 276-311 (1961).
7. G. J. Harvey, *J. Australian Inst. Metals*, **7**, 17 (1962).

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