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*FURTHER SURFACE TREATMENT ASPECTS
IN GALVANIZING IRON SINGLE CRYSTALS*

by

G. E. Ruddie and J. J. Sebisty

Physical Metallurgy Division

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GALVANIZING IRON SINGLE CRYSTALS

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G. E. Ruddie* and J. J. Sebisty*

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ABSTRACT

Hydrogen-atmosphere galvanizing of single-crystal and polycrystal samples of four different types of iron with various surface pretreatments was investigated to more conclusively identify the reaction effects of substrate crystallographic orientation and surface treatment. This work forms part of a broader program, supported by the Canadian Galvanizing Research Association, to investigate the role of various parameters of the steel base in the galvanizing reaction.

A relationship between galvanizing reactivity and iron crystallography was established for only the Cambridge iron containing 0.02% silicon. Electropolished crystals of this material showed unusually high reactivity which varied on the principal low-index surfaces, decreasing in the order (111), (110) and (100). Electropolished samples of Cleveland (Armco), Ferrovac E and enamelling iron galvanized normally, independent of crystallographic orientation.

Reaction on smooth-surfaced crystals generally proceeded in two stages defined by a rate change near the 2.5-min immersion time.

Roughening of the crystal surface by shot blasting reduced the reactivity of the Cambridge iron almost to the level obtained for the "normal" galvanizing materials and largely eliminated the differences related to crystallographic orientation.

In supplementary tests, electropolished and mechanically polished Cambridge (110) crystals showed identical orientation-related reaction behaviour at short, but not at long, immersion times, depending on the method of galvanizing.

X-ray analyses of surface strain in a mechanically polished and hydrogen-annealed Cambridge (110) crystal indicated that no recrystallization had occurred. Thus the crystallographic effect on galvanizing was unchanged.

Variable reaction effects found with the Cambridge iron emphasize the importance of the substrate surface in the galvanizing reaction. The exceptionally high response of specific crystallographic orientations may have possible connection with outbursts of iron-zinc alloy growth which frequently occur in galvanized coatings on commercial steels.

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RÉSUMÉ

RAPPORT R 271 DE RECHERCHE DE LA DIRECTION DES MINES

AUTRES ASPECTS DU TRAITEMENT DE SURFACE DANS

LA GALVANISATION DE CRISTAUX UNIQUES DE FER

par

G.E. Ruddie* et J.J. Sebisty*

On a étudié la galvanisation sous atmosphère d'hydrogène d'échantillons à cristaux uniques et multiples de quatre différents types de fer dont on a traité la surface de diverses façons, afin d'identifier avec plus de précision les effets de réaction de l'orientation cristallographique du substrat et du traitement de surface. Ce travail s'inscrit dans un vaste programme appuyé par la Canadian Galvanizing Research Association et visant à étudier le rôle de divers paramètres de la base d'acier dans la réaction de galvanisation.

On a établi, uniquement pour le fer Cambridge contenant 0.02% de silicium, une relation entre la réactivité de la galvanisation et la cristallographie du fer. Les cristaux de cette substance polis par électrolyse ont présenté une réactivité anormalement élevée qui variait sur les principales surfaces à faible indice, décroissant dans l'ordre (111), (110) et (100). Les échantillons de Cleveland (Armco), de Ferrovac E et de fer à émaillage polis par électrolyse, se sont galvanisés normalement, indépendamment de l'orientation cristallographique.

La réaction sur les cristaux à surface unie se faisait habituellement en deux étapes caractérisées par un changement de taux après 2.5 minutes d'immersion.

L'augmentation de la rugosité de la surface des cristaux par grenaillage réduisait la réactivité du fer Cambridge presque au niveau des substances qui se galvanisent "normalement" et éliminait en grande partie les différences reliées à l'orientation cristallographique.

Lors de tests additionnels, les cristaux de Cambridge (110) polis par électrolyse et par des moyens mécaniques ont démontré la même réaction reliée à l'orientation, mais pendant de courtes périodes d'immersion seulement, selon les méthodes de galvanisation.

Des analyses aux rayons X de la déformation de la surface d'un cristal Cambridge (110) poli mécaniquement et recuit à l'hydrogène, ont démontré qu'il n'y avait pas eu recristallisation. L'effet cristallographique sur la galvanisation n'avait donc pas été modifié.

Les effets variables de réaction observés dans le fer Cambridge soulignent l'importance de la surface du substrat dans la réaction de galvanisation. L'effet particulièrement marquant de certaines orientations cristallographiques peut être relié à la croissance accélérée de l'alliage fer-zinc fréquemment observée dans les revêtements galvanisés d'aciers commerciaux.

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INTRODUCTION

The effects of substrate crystallographic orientation and surface treatment in galvanizing of iron single crystals were previously investigated (1,2) to determine the influence of the physical condition of the iron surface on the kinetics of the galvanizing reaction. Significant differences in reactivity were found on the principal low-index surfaces of electropolished commercial single crystals. The corresponding surfaces of enamelling-iron crystals did not exhibit the same orientation-dependent galvanizing response, but reacted normally for most of the orientations examined, similarly to a polycrystalline sample of the same material. Roughening of the substrate surface, especially by shot blasting, reduced the orientation-related reactivity differences on the commercial crystals. On the other hand, the reactivity was unaffected by the surface work-hardening produced by a mechanical polishing treatment.

The investigation was extended on these and other iron materials of different purity to permit more conclusive identification of the crystallographic-orientation effect and of the alteration of galvanizing reactivity by surface roughening. To explain the minimal effect of surface work-hardening on the orientation-related galvanizing behaviour, as previously demonstrated by electrolytically and mechanically polished commercial crystals, the strain condition of these surfaces was examined by X-ray diffraction analyses.

Galvanizing experiments were done in a hydrogen atmosphere as well as by the conventional open-pot process. Iron single crystals and polycrystals were pretreated by different methods and galvanized in unalloyed zinc baths at 450°C (840°F) over a range of immersion times. Surface pretreatment was done by electro-polishing, mechanical polishing and shot blasting to produce different surface-hardness and roughness conditions.

EXPERIMENTAL PROCEDURE

(a) Materials

Single-crystal and polycrystal samples of iron were obtained from four materials of different purity. These are designated as Cambridge, Cleveland (Armco iron), Ferrovac E and enamelling iron. The chemical compositions are given in Table 1.

Commercial single crystals designated as Cambridge (100) and (110) and Cleveland (111) from the prior studies ^(1,2) were re-used in this investigation. One of the Cambridge (110) crystals was spark-cut along a (111) plane to provide the third of the three principal low-index orientations in this material. Samples of the same three orientations were spark-machined from a new commercial crystal designated as Cleveland A. (Refer to Figures 1 and 2).

Large single-crystal grains of Ferrovac E iron were produced by a cross-rolling strain-annealing process. Details are given in Appendix A. Single crystals with surface orientations (100), (320), near (110) and near (100), as well as polycrystal samples with an average grain diameter of approximately 0.1 mm, were obtained.

Samples of polycrystalline enamelling-iron prepared for the prior work ⁽¹⁾ were also used. These, likewise, had an average grain diameter of approximately 0.1 mm.

(b) Pretreatment

Small crystal samples of the four iron materials were prepared as follows:

1. Elliptical disc-shaped samples were spark-machined from the 0.27-in. (7-mm) diameter Cleveland A crystal as illustrated in Figure 1. Machining along the desired crystallographic planes was accomplished by (i) cementing one end of the crystal rod to a goniometer stage, (ii) orientation of the staged crystal by the Laue X-ray diffraction technique, (iii) transfer of the stage to a spark machining apparatus, and (iv) making a series of cuts through the crystal to produce discs of approximately 0.04 in. (1 mm) thickness. A small suspension hole was drilled in each disc.

The Cleveland (111) crystals were the portions remaining from the original tests ^(1,2).

2. The Cambridge (100) and (110) crystals were the pieces remaining from the original tests ^(1,2). One of the Cambridge (110) crystals was spark-machined along a (111) plane (Figure 2) in the same manner as described above.

3. Polygon-shaped crystal samples were cut from the strain-annealed Ferrovac E iron with a jeweller's saw. These were approximately 0.015 in. (0.4 mm) thick and in areas equivalent to 0.07 in.² (45 mm²) or less. Suspension holes were provided by drilling.
4. The polycrystalline samples of enamelling iron were in the form of rectangular prisms, 0.50 x 0.25-0.50 x 0.035 in. (13 x 6.5-13 x 0.9 mm).

Based on the results of the prior studies (1,2), electro-polishing and shot blasting were used as the principal pre-galvanizing surface treatments. The electropolishing treatment actually consisted of initial levelling by mechanical polishing followed by successive chemical and electrolytic polishings to provide the micro-smooth strain-free surface condition desired (1). The shot-blasting treatment, incorrectly referred to as grit blasting in the previous report (2), was performed as described with 100/230 mesh (149/62 μ) glass beads at a pressure of 90 psi (6×10^5 N/m²) to produce a rough irregular surface.

Talysurf CLA roughness and micro-indentation hardness measurements were made on representative crystals of the Cleveland A and Ferrovac E materials after each surface pretreatment.

For supplementary galvanizing tests to study the effect of surface work-hardening, Cambridge (110) and Cleveland (111) crystals were prefinished by the mechanical polishing procedure

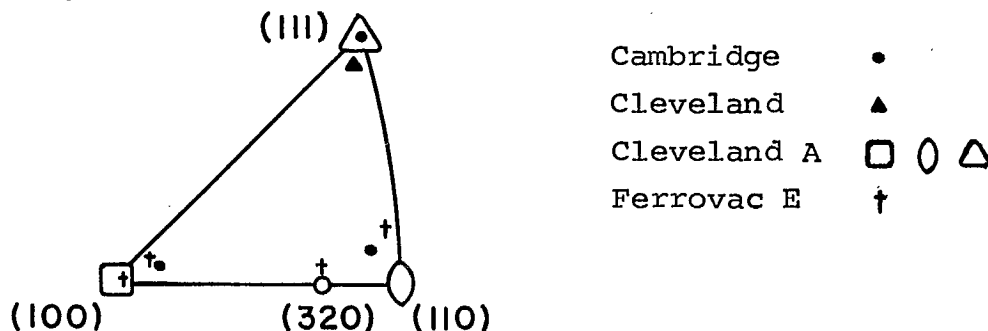
described previously ⁽²⁾. In conjunction with this study, two Cambridge (110) crystals were prepared for X-ray analyses of the surface strain resulting from the pre-galvanizing treatment. One of these was electropolished to provide a relatively unstrained surface. The other was mechanically polished and annealed in purified hydrogen for 3 hr at 400°C (750°F) to produce a surface condition corresponding to that obtained in the hydrogen-atmosphere galvanizing tests. X-ray diffraction line profiles from 2θ , ω and χ scans through the (110) reflection were obtained to measure lattice strain and mosaic angular spread in the prepared surfaces ⁽³⁾. Analyses of the data included correction for the X-ray source, absorption and wave-length contributions.

As part of the hydrogen-atmosphere galvanizing operation, the final pretreatment step entailed reduction of the crystal surface in purified hydrogen at 400°C (750°F) for 2-3 hr to ensure a clean, oxide-free condition. The resulting annealing effect, as shown for example with the mechanically polished surface ⁽²⁾, had caused only a minor decrease in surface hardness. For comparison, some conventional open-pot galvanizing experiments were done to avoid the reduction-anneal pretreatment. The crystals in this case were finally pretreated by pickling for 2 min in a 5% HCl solution at room temperature followed by drying in a warm air-stream. The chloride pickling residue remaining on the surface acted as a fluxing agent and reaction with the zinc bath was initiated within 10 sec after immersion.

(c) Galvanizing Experiments

The bulk of the galvanizing experiments were done in a hydrogen-atmosphere apparatus ⁽¹⁾. Following the pre-galvanizing reduction treatment described in the preceding section, the samples were lowered to the coolest zone in the apparatus chamber, where they were maintained at approximately 175°C (345°F) before immersion in the zinc bath. After withdrawal from the bath, they were returned to this zone and furnace-cooled. A few supplementary tests were made by the conventional open-pot method which involved the mild pickling pretreatment noted in the previous section. The samples were immersed and withdrawn manually and water-quenched immediately after withdrawal. In both series, galvanizing was done in special high-grade (99.99%) zinc baths at $450 \pm 2^\circ\text{C}$ ($840 \pm 4^\circ\text{F}$) for immersion times of 0.25 to 10 min.

The experiments are listed in Table 2. These covered the Cambridge, Cleveland, Cleveland A and Ferrovac E crystals with surface orientations at or near (110), (100) and (111), representing the corner points of the stereographic triangle as shown below. Polycrystalline samples of Ferrovac E and enamelling iron were included for comparison of their galvanizing properties with those of the single crystals in this and the prior investigation ⁽¹⁾.



Evaluation of galvanizing behaviour was made by metallographic examination and iron weight-loss measurements. Established techniques of metallographic sectioning, mounting, polishing and etching were used ⁽¹⁾. Crystal sections required for succeeding experiments were stripped of their zinc coating in a 12.5% HCl solution.

RESULTS

(a) Surface Hardness of Crystals

The results of Knoop and Vickers micro-indentation hardness tests for the Cleveland A (100), (110) and (111), and the Ferrovac E polycrystalline surfaces are presented in Table 3. The hardness of the electropolished Cleveland A surfaces was independent of crystallographic orientation and was of similar magnitude to that found previously for the Cambridge and Cleveland crystals ⁽²⁾. Lower hardness was indicated for the Ferrovac E iron. A marked increase in surface hardness resulted from shot blasting. The values obtained in this and the prior work ⁽²⁾ were of the same order, being independent of crystallographic orientation and type of iron.

It should be noted that with the low load and shallow indenter used in the Knoop tests, the indentation depths were generally equal to or less than the thickness of substrate material consumed in the galvanizing reaction.

(b) Surface Roughness of Crystals

CLA (centre line average) values of surface roughness obtained from Talysurf traces on Cleveland A (100), (110) and (111) surfaces and Ferrovac E polycrystalline samples are given in Table 4. Typical traces are shown in Figure 3. It was observed that the topography of the electropolished surfaces was not accurately reproduced because the diamond stylus tended to gouge and skip over the soft iron surface. The roughness of these surfaces can therefore be assumed to be somewhat less than the tabled value of $18\mu\text{in.}$ ($0.46\mu\text{m}$). Roughness values for the shot-blasted surfaces ranged between 74 and 95 $\mu\text{in.}$ (1.88 and $2.24\mu\text{m}$). This variable response was probably due to the softness of the original iron surfaces and the manual control of the blasting treatment. Topographic features of the Cambridge (110) and (100) and Cleveland (111) crystals with electropolished and shot-blasted surfaces were described in the previous report ⁽²⁾.

(c) Surface Work-hardening Due to Mechanical Polishing

The X-ray diffraction line profile analyses characterized the strains in the Cambridge (110) surfaces by two components, namely, the strains accommodated in the boundaries and those in the interior of the surface subgrains. The corresponding measurements, reported in more detail elsewhere ⁽³⁾, are presented in terms of mosaic angular spread and lattice strain in Tables 5 and 6, respectively. Diffraction from the electropolished surface showed a low degree of lattice strain and a mosaic subgrain

structure which is typical of an annealed crystal. In comparison, the mechanically polished and annealed crystal was characterized by a considerably increased mosaic spread of $\pm 1.16^\circ$ about the mean orientation, confined to a surface layer of less than 5μ , and with a somewhat higher lattice strain. (The difference in lattice strain reported in Table 6 for the two crystal surface treatments was considered to be small). This well-defined and relatively strain-free subgrain structure indicated that the annealed surface had been stress-relieved without recrystallization. Although no analyses were made of a mechanically polished surface before annealing, it is probable that a highly strained and misoriented type of structure constituted the surface deformation layer.

(d) Iron Weight Loss Measurements

Iron weight losses were calculated from the average iron-zinc alloy thickness as measured on representative microsections. An average iron-zinc alloy density of 7.18 g/cc with an average iron content of 7% was assumed. The results are plotted on logarithmic co-ordinates in Figures 4 to 9. For the following discussion of the graphs, it should be noted that "reactivity" is indicated by the magnitude of iron loss for a particular immersion time. The slope of the iron-loss: immersion-time curve represents the "reaction rate" and is defined by the exponent m in the general kinetics relation

$$w = ct^m$$

where the iron loss w is a function of immersion time t , and c is a proportionality constant.

The iron losses on electropolished and shot-blasted surfaces are shown for the four iron materials in Figures 4 to 7. The curves were plotted by visual fit of the data. Two reaction stages were generally indicated by a rate change near the 2.5-min immersion time. A tabulation of the reaction rates is given below. Electropolished samples of the Cleveland, Ferrovac E and enamelling-iron materials reacted at rates ranging from 0.27 to 0.60 for the shorter immersion times while for the longer times the rates were more constant at 0.56 to 0.60. This behaviour is consistent with the parabolic reaction kinetics ($m \sim 0.5$) usually reported for pure iron at 450°C (840°F) (4). However, the lower rate shown for the Cleveland and enamelling iron at immersion times of less than 2.5 min is similar to the results of other studies (5,6). All three materials exhibited similar reactivities regardless of crystallographic orientation (Figures 4 and 6). The shot-blasted Cleveland crystals (Figure 5) were slightly more reactive at the shorter immersion times and less reactive at the longest time, with reaction rates of 0.26 and 0.35, respectively.

<u>Reaction Rate (m)</u>				
	<u>Electropolished</u>		<u>Shot-blasted</u>	
	<u><2.5 min</u>	<u>>2.5 min</u>	<u><2.5 min</u>	<u>>2.5 min</u>
Cleveland (111)	} 0.34	0.59	0.26	0.35
Cleveland A (111), (110), (100)				
Ferrovac E $\sim(110)$, $\sim(100)$, (100), (320), polycrystal	} 0.60	0.60		
Enamelling-iron polycrystal	0.27	0.56		
Cambridge (111)		0.96		
Cambridge (110)	0.79	0.93	0.32	0.32
Cambridge (100)	0.51	0.20	0.30	0.37

The Cambridge iron was much more reactive than the other materials and the response of the electropolished surfaces varied with crystallographic orientation as shown in Figure 7. Although the reaction rate and the high level of reactivity were indicated to be slightly lower for the (110) orientation than for (111), these characteristics were markedly decreased on (100). Initial and final rates for the latter were 0.51 and 0.20 compared to 0.79 and 0.93 for the (110) orientation. On the shot-blasted surfaces, the reaction behaviour was nearly independent of orientation. The rates were similar to, and the reactivities slightly higher than, those for the shot-blasted Cleveland crystals.

Results of the experiments comparing hydrogen-atmosphere and conventional galvanizing reactions for the four iron materials are given in Figures 8 and 9. Reaction rates for the two processes were generally similar for all materials except the Cambridge iron.

The magnitude of iron losses were only slightly lower for the conventional process except with the mechanically polished Cambridge (110) crystals at the maximum immersion time of 10 min. A pronounced decrease was found in this case as indicated in Figure 9. Possible explanations are discussed later.

(e) Metallographic Observations

Photomicrographs of representative coating microstructures are presented in Figures 10 to 17. Normal coating structures, as commonly found on electrolytic iron and low-carbon steels, were formed on the Cleveland, Ferrovac E and enamelling-iron materials with electropolished surfaces (Figure 10). No significant differences were observed between samples of Cleveland and Ferrovac E iron, regardless of crystallographic orientation. With the electropolished enamelling iron also, the galvanizing characteristics of the polycrystalline material were shown to be identical with most of the single-crystal orientations examined previously ⁽¹⁾ for immersion times up to 2.5 min. (The single exception to be recalled was the (111) surface of enamelling iron which exhibited somewhat higher reactivity than the other five orientations tried). All of the coating structures were generally uniform and compact, consisting of the Γ , δ_1 and ζ iron-zinc alloy layers in sequence from the iron substrate. Rapid ζ growth in the early stages up to about 1 min, and predominant δ_1 growth thereafter, were principal features. Discontinuous formation of Γ was distinguished on only the enamelling-iron coatings.

Representative coatings on the shot-blasted surfaces for the Cleveland and Ferrovac E materials are illustrated in Figure 11. As with the electropolished surfaces, there was no dependence on substrate crystallography. However, the shot-blasting treatment caused changes in the growth rates of individual alloy layers. More rapid and irregular ζ growth occurred during the first minute of the reaction followed by a higher rate of δ_1 growth than for the electropolished surfaces. The increased δ_1 growth and the accompanying reduction in ζ -layer thickness for the 10-min immersion decreased the over-all alloy thickness.

As noted in the last section and from the prior work ^(1,2) for the electropolished Cambridge crystals, unusually high reactivity on the (110) orientation and significantly lower response on (100) was confirmed by the microstructures illustrated in Figure 12. The aggressive attack on (110) was, however, not unique, being duplicated on the (111) orientation as shown in Figure 14. This similarity was further evident from the equivalently high reactivity obtained on surfaces with these orientations forming adjacent faces of the taper crystal in Figure 15 (cf. Figure 2). The coating structures indicated that reactivity decreases in the orientation order (111), (110) and (100). (A different order was reported in the previous work ^(1,2) which involved Cleveland (111) instead of Cambridge (111) crystals). In correspondence with the earlier work, the iron-zinc alloy structures on the Cambridge crystals were composed almost wholly of a thick, compact, fine-grained ζ layer, similar to that on iron-base alloys containing

0.03 - 0.08% Si (7). A distinctly granular ζ -growth habit on the (111) orientation distinguished it from a vertically-striated structure on (110). All coatings featured a very thin δ_1 layer which showed negligible growth for immersion times to 10 min. On the less reactive (100) orientation (Figure 12), the coatings were characterized, particularly at shorter immersion times, by a stratified ζ structure which suggested a periodic variation in the growth rate of this phase. Between 2.5 and 5 min, a distinct rate change in the reaction occurred which was reflected in prominent δ_1 growth. Further formation of ζ was thereby largely stifled and the ζ - δ_1 structure produced was more nearly representative of a normal coating.

Reaction with the shot-blasted Cambridge (110) and (100) surfaces is illustrated by the coatings in Figure 13. Reactivity was dramatically decreased almost to the level exhibited on the similarly-treated Cleveland crystals (Figure 11) so that differences with crystallographic orientation were nearly eliminated. The principal alloy phases, δ_1 and ζ , were present in characteristic uneven formations for all immersion times as shown. As with the Cleveland reaction, irregular ζ growth was most prominent at shorter immersion times, after which this was combined with rapid and equally irregular δ_1 growth.

Coatings produced by hydrogen-atmosphere and conventional galvanizing are compared in Figures 16 and 17. Reaction on the mechanically polished Cambridge (110) surfaces was identical for the two processes up to the 2.5-min immersion. Typically

uniform fine-grained structures showing equivalent thicknesses, and composed almost entirely of ζ , were obtained. The 10-min immersion produced a marked reduction in reactivity with conventional galvanizing, represented in the respective microstructures by a 50% difference in the total iron-zinc alloy thickness. Significant δ_1 growth and reciprocal stifling of ζ between 2.5 and 10 min can be seen (Figure 17). Reaction behaviour on the mechanically polished Cleveland (111) and on the electropolished Ferrovac E and enamelling-iron polycrystalline samples was similar for the two processes. The Ferrovac E coatings indicate the slightly lower reactivity generally observed with these materials when galvanized conventionally.

Figures 12 and 16 illustrate the identical reaction structures obtained by hydrogen-atmosphere galvanizing for the electrolytically and mechanically polished Cambridge (110) surfaces. The degree of deformation in the mechanically polished surface was evidently not sufficient to alter the high reactivity on this orientation.

(f) Summary of Results

Examination of the galvanizing reaction on electropolished single crystals of four different types of iron revealed a dependence on crystallographic orientation with only one of the materials. Normal reaction behaviour was found on all single-crystal and polycrystal samples of Cleveland (Armco), Ferrovac E and enamelling iron (except (111) orientation ⁽¹⁾). The Cambridge iron crystals, on the other hand, exhibited much higher reactivity

which varied with the principal low-index surface orientations, decreasing in the order (111), (110) and (100).

For all four materials, two reaction stages were generally indicated by a rate change near the 2.5-min immersion time.

Surface roughening by shot blasting altered coating formation on the materials otherwise exhibiting normal galvanizing response. It also markedly reduced the reactivity on the Cambridge crystals to lower levels such that differences with orientation were almost eliminated and more nearly normal coating structures were formed.

The "normal" galvanizing materials were slightly less reactive but otherwise responded similarly in the conventional open-pot process as in the hydrogen-atmosphere experiments. Reaction with mechanically polished Cambridge (110) crystals was identical in both processes except for the sharply reduced reactivity with the sample galvanized for 10 min by the open-pot process.

Surface strain analyses of electrolytically and mechanically polished Cambridge (110) crystals indicated that the latter treatment, followed by an anneal in hydrogen, resulted in a more widely misoriented subgranular surface layer without loss of the single-crystalline structure. However, the galvanizing behaviour was identical for both crystals. Even with conventional galvanizing, which avoided the pre-anneal, similar coatings were formed at immersion times up to 2.5 min, although not at 10 min as noted above. Thus, the orientation-dependent reaction was

apparently unaffected by the strain induced by mechanical polishing.

DISCUSSION

The galvanizing responses on the electropolished (111), (110) and (100) Cambridge surfaces must be related to crystallographic orientation. This follows from the fact that a (100) surface spark-cut from a (110) crystal gave the same result as a separate (100) crystal ⁽¹⁾. Therefore, material and processing variables could not have been involved. Similarly, the reaction reproducibility on the (110) as well as (100) orientations after repeated re-galvanizing of the same crystal sections ruled out any homogeneity effect.

The Cambridge coatings were previously interpreted ^(1,2) to indicate a structure-sensitive passage of the reacting elements, most likely an intergranular passage of zinc, through the ζ layer. The ease of zinc movement was presumed to be dependent on the way in which the ζ growth was crystallographically initiated and continued from the iron substrate. An apparent modification in ζ growth was evident in the (100) coatings at intermediate immersion times in the range tried (Figure 12). The stratified appearance of the ζ structure suggested a periodic slowing down of the reaction and therefore of the rapid inward movement of zinc. At the longer immersion times, the stratification disappeared and feeding of the zinc through the ζ layer was apparently reduced as indicated by increased δ_1 and retarded ζ growth.

In contrast to the high orientation dependence of the Cambridge iron, the electropolished low-index surfaces of the Cleveland, Ferrovac E and enamelling-iron ⁽¹⁾ crystals, as well as polycrystalline surfaces of the two latter materials, generally developed normal coating structures with characteristic, layered alloy-growth. For reasons unknown, prominent growth of δ_1 and accompanying retardation of ζ was initiated early in the reaction. This may have been related to prominent physical and chemical inhomogeneities indicated in the Cleveland and enamelling iron by the distribution of insoluble inclusions. However, this reasoning is not consistent with respect to the Ferrovac E iron which appeared to have a more homogeneous impurity distribution, similar to the reactive Cambridge material. On the other hand, the significant content of silicon (0.019%), which distinguished the Cambridge iron from the three other materials, may have in some way made the reaction with zinc more sensitive to the substrate crystallography. Structurally, the thick fine-grained ζ growth on the smooth Cambridge surfaces is similar to that which formed on polycrystalline iron materials containing 0.03-0.08% silicon ⁽⁷⁾.

Surface roughening of the Cambridge crystals by shot blasting effectively altered the growth of the individual alloy layers to more normal proportions and reactivity was reduced almost to that of the Cleveland material. This result is in contrast to increased attack and coating thickness which have usually been reported for roughened polycrystalline surfaces as

referenced elsewhere ⁽²⁾. Recent tests with 0.03 and 0.08% silicon-containing irons ⁽⁸⁾ have also shown reduced reactivity when surfaces were prepared by a similar shot-blasting treatment.

The marked reduction in overall alloy growth on the Cambridge surfaces roughened by shot blasting was hypothetically explained ⁽²⁾ in terms of the growth of ζ by intergranular passage of zinc through this phase. The irregular peak-and-valley contouring of the surface, in combination with the vertical growth habit of the iron-zinc alloy phases, promoted compact growth of the predominant ζ phase in the valleys as well as interference growth of this phase from the closely spaced peaks. Intergranular feeding of zinc would thereby be effectively stifled at an early stage in the reaction. It was suggested that the crystallographic orientation effect would gradually have increasing influence as dissolution levelling of the surface irregularities progressed and more regular vertical alignment of ζ grains was established.

In order to test for this effect, the 2.5-min immersion samples of the shot-blasted Cambridge (110) and (100) crystals were stripped of their coatings and regalvanized in the hydrogen-atmosphere apparatus for the same period of time. In all such tests, initial and regalvanized structures were similar. When it is considered that the irregularities initially present on the shot-blasted surface consisted of valley-to-peak heights as large as 400 $\mu\text{in.}$ (10 μm) (Figure 3), then the average 80 to 120 $\mu\text{in.}$ (2 to 3 μm) of iron consumed in the first 2.5 min would not have reduced the surface contour appreciably. Even with 160 to 200 $\mu\text{in.}$ (4 to 5 μm) of the iron reacted at 10 min, there was no

significant increase in the reaction rate (Figure 7) and no orientation effect was apparent in the microstructures (Figure 13). Furthermore, in view of the irregular coatings still present at 10 min, it must be assumed that much longer immersion times would be required to eliminate the substrate contour effect on iron-zinc alloy formation.

The possible reaction effects of surface deformation due to the shot-blast treatment cannot be disregarded. Impacting by the glass shot would have produced a hardened layer of several microns thickness, although this would have been stress-relieved to some degree by the pre-galvanizing anneal. Nevertheless, until complete levelling is achieved, the irregularly contoured substrate together with the characteristic growth habit of the iron-zinc phases would be the overriding factors determining the uniformity and thickness of the ζ layer. The importance of topography over any work-hardening effects on alloy growth was confirmed in the previous study ⁽²⁾ by the coating structures obtained on strain-free crystal surfaces roughened by a chemical etching pretreatment.

The identical orientation-related response obtained for the mechanically polished as well as the electropolished Cambridge (110) crystals (Figures 16 and 12, respectively), regardless of the surface deformation induced, may be explained by the results of the X-ray strain analyses. These measurements indicated that the mechanically worked surface, after a typical pre-galvanizing anneal (Tables 5 and 6), had undergone stress-relief without recrystallization,

1

which could account for the crystallographic effect on galvanizing being maintained. Moreover, this effect with the Cambridge (110) crystal, for reaction times up to at least 2.5 min, was also obtained by conventional galvanizing (Figure 17) in which there was no preceding anneal. This was, however, not applicable at 10 min, as discussed below.

With the mechanically polished Cambridge (110) crystals, the marked reduction in reactivity indicated for 10 min immersion by the conventional process (Figures 9 and 17) is a notable variation from the corresponding hydrogen-atmosphere galvanizing tests (Figures 9 and 16). A partial explanation for the observed variation is provided by the different cooling conditions involved, namely, by quenching in the conventional process and by furnace cooling in the hydrogen-atmosphere apparatus. The result of the latter would be an effective increase in the reaction time. Moreover, with such a highly reactive substrate, the effect of slow cooling would be proportionately greater at longer immersion times because of the very thick coating formed and the consequent increase in sample bulk.

On the other hand, it is clear from the microstructural evidence in Figures 16 and 17 that the lower Cambridge reactivity with conventional galvanizing was directly related to changes in growth rates of the ζ and δ_1 phases between 2.5 and 10 min. Therefore, one or a combination of the different pretreatment conditions must have been primarily responsible. The difference in sample temperature immediately before immersion, approximately

175°C (345°F) in the hydrogen-atmosphere apparatus and ambient room-temperature with the conventional process, may not have had much effect on the reaction with the small, thin samples used.

Similarly, the mild pickling pretreatment was probably not a major factor. Nevertheless, the samples would have been oxidized to some degree before pickling and the pickling residue depended on to provide a fluxing action may not have been as effective in providing a chemically clean iron surface as the hydrogen reduction. More significant is the deformation due to mechanical polishing. X-ray diffraction analyses were done on annealed samples only and the true strain condition of the unannealed surfaces was not established. Microhardness differences for the respective conditions were indicated to be minor in previous work (2). However, from the conventionally galvanized 10-min coating structure obtained (Figure 17) it is possible that the deformed subsurface state of the unannealed sample may have been principally responsible for promoting δ_1 growth, and reciprocal stifling of ζ , at some time beyond 2.5-min immersion.

The examination of a substrate orientation effect on the galvanizing reaction was of interest with regard to the possibility of developing improved galvanized coatings on sheet steel. The reactions with the Cleveland (Armco), Ferrovac E and enamelling-iron materials in this study have shown no variation with substrate orientation, but have been generally similar to those commonly found with low-carbon mild steels. On the other hand, the unusually high reactivity found with specific orientations of the Cambridge iron suggests that there may be a possible connection

with anomalous local reaction effects which occur in continuous-strip coatings and more frequently in conventionally galvanized coatings where longer immersion times are involved. However, more extensive study is needed on a wider range of materials to show that an effect of practical significance does exist. Anomalies found in this investigation highlight the importance of the surface layers in the galvanizing reaction.

CONCLUSIONS

Cleveland (Armco), Ferrovac E and enamelling iron with electropolished surfaces galvanize normally, independent of crystallographic orientation.

Electropolished Cambridge iron crystals containing 0.02% silicon have higher reactivities which vary significantly with the principal low-index surface orientations, decreasing in the order (111), (110) and (100). The characteristics of the predominant ζ iron-zinc layer in the coatings suggest a crystallographic effect of the substrate on the nucleation and growth mode of this phase.

All four iron materials tend to react in two stages defined by a rate change, usually an increase, near the 2.5-min immersion time. The "normal" galvanizing materials generally do not attain parabolic reaction kinetics before 2.5 min.

Roughening of the iron surface by shot blasting effectively reduces the reactivity of the Cambridge crystals almost to that of the "normal" galvanizing materials and more normal proportions

of the iron-zinc phases are formed. Differences of reactivity with crystallographic orientation are almost eliminated by this treatment.

Reaction with mechanically polished Cambridge (110) crystals is identical for immersion times up to 2.5 min when galvanizing is done in either a hydrogen-atmosphere or by the conventional open-pot process. However, coating thickness is significantly reduced with 10-min immersion by the conventional method.

Electropolished and mechanically polished Cambridge crystals galvanize identically in the hydrogen-atmosphere process. The cold-worked surface layer produced by the latter treatment undergoes stress-relief without recrystallization in the pre-galvanizing anneal and the crystallographic effect on galvanizing is thereby maintained.

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REFERENCES

1. Ruddle, G.E. and Sebisty, J.J. (1972), Mines Branch Research Report R247, Department of Energy, Mines and Resources, Ottawa.
2. Ruddle, G.E. and Sebisty, J.J. (1972), Mines Branch Research Report R258, Department of Energy, Mines and Resources, Ottawa.
3. Mitchell, C.M. (1973), Physical Metallurgy Division Internal Report PM-T-73-5, Mines Branch, Department of Energy, Mines and Resources, Ottawa.

4. Hershman, A.A. (1969), Proc. Eighth International Conf. on Hot-Dip Galvanizing (London), London, Industrial Newspapers Ltd., pp. 3-29.
5. Blickwede, D.J. (1953), J. of Metals 5, 807.
6. Guttman, H. and Niessen, P. (1972), Can. Met. Quarterly 11, 609.
7. Sebisty, J.J. and Ruddie, G.E. (1972), Mines Branch Research Report R255, Department of Energy, Mines and Resources, Ottawa.
8. Sebisty, J.J. (1973), Physical Metallurgy Division Internal Reports PM-R-73-5 and PM-R-73-10, Mines Branch, Department of Energy, Mines and Resources, Ottawa.
9. Stein, D.F. and Low, Jr., J.R. (1961), Trans. Met. Soc. AIME 221, 744.
10. Keh, A.S. (1965), Phil. Mag. 12, 9.
11. Packwood, R.H. (Jan. 1973), private communication.
12. Takeuchi, T. (1966), Trans. Nat. Res. Inst. for Metals 8, 1.
13. Kranzlein, H.H., Burton, M.S. and Smith, G.V. (1968), Mem. Sci. Rev. Metallurg. 65, 361.

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TABLE 1

Chemical Composition of Iron Crystals

Element (%)	Cambridge Crystals (110), (100)†	Cleveland Crystals (111), A(110), A(100), A(111)†	Ferrovac E Iron ††	Enamelling Iron ††
C	.005	.012	.004*	<.01
Mn	.03	.017	<.025	.295
Si	.03	Trace	<.005	<.005
	.019**	<.001**		.014***
P		.005	<.002	.010
S		.025	<.005	.018
Al			<.005	.005
Ni			.020	.038
Cr	.03		<.005	.021
Sn			<.002	.018
Cu			<.005	.040
Mo			<.005	.017
Others	<.01		<.016	
Fe(by diff.)	99.91	99.94	99.90	99.51

† Suppliers' analyses.

†† Quantometer analyses of stock material.

* Conductometric carbon determination.

** DC arc spectrographic determination (National Research Council, Ottawa)

*** Modified quantometer analyses on crystal samples (solution method).

TABLE 2

Galvanizing Experiments

Run and Sample No.	Crystal Sample Data			Galvanizing	
	Material	Orientation	Surface Treatment*	Temp. °C (°F)	Time (min)
102 (1A, 2A, 3A, 5A) (7A, 8A, 9A, 11A) (13A, 14A, 15A, 17A) (19F, 20F)	Cleveland A Cleveland A Cleveland A Ferrovac E	(110) (100) (111) 9° off (110), 7° off (100)	mp, cp (2 hr), ep (4 min)	450 (840)	$\frac{1}{2}$, 1, 2 $\frac{1}{2}$, 10 $\frac{1}{2}$, 1, 2 $\frac{1}{2}$, 10 $\frac{1}{2}$, 1, 2 $\frac{1}{2}$, 10 2 $\frac{1}{2}$, 2 $\frac{1}{2}$
103 (6A, 4A) (12A, 10A) (18A, 16A) (2, 1) (8, 7) (15, 14)	Cleveland A Cleveland A Cleveland A Cambridge Cambridge Cleveland	(110) (100) (111) 7° off (110) 8° off (100) 1 to 7° off (111)	mp, cp (2 hr), ep (4 min)	448 (840)	1, 5 1, 5 1, 5 5, 10 5, 10 5, 10
104 (1A, 2A) (7A, 8A) (13A, 14A) (18A) (3A, 9A, 15A) (2) (15)	Cleveland A Cleveland A Cleveland A Cleveland A Cleveland A Cambridge Cleveland	(110) (100) (111) (110), (100), (111) 7° off (110) 1 to 7° off (111)	sb (5 sec) repeat of sample 103-18A as stripped (from run 102) sb (5 sec)	450 (840)	$\frac{1}{2}$, 1 $\frac{1}{2}$, 1 $\frac{1}{2}$, 1 1 2 $\frac{1}{2}$, 2 $\frac{1}{2}$, 2 $\frac{1}{2}$ 5 5
105 (6A, 3A, 4A) (12A, 9A, 10A) (18A, 15A, 16A) (3) (9, 8) (16) (19F, 20F) (21F, 22F) (23F)	Cleveland A Cleveland A Cleveland A Cambridge Cambridge Cleveland Ferrovac E Ferrovac E Ferrovac E	(110) (100) (111) 7° off (110) 8° off (100) 1 to 7° off (111) 9° off (110), 7° off (100) 3° off (320), 2° off (100) polycrystalline	sb (5 sec) mp, cp (2 hr), ep (4 min)	449 (840)	1, 2 $\frac{1}{2}$, 5 1, 2 $\frac{1}{2}$, 5 1, 2 $\frac{1}{2}$, 5 2 $\frac{1}{2}$ 2 $\frac{1}{2}$, 5 2 $\frac{1}{2}$ 2 $\frac{1}{2}$, 2 $\frac{1}{2}$ 2 $\frac{1}{2}$, 2 $\frac{1}{2}$ 2 $\frac{1}{2}$

TABLE 2 (cont'd.)

Galvanizing Experiments

Run and Sample No.	Crystal Sample Data			Galvanizing	
	Material	Orientation	Surface Treatment*	Temp. °C (°F)	Time (min)
106 (3A,9A,15A) (5A,11A,17A) (1, 7) (3,9) (14) (16) (61,62) (21F,22F) (23F)	Cleveland A	(110),(100),(111)	as stripped (from run 105) sb(5 sec)	450 (840)	2½, 2½, 2½ 10, 10, 10
	Cambridge	7° off(110),8° off(100)			10, 10
	Cleveland	1 to 7° off (111)	as stripped (from run 105) sb(5 sec)		2½, 2½ 10
	Cambridge	(111)	as stripped (from run 105) mp,cp(1 hr),ep(5 min)		2½ 3½, 3½
	Ferrovac E	3° off(230),2° off (100)	sb(5 sec)		2½, 2½
	Ferrovac E	polycrystalline			2½
107 (2) (3) (61,62) (24F,25F) (26F,27F) (28F,29F) (30F, 31F) (32E,33E)	Cambridge	7° off (110)	sb(5 sec) mp	450 (840)	5 10
	Cambridge	(111)	ep(3 min)		2½, 10
	Ferrovac E	9° off (110)	mp,cp(1 hr),ep(5 min)		1, 10
	Ferrovac E	7° off (100)			1, 10
	Ferrovac E	2° off (100)			1, 10
	Ferrovac E	polycrystalline			1, 10
	Enamelling iron	polycrystalline			5, 10
VU (1,2,3) ** (15,16,14) (34F,35F,36F) (6E,9E,3E)	Cambridge	7° off (110)	mp	450 (840)	1, 2½, 10
	Cleveland	1 to 7° off (111)			1, 2½, 10
	Ferrovac E	polycrystalline	mp,cp(1 hr),ep(5 min)		1, 2½, 10
	Enamelling iron	polycrystalline			1, 2½, 10

* mp,cp,ep,sb - mechanical, chemical, and electrolytic polish, and shot blasting, respectively.

** conventional open-pot galvanizing experiment.

TABLE 3

Surface Micro-indentation Hardness Tests*

Substrate Surface Treatment	Knoop (H _K) and Vickers (H _V) Hardness (kg/mm ²)			
	Cleveland A (100) H _K , H _V	Cleveland A (110) H _K , H _V	Cleveland A (111) H _K , H _V	Ferrovac E polycrystal H _K , H _V
electropolished	86,96	91,106	97,99	80,78
shot-blasted	233,217	222,217	206,217	222,210

* Knoop indenter with 10-g load; indentation depth ranged from 0.8 to 1.4 μ m (3 to 6 X 10⁻⁵ in.).

Vickers indenter with 15-g load; indentation depth ranged from 1.7 to 2.8 μ m (7 to 11 X 10⁻⁵ in.).

TABLE 4

CLA Surface Roughness*

Substrate Surface Treatment	Cleveland A (100) μ in. (μ m)	Cleveland A (110) μ in. (μ m)	Cleveland A (111) μ in. (μ m)	Ferrovac E polycrystal μ in. (μ m)
electropolished	18(0.46)	**	**	18(0.46)
shot-blasted	88(2.24)	95(2.41)	74(1.88)	91(2.31)

* Talysurf cut-off width of 0.030 in. (0.08 cm); centre line average obtained from planimeter measurement of Talysurf trace.

** Talysurf traces indicated a roughness equivalent to other electropolished surfaces.

Table 5

Mosaic Angular Spread in Cambridge (110) Surfaces

Crystal Surface Treatment	X-ray Penetration Depth at 95% Absorption* μ in. (μ m)	Mosaic Angular Spread About Mean** degrees
electropolished	276 (7.0)	\pm 0.37
mechanically polished and annealed in purified H ₂ for 3 hr at 400°C (750°F)	185 (4.7)	\pm 1.16

* 95% of the X-rays contributing to the diffracted line originate within this depth from the crystal surface.

** represents angular misorientation of surface subgrains about the mean as measured from the half width at half maximum of the corrected X-ray diffraction profile.

TABLE 6

Lattice Strain in Cambridge (110) Surfaces

Crystal Surface Treatment	Direction of X-ray Scan *	Incident Angle from Surface degrees	X-ray Penetration Depth at 95% Absorption** μ in. (μ m)	Lattice Strain *** μ in./in. (μ m/m)
electropolished	longitudinal	5.6	272 (6.9)	\pm 3150
	transverse	5.6	272 (6.9)	\pm 3070
mechanically polished and annealed in purified H ₂ for 3 hr at 400°C (750°F)	longitudinal	2.5	150 (3.8)	\pm 5490
	longitudinal	6.4	295 (7.5)	\pm 5890
	transverse	5.6	276 (7.0)	\pm 5200

* Longitudinal and transverse are orthogonal directions in the (110) surface through which 2 θ X-ray scans were made.

** 95% of the X-rays contributing to the diffracted line originate within this depth from the crystal surface.

*** represents strain in the interiors of the surface subgrains as measured from the half width at half maximum of the corrected X-ray interference distribution.

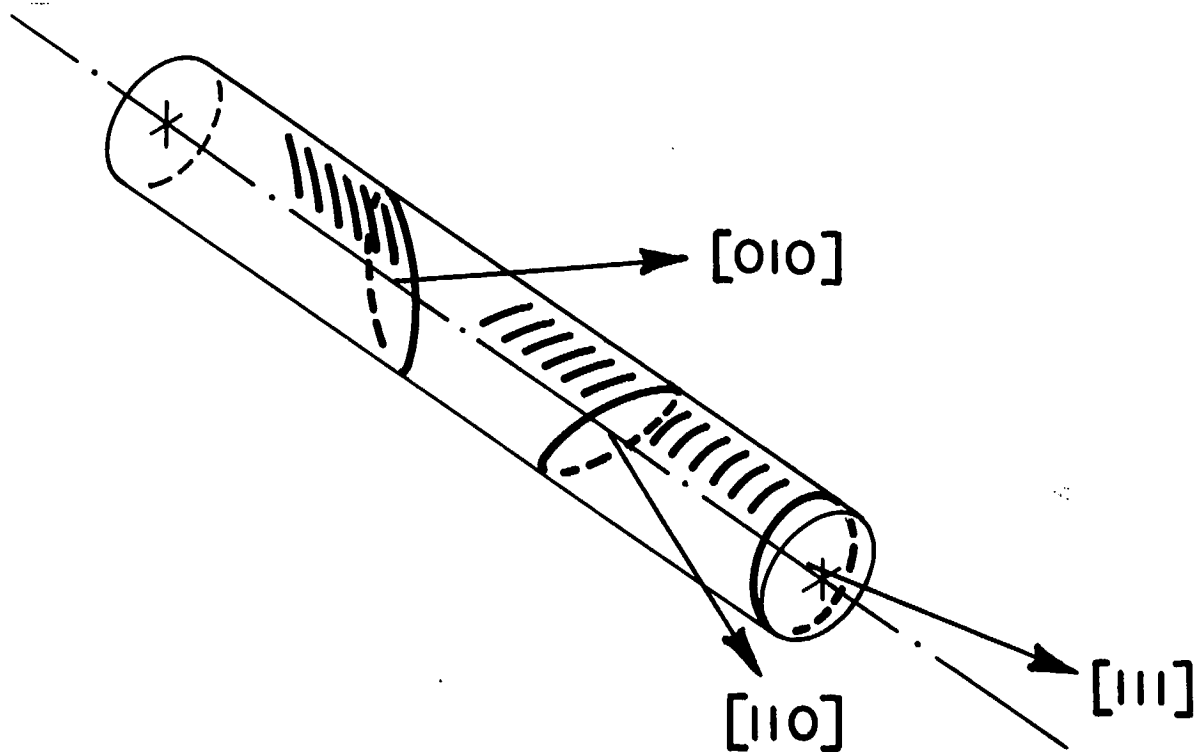


Figure 1. Diagram of Cleveland A crystal with spark-cuts along the (111), (110) and (010) planes shown in heavy outline. (Note that the (010) plane is equivalently designated as (100) throughout this report).

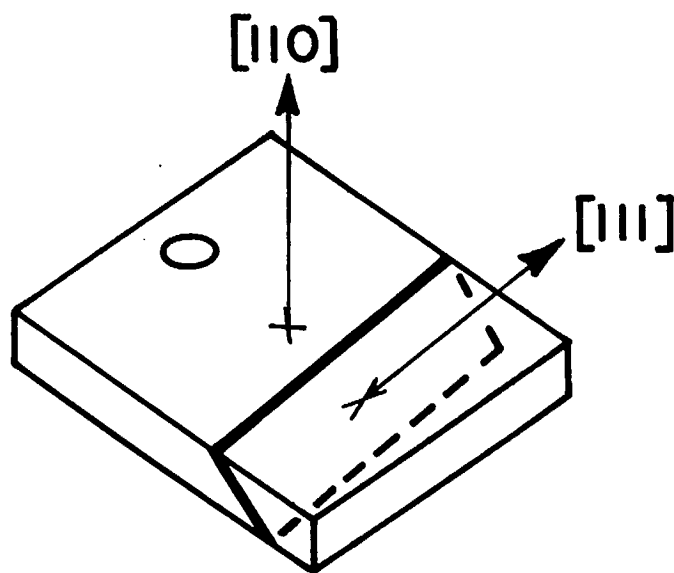


Figure 2. Diagram of Cambridge (110) crystal with spark-cut along the (111) plane shown in heavy outline.

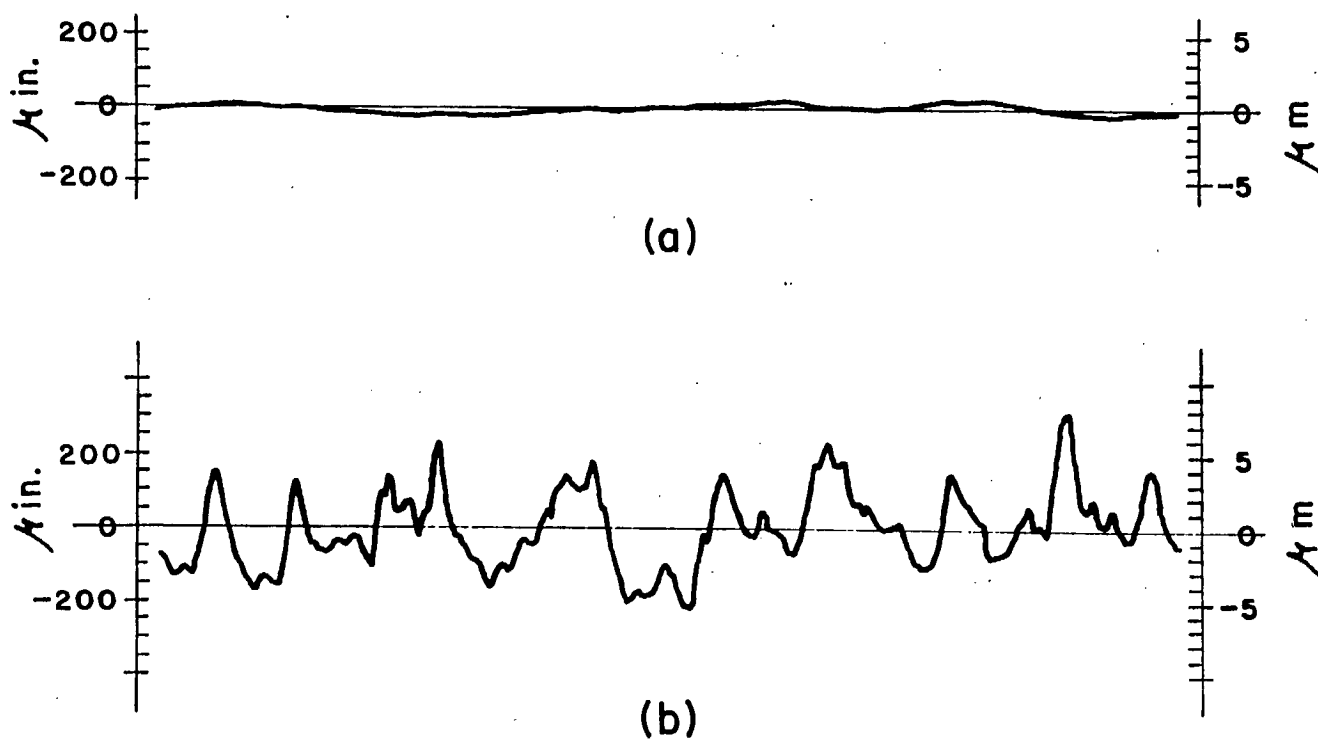


Figure 3. Talysurf traces of (a) electropolished and (b) shot-blasted surfaces of Ferrovac E iron. Vertical magnification X2000, horizontal magnification X100.

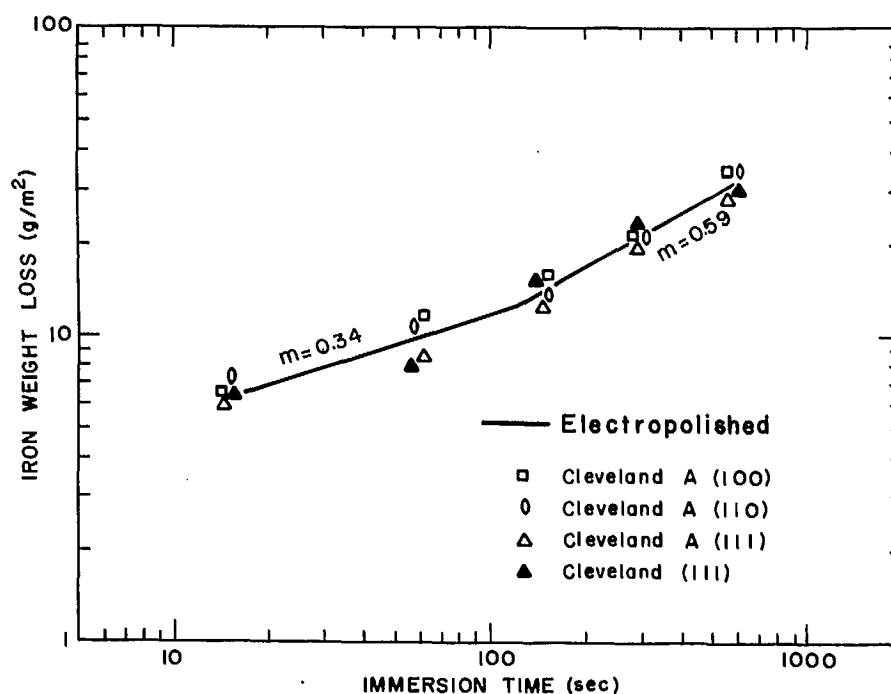


Figure 4. Iron loss vs. immersion time for Cleveland A (100), (110), (111), and Cleveland (111) crystals with electropolished surfaces.

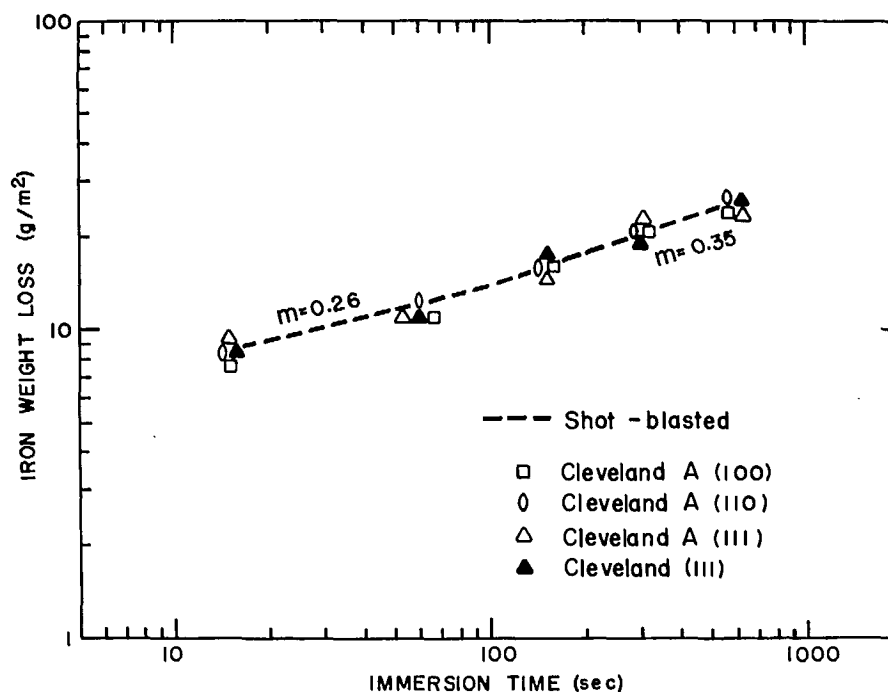


Figure 5. Iron loss vs. immersion time for Cleveland A (100), (110), (111) and Cleveland (111) crystals with shot-blasted surfaces.

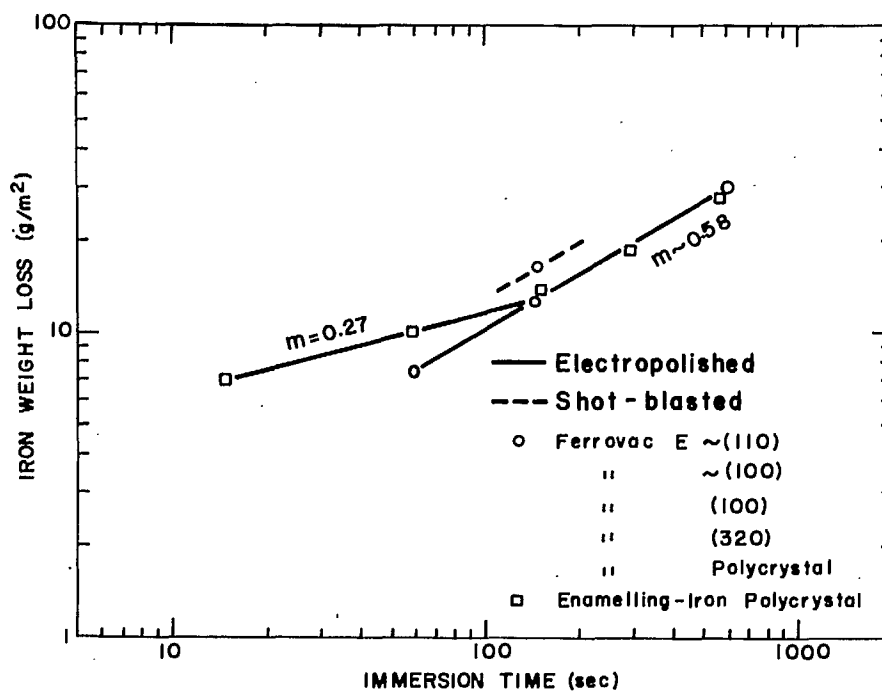


Figure 6. Iron loss vs. immersion time for Ferrovac E $\sim(110)$, $\sim(100)$, (100), (320), polycrystal, and enamelling-iron polycrystal samples with surface treatments as indicated.

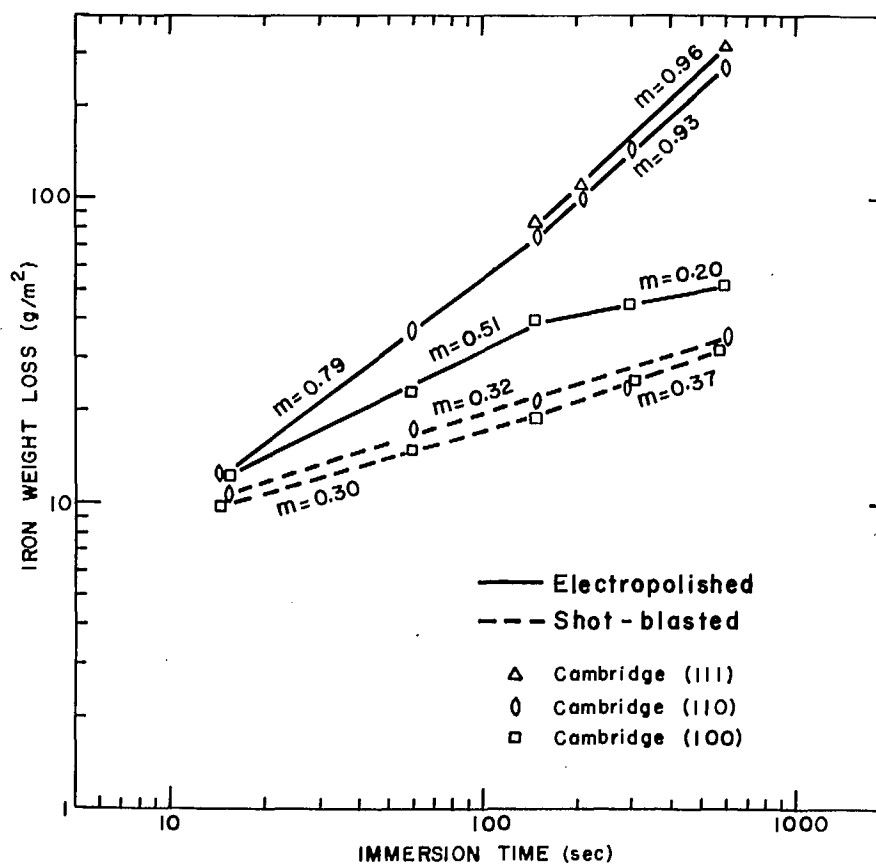


Figure 7. Iron loss vs. immersion time for Cambridge (111), (110) and (100) crystals with surface treatments as indicated.

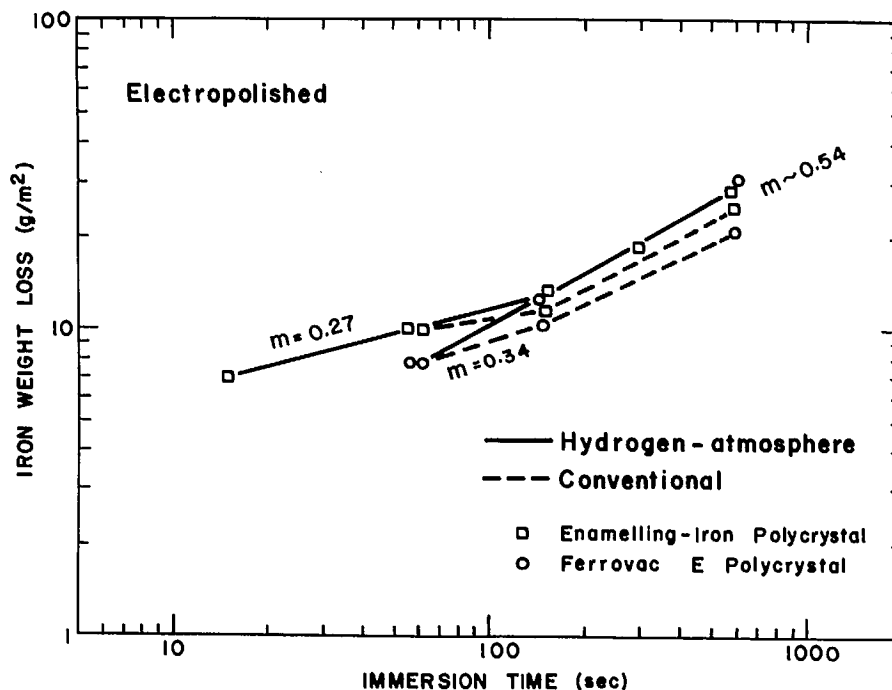


Figure 8. Iron loss vs. immersion time for hydrogen-atmosphere and conventionally galvanized enamelling-iron and Ferrovac E polycrystals with electropolished surfaces.

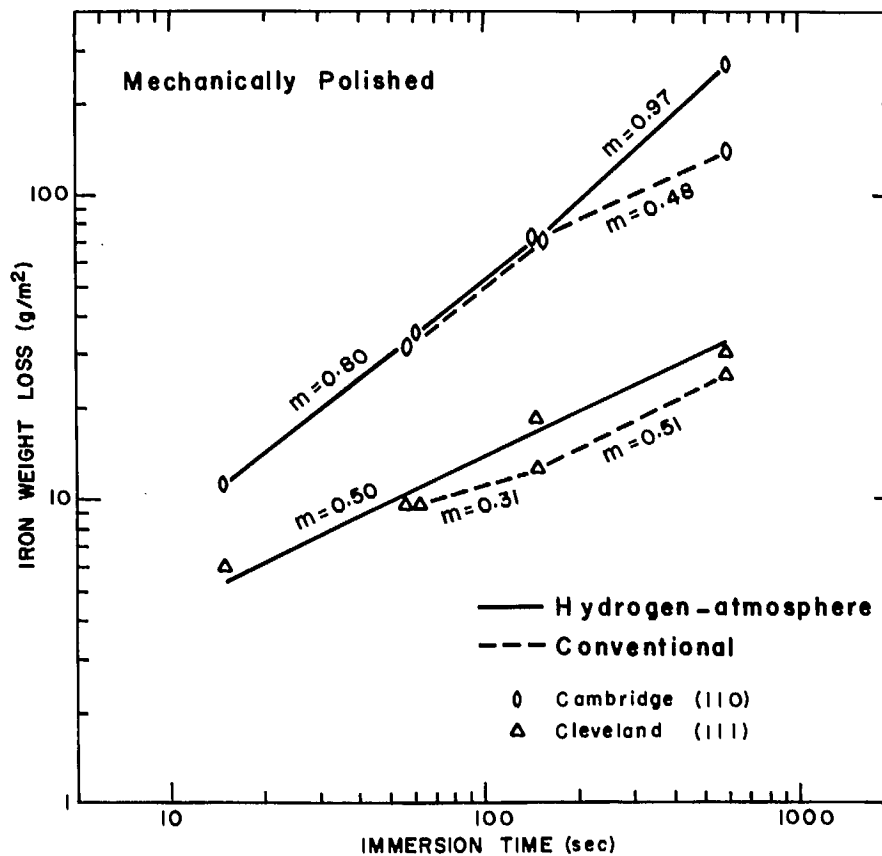


Figure 9. Iron loss vs. immersion time for hydrogen-atmosphere and conventionally galvanized Cambridge (110) and Cleveland (111) crystals with mechanically polished surfaces.

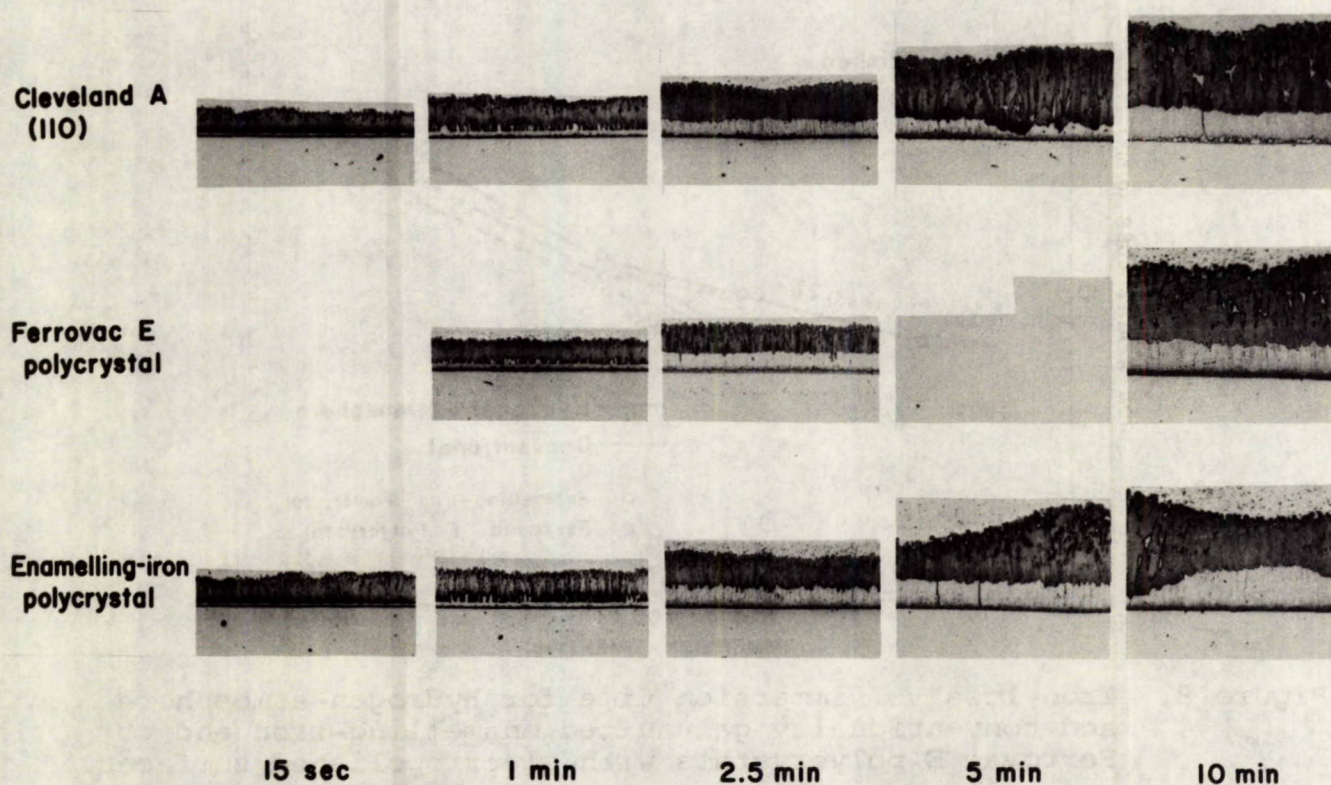


Figure 10. Representative coatings on electropolished iron crystals at 450°C (840°F) and immersion times as indicated. X250.

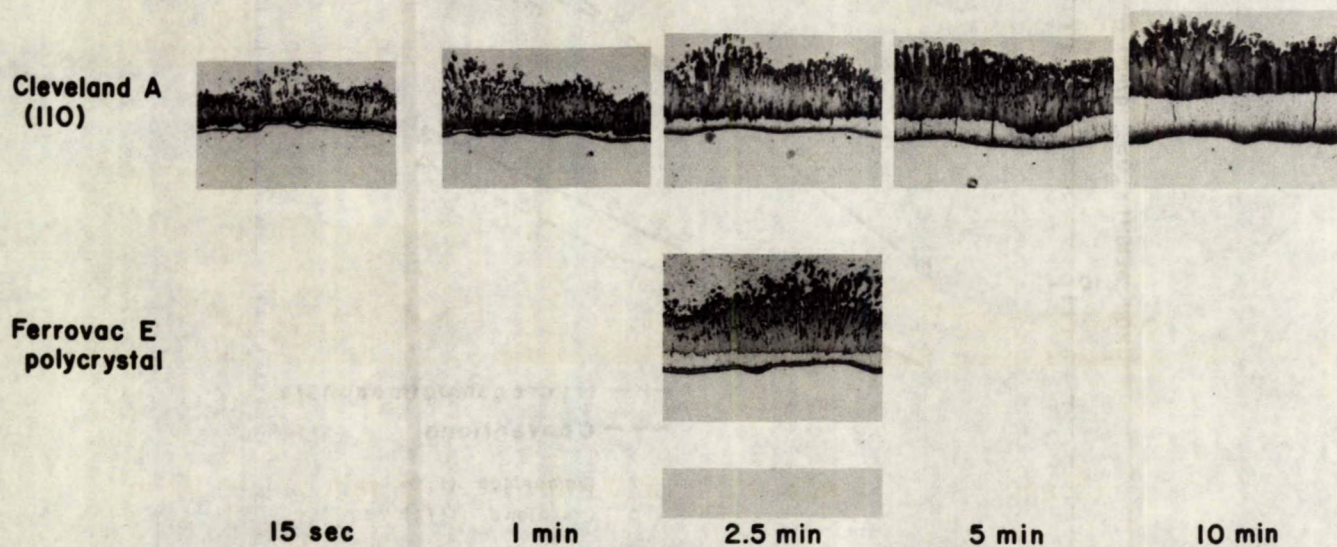


Figure 11. Representative coatings on shot-blasted iron crystals at 450°C (840°F) and immersion times as indicated. X250

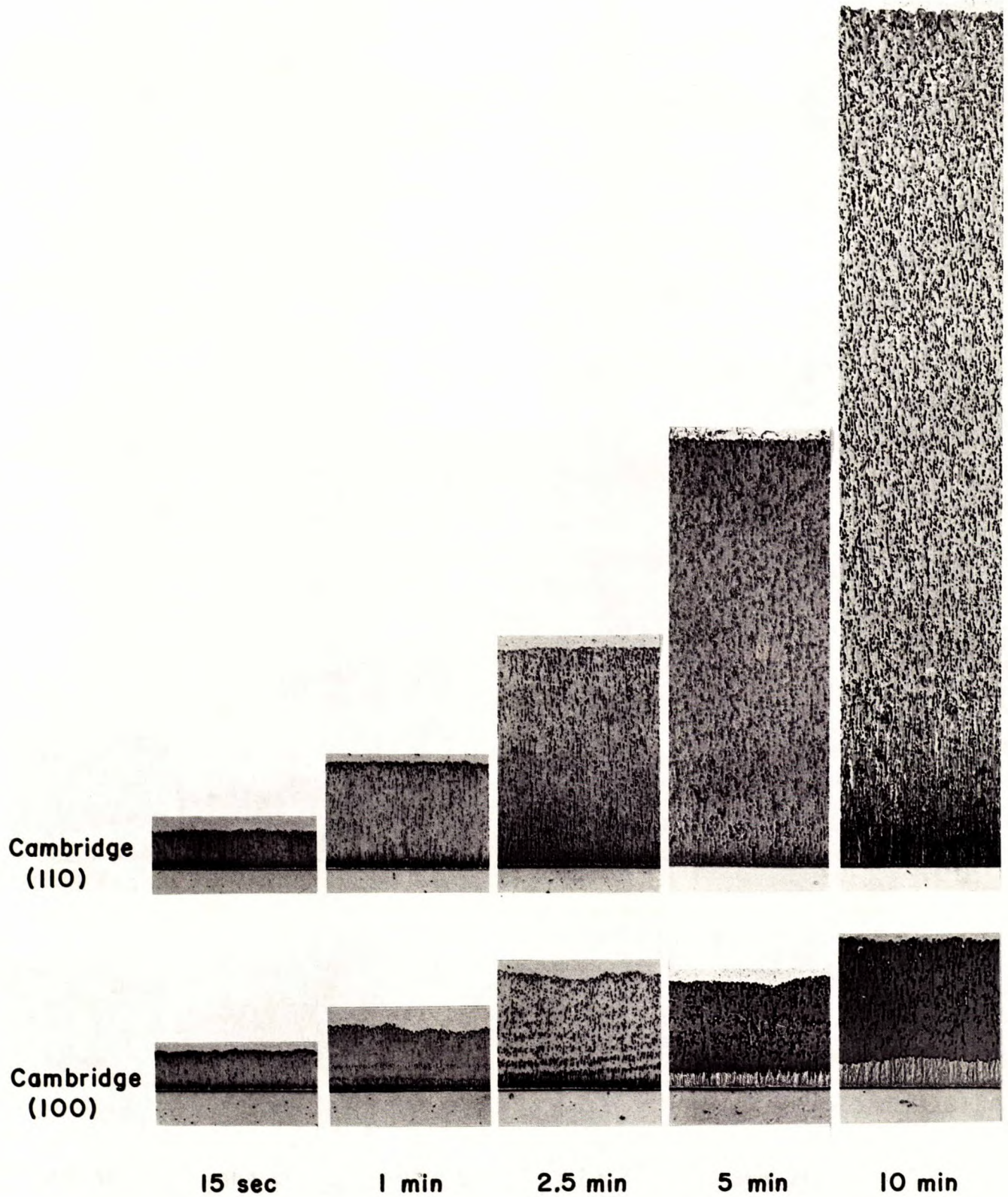


Figure 12. Coatings on electropolished Cambridge iron crystals at 450°C (840°F) and immersion times as indicated. X250.

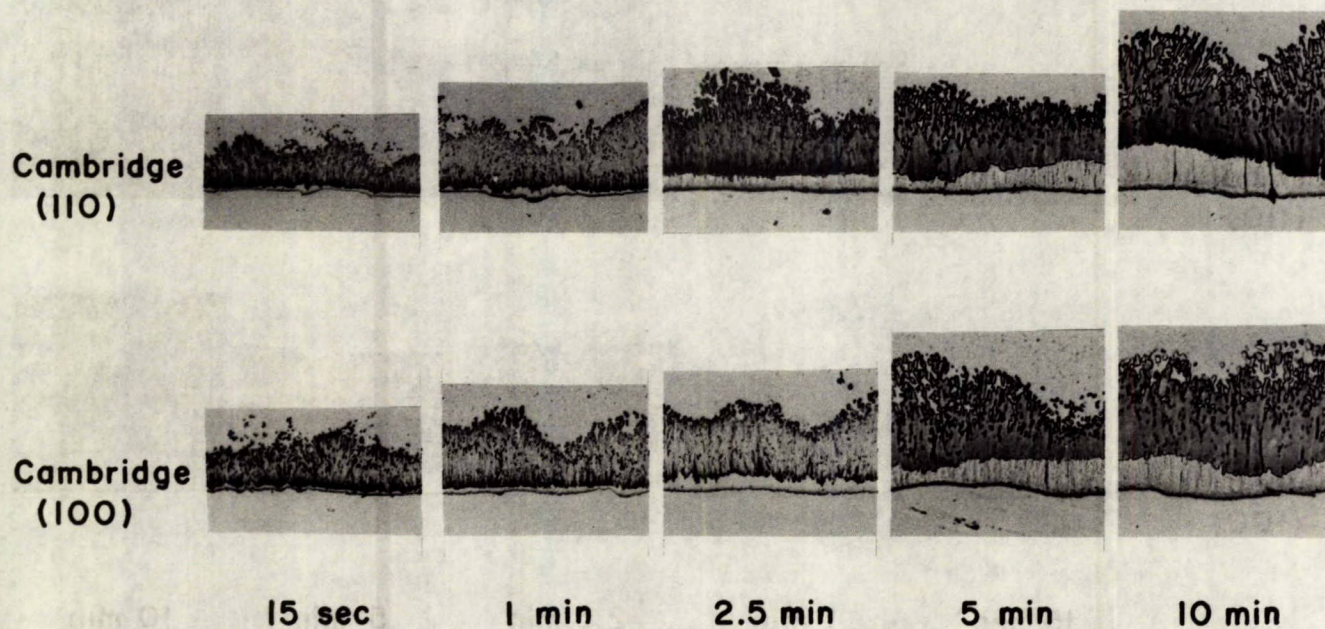


Figure 13. Coatings on shot-blasted Cambridge iron crystals at 450°C (840°F) and immersion times as indicated. X250.

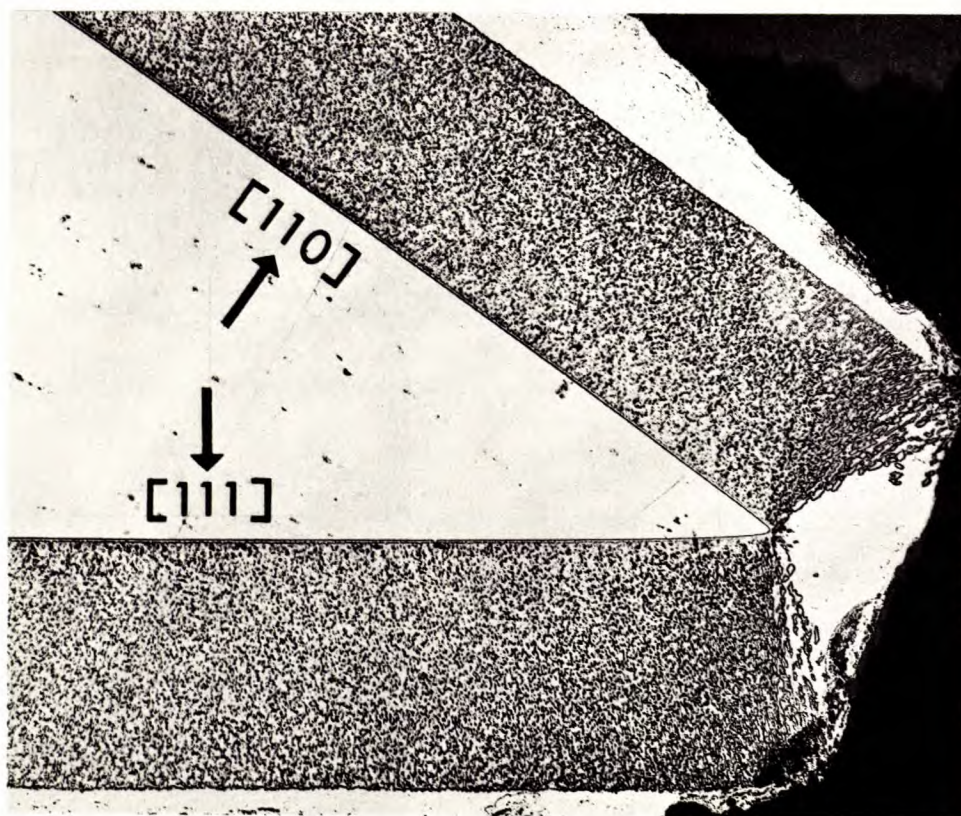
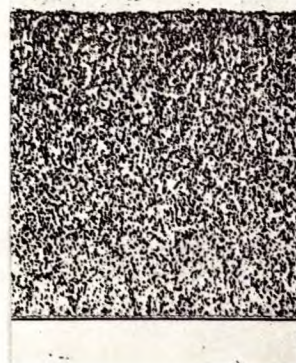


Figure 15. Coatings on electropolished faces of Cambridge (110) iron crystal as indicated: 2.5-min immersion at 450°C (840°F). X200.

Cambridge (111)



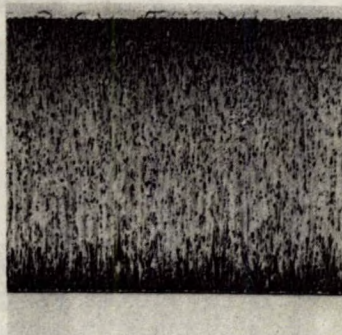
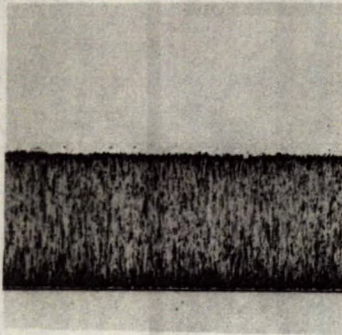
2.5 min



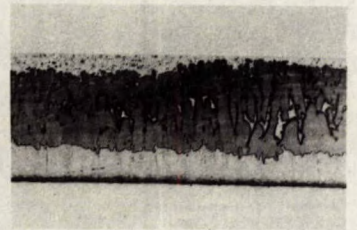
10 min

Figure 14. Coatings on electropolished Cambridge (111) iron surface at 450°C (840°F) and immersion times as indicated. X250. Coating at 2.5 min is from same sample as Figure 15.

Cambridge (110)
Mechanically
polished



Ferrovac E
polycrystal
Electropolished



1 min

2.5 min

10 min

Figure 16. Hydrogen-atmosphere-galvanized coatings on iron crystals at 450°C (840°F) for surface treatments and immersion times as indicated. X250.

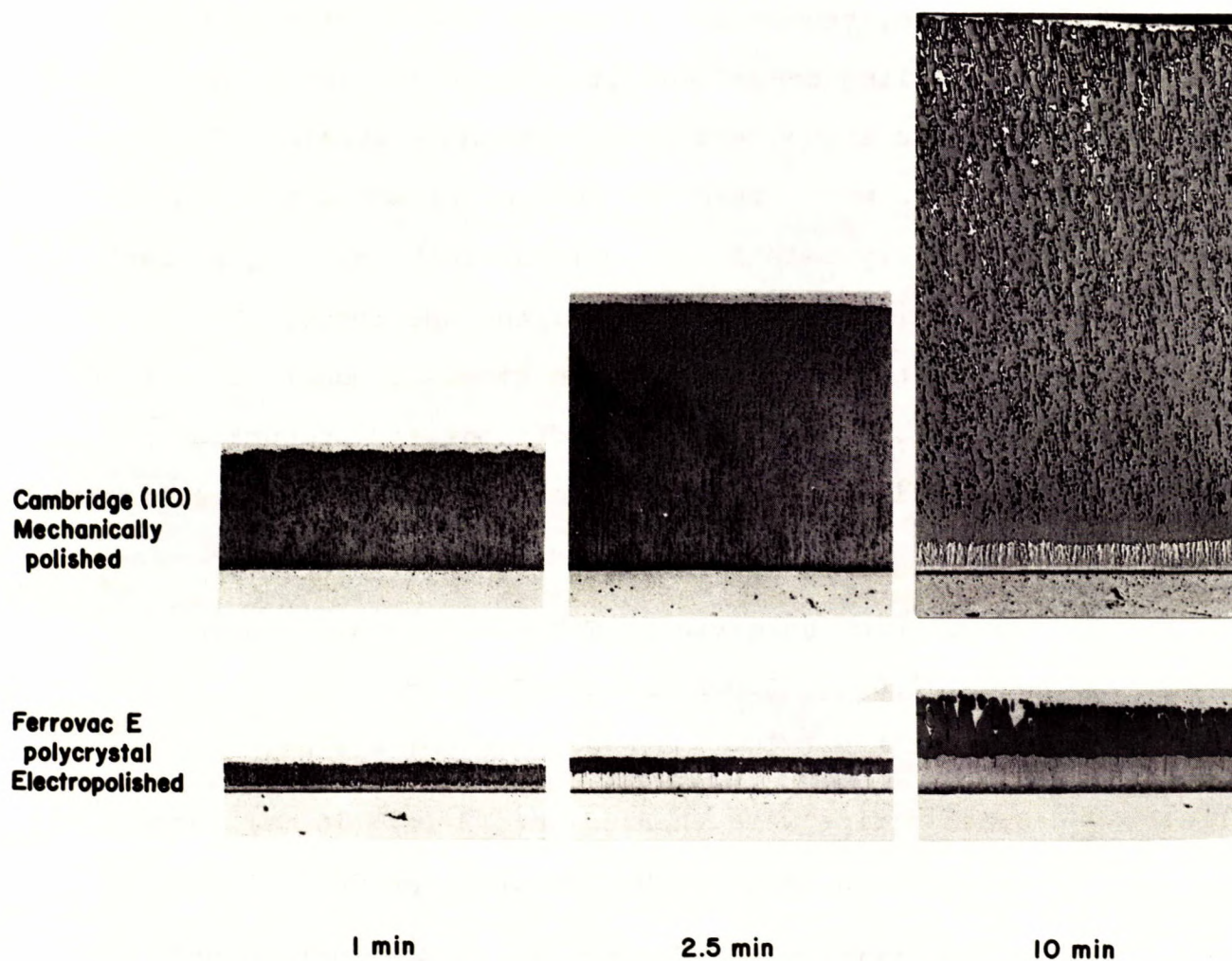


Figure 17. Conventionally galvanized coatings on iron crystals at 450°C (840°F) for surface treatments and immersion times as indicated. X250.

APPENDIX A

Production of Ferrovac E Iron Single Crystals

Procedures for the growth of large single crystals by strain-annealing have been described for Ferrovac E (9-11), electrolytic (12) and zone-refined electrolytic irons (13). Successful crystal growth of high-purity iron is critically dependent on material and process parameters such as the carbon content of the iron, the amount of material reduction by cold rolling, the annealing conditions of time, temperature and atmosphere, and the amount and rate of tensile strain. Some of these parameters were varied in several attempts to produce Ferrovac E single crystals for this investigation. Significant grain growth occurred in only a few of the specimens. The procedure is outlined below giving the range of conditions tried for each parameter. The specific conditions for production of the crystals used in the investigation are given in square brackets.

1. Stock materials: Ferrovac E iron with chemical composition as given in Table 1. Carbon contents were [0.004], 0.006 and 0.007%. Stock was in the form of $\frac{1}{4}$ x 1/16-in. (6.3 x 1.6 mm) strips.
2. Stock strips were sheared into 3-in. (76 mm) lengths and cleaned in a 50% HCl solution at 80°C (180°F).
3. These strips were reduced 60-[75]% by cold cross-rolling.
4. Tensile specimens were machined from the reduced strip.

5. Specimens were degreased in trichloroethylene vapor and then annealed at [820]-850°C ([1510]-1560°F) for 3 hr in [argon], hydrogen or vacuum and furnace-cooled.
6. Specimens were pickled in 50% HCl solution to remove the anneal-formed oxide scale and chemically polished in an 80% H₂O₂ - 5% HF-15% H₂O solution to provide a bright, smooth surface finish. Microscopic examination indicated average grain diameters of 0.03-0.15 mm [<0.1 mm]. Tensile straining of the specimens followed at a rate of 1%/min to a strain of 3.0% or more until Lüders bands were visible over the entire gauge length.
7. Final annealing for recrystallization into large grains was at 850-890°C (1560-1630°F) [880°C (1620°F)] for 18-26 hr [24 hr] in [argon], hydrogen or vacuum and followed by furnace cooling.
8. The recrystallized specimens were pickled in 50% HCl solution and etched in 25% HNO₃ solution to reveal their grain structure.
9. The crystallographic orientations of large grains were determined by Laue back-reflection X-ray diffraction with radiation from a Co target generated at 40 kV and 10 mA.

