CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH

OTTAWA

STUDY OF SURFACE TREATMENT EFFECTS
IN GALVANIZING IRON SINGLE CRYSTALS

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PHYSICAL METALLURGY DIVISION

NOVEMBER 1972

Mines Branch Research Report R 258

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by

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ABSTRACT

Single crystals of iron with basic low-index surface orientations were given various pretreatments to produce a range of surface roughness and hardness conditions and then galvanized in pure zinc in a purified hydrogen atmosphere.

Significantly different reaction effects previously found on electropolished (110), (100) and (111) surfaces of commercial single crystals were confirmed in tests involving pretreatment by thermal faceting and mechanical polishing. A relationship between galvanizing reactivity and crystallographic orientation of the iron surface was thereby more conclusively established.

Increasing the roughness of the crystal surfaces by grit blasting, and to a lesser extent by chemical etching, significantly reduced the dependence of the reactivity on crystallographic orientation. Fine surface irregularities and larger-scale unevenness, especially as produced by grit blasting, in combination with the growth habit of the iron-zinc alloy layers, were the predominant factors determining the galvanizing behaviour.

Surface work-hardening by the mechanical polishing and grit-blasting pretreatments had no apparent effect on the galvanizing reaction.

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Direction des mines

Rapport de recherches R 258

UNE ÉTUDE SUR LES EFFETS DU TRAITEMENT DE SURFACE DANS LA GALVANISATION DES MONOCRISTAUX DE FER

par

G. E. Ruddle* et J. J. Sebisty*

RÉSUMÉ

Les auteurs ont tout d'abord donné de divers traitements préliminaires aux monocristaux de fer avec des orientations de surface de base à indices faibles afin de pouvoir produire des gammes de rudesse de surface et de dureté. Ensuite ils ont galvanisé ces monocristaux dans du zinc pur dans une atmosphère d'hydrogène purifié.

Ils ont pu confirmer les effets de réaction significativement différents trouvés auparavant sur les surfaces polies électrolytiquement des monocristaux commerciaux (110), (100) et (111) dans des essais qui impliquaient le traitement préliminaire par le facettage thermique et par le polissage mécanique. Ils ont pu donc établir, d'une manière plus concluante, une relation entre la réactivité de galvanisation et l'orientation cristalographique de la surface de fer.

Les auteurs ont trouvé que s'ils augmentaient la rudesse des surfaces de cristal par le grenaillage, et de façon moins extrême c'est-à-dire par l'attaque chimique, ils pourraient réduire significativement la dépendance qu'il y a entre la réactivité et l'orientation cristalographique. Ils ont aussi trouvé que les petites irrégularités de surface et l'inégalité à une plus grande échelle, particulièrement produites par le grenaillage, en combinaison avec la façon de croissance des couches d'alliage fer-zinc, étaient les facteurs prédominants qui ont déterminé le comportement de galvanisation.

Les auteurs montrent que l'écrouissage par les traitements préliminaires de polissage mécanique et de grenaillage n'ont pas eu d'effects apparents sur la réaction de galvanisation.

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INTRODUCTION

In an exploratory investigation of the effects of crystallographic orientation on the galvanizing reaction [1], differences in the rate of zinc attack were found on the principal low-index planes of electropolished iron single crystals. The orientation of the substrate appeared to affect the nucleation and growth mode of the predominant ζ phase in coatings at 450°C (840°F) and thereby modified the galvanizing reaction rate and the final coating microstructure.

Studies on the effect of altering the physical condition of the substrate surface by various pretreatments have generally shown that the galvanizing reaction is significantly influenced by the surface roughness [2-6] and, in some cases, by severe cold-working of the surface [2,7,8]. The way in which the substrate surface is physically altered by pretreatment is expected to be dependent to some extent on its crystallographic orientation. Therefore, the prior exploratory investigation of crystallographic orientation effects on the kinetics of the galvanizing reaction was extended to determine the effects of surface pretreatment in combination with crystallographic orientation of the substrate. Examination of the diffusional, topographical, and work-hardening aspects of substrate orientation on the formation of galvanized coatings was of primary interest.

The investigation involved galvanizing experiments in a specially built hydrogen-atmosphere apparatus [1] in which iron single crystals having principal low-index surface orientations and pretreated by different methods were coated in unalloyed zinc baths at 450°C (840°F) over a range of immersion times. Crystal surface pretreatment was by thermal faceting, chemical etching, mechanical polishing, and grit blasting to produce a range of conditions of surface strain and roughness. The results obtained with the electropolished crystals in the previous investigation have been included in this report.

EXPERIMENTAL PROCEDURE

Iron Single Crystals

(a) Materials

Commercial single crystals of iron, used in the prior crystallographic orientation study [1], were re-used in this investigation. These are designated as Cambridge crystals, 7° off (110) and 8° off (100), and as Cleveland crystals, up to 7° off (111). They were intended to represent three of the principal low-index plane orientations in the body-centred cubic structure of alpha iron. The crystals were equivalent to Armco iron in

purity as shown by the suppliers' analyses given in Table 1.
The presence of a small amount of silicon (0.019%) in both
Cambridge crystals was confirmed by dc arc spectrography
(Analytical Chemistry Section, Chemistry Division, National
Research Council, Ottawa).

(b) Pretreatment

The Cambridge crystals were in the form of rectangular
prisms, 0.50 x 0.50 x 0.04 in. (13 x 13 x 1 mm). The Cleveland
crystals were discs, 0.375 x 0.08 to 0.10 in. (10 x 1.0 to 2.5 mm).

Five surface pretreatment and galvanizing tests were
done in a sequence to best utilize the limited amount of crystal
material. Considering the surface strain and roughness caused
by the pretreatments, the sequence below was arranged to enable
repeated use of individual crystal samples for the five tests.
It should be noted that a thin layer of the substrate was
dissolved by the galvanizing and coating stripping operations
between each pretreatment.

Pre-galvanizing Treatment	Surface Strain	Surface Roughness
1. Electropolishing (previous experiments)	strain-free	micro-smooth
2. Thermal faceting	strain-free	micro-smooth, faceted
3. Chemical etching	strain-free	slightly rough, micro-faceted
4. Grit blasting	highly strained	rough, irregular
5. Mechanical polishing	less highly strained	smooth, micro-scratched

In preparation for the thermal faceting treatment, maximum
surface smoothness was produced on the crystals by chemical and
electrolytic polishing techniques [1]. Analyses of iron surfaces
by Sewell et al [9,10] have shown that, on a sub-microscopic
scale, the topography produced by the electropolishing process is
not smooth. Annealing of the iron in a reducing atmosphere at
temperatures above 500°C (930°F) effected a rearrangement of the
surface atoms into a regular micro-faceted structure. Relatively
rapid thermal faceting was observed at annealing temperatures of
800 to 850°C (1470 to 1560°F) [10,11]. In the present work,
the iron crystals were annealed in a tube furnace for 3 hr at
800°C (1470°F) in an atmosphere of hydrogen of ultra-high purity
grade. The furnace was vacuum-degassed at 300°C (570°F) and
5×10^{-3} Torr for 3 hr before the crystals were inserted.

The chemical etching treatment involved immersion of the crystals for 10 min in a 1:1 solution of HCl and H_2O at room temperature.

For the grit blasting treatment, the crystals were mounted on a brass plate by Pellon "KK" adhesive. Blasting of the crystal surfaces was performed with a dry-honing machine using 100/230-mesh (149/62 μ) glass beads at an operating pressure of 90 psi (6 x 10^5 N/m^2). The nozzle was held 2 to 3 in. (5 to 8 cm) directly above each crystal for approximately 5 sec to produce a uniformly rough surface. Finally, the adhesive was softened by heating to permit separation of the crystals from the support plate and then dissolved in methyl ethyl ketone. Both surfaces of each crystal sample were similarly treated.

The mechanical polishing procedure involved mounting the samples on support discs as described above, grinding by dry lapping on 400-grit silicon carbide paper until the roughness originating from the prior experiment was removed, and then by successive lappings on 600-grit and 600-soft papers.

Following each pretreatment, representative (110), (100), and (111) surfaces were examined by optical microscopy, scanning electron microscopy, and replica electron microscopy as appropriate for the various topographies. Though the roughest surfaces were best displayed by scanning electron microscopy, the higher-resolution technique of replica electron-microscopy was necessary for the smoother surfaces. Surface replica preparation was done as before [1] except that, in the second stage of the process, carbon was deposited at an angle of 45° as the plastic replica was rotated.

Measurements of surface hardness were made after each pretreatment using a Tukon Knoop indenter at 10-g load and a Leitz Miniload Vickers indenter at 15-g load. Although these tests at such low loads did not give absolute micro-hardness values, the relative values served as an indication of the amount of surface strain.

The final pretreatment step was part of the galvanizing operation that entailed reduction of the crystal surface in a purified hydrogen atmosphere at 400°C (750°F) for between 2 and 3 hr. This removed any surface oxide, formed during or after the surface preparation. The annealing effect of this treatment caused a minor reduction in surface hardness as noted later.

Galvanizing Experiments

All galvanizing experiments were done in the hydrogen-atmosphere apparatus described in the previous report [1]. This permitted integration of the operations of reduction of the iron surfaces, melting and filtering of the zinc bath, and immersion of the crystal samples, all in a purified-hydrogen atmosphere.

The conventional pickling and fluxing pretreatments were thereby eliminated, and samples with clean oxide-free surfaces were immersed into the filtered bath through a clean surface.

The experiments completed are listed in Table 2. These covered the commercial crystals with surface orientations near (110), near (100), and near (111), representing the corner points of the stereographic triangle as shown below, and with surface treatments of thermal faceting, chemical etching, grit blasting and mechanical polishing. Selection of these orientations was based on the
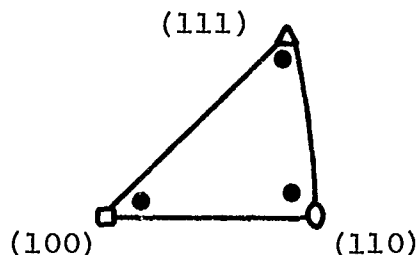
prior study [1] in which marked differences in galvanizing reactivity were found with the same materials after they had been pretreated by electropolishing. Special high-grade (99.99%) zinc at a bath temperature of $450 \pm 2°C$ ($840 \pm 4°F$) was used for all experiments. Crystal samples were suspended vertically in pairs, one sample for metallographic examination and the second for iron weight loss measurement , and galvanized at immersion times of 15 sec, 1, and 2.5 min.

Evaluation of the galvanizing behaviour of the crystals was made by metallographic examination, and by determining the loss of iron in every case except the 15-sec and 1-min immersion times for the Cambridge (100) orientation for which a complete set of samples was not available. Established techniques of metallographic sectioning, mounting, polishing, and etching were used. The crystals on which iron loss was determined were weighed before galvanizing, stripped after galvanizing in a 1:7 solution of HCl and H_2O, weighed and measured for surface area to determine the iron loss per unit of surface area. Alternative iron loss data were obtained from measurements of iron-zinc alloy thickness.

RESULTS

Surface Hardness of Crystals

The results of Knoop and Vickers micro-indentation hardness tests of the (110), (100), and (111) surfaces are presented in Table 3 for the series of five surface pretreatments in the sequence in which they were applied to the crystals. The relative

hardnesses of the differently treated surfaces can be seen to be independent of crystallographic orientation and type of test. Both the Knoop and Vickers tests provided similarly sensitive measures of the surface hardness.

In comparison to the relatively low hardness obtained on the electropolished surfaces, the thermally faceted surfaces were still softer, presumably because of an annealing effect at or near the surface. Chemical etching effectively removed part of the anneal-softened layer from each crystal and exposed a slightly harder surface. Surface hardness was increased drastically by grit blasting but decreased after removal by mechanical polishing of the highly roughened surface. With reference to galvanizing effects described later, it should be noted that the mechanically polished surfaces were at least 1.5 times harder than the relatively strain-free surfaces produced by the first three treatments in the series. Separate tests were made on the mechanically polished surfaces to ensure that there were no major annealing effects in the pre-galvanizing reduction treatment. The results given in Table 3 indicate that the hardness was decreased only slightly.

It is of interest to note that with the low test loads used, the indentation depths were generally less than the thickness of substrate material consumed in the galvanizing reaction.

Surface Topography of Crystals

Photomicrographs illustrating the topographic features produced by the different pretreatments are presented in Figures 1 to 4. The replicas of the electropolished surfaces in Figure 1 revealed grooved, dimpled, and finely eroded features for the (110), (100), and (111) orientations, respectively. Similar electropolished surface structures were found by Sewell et al [9,10].

It has been reported that annealing an electropolished surface in hydrogen for 3 hr between 800 and 850°C (1470 and 1560°F) modifies the surface structure by reducing the thin oxide film which is anodically formed during electropolishing, and by re-arranging surface iron atoms.[10,11]. The modified structure consisted of well-defined smooth facets related to the crystallographic orientation of the surface. The results of the thermal faceting treatment, as shown in Figure 1, were less than desirable in that the smooth underlying surfaces of the (110) and (100) crystals appeared to be covered by a uniform distribution of crystallites. This is interpreted on the basis of other results [10] to be oxide contamination. This oxide growth might have been minimized by improved vacuum-degassing of the tube furnace and by purification of the hydrogen gas. On the other hand, the smooth appearance of the (111) surface is not necessarily an indication that it was less contaminated. The absence of

similar crystallites in this case may be due to a chemical impurity such as carbon, for example, which can prolong the induction period for oxide nucleation when present on the surface (9). However, there is reason (1) to believe that the oxide particles were effectively removed in the pre-galvanizing reduction treatment with purified hydrogen at 400°C (750°F); hence, the surface contacting the zinc would be much smoother than that indicated in Figure 1.

An example of a relatively uncontaminated faceted structure obtained in a trial hydrogen anneal on an enamelling-iron surface of higher-index orientation is illustrated in the bottom of Figure 1. In this case, the crystallographic surface steps are much deeper and more closely spaced than would be expected on surfaces near the low-index orientations.

Mechanical polishing produced a finely scratched surface structure for all three orientations. The typical structure is illustrated by the surface replica in Figure 2.

More pronounced orientation-related topographic features were observed on the chemically etched surfaces. The (110), (100), and (111) surfaces were characterized by the irregularly stepped, regularly pitted, and hill-and-valley types of structure, respectively, as shown in Figure 2. The individual features reflected the crystallographic symmetry of the respective surfaces.

As with mechanical polishing, grit blasting produced the same topography on all three orientations. Surface replication, as shown by the example in Figure 2, provided an indication of the coarseness of the grit-blasted structure but did not record topographic details as well as the scanning electron microscope. Scanning electron micrographs, together with optical photomicrographs, are shown in Figures 3 and 4 to illustrate the comparative roughness of the mechanically polished and grit-blasted surfaces. At low magnification (Figure 4), the topographic result of grit blasting appeared to be a surface of irregular gouges and depressions, but high magnification (Figure 3) revealed sharp ridges, folds, and fissures.

Iron Loss Measurements

Iron losses as determined by chemical stripping of the galvanized coatings are presented in Table 4. Whereas these data correlated well with the coating microstructures of the Cambridge crystals, there were inconsistencies for the Cleveland (111) orientation. The iron loss discrepancies for the Cleveland crystals were presumed largely due to the smaller sample size and the larger proportion of edge surface to total surface area, as discussed in the previous report (1). For this reason and because of the limited stripping data on the Cambridge (100) crystals, alternative iron loss values were calculated from the

average iron-zinc alloy thickness as measured on representative
micro-sections. An average density of 7.18 g/cc and an
average iron content of 7% for the alloy layers was assumed.
Except for the grit-blasted and chemically etched Cambridge
crystal surfaces, alloy growth was generally of uniform thickness
and reliable measurements were possible. The results obtained
from these measurements are considered to be more representative
than the stripping measurements and are graphically presented
on logarithmic co-ordinates in Figures 5 to 12.

In the following discussion, it should be noted that
"reactivity" is indicated by the magnitude of the iron loss
for a particular immersion time. The "reaction rate" is
represented by the slope of the iron loss:immersion time curve
and is defined by the exponent m in the general kinetics
relation

$$w = ct^m$$

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

The iron losses for the three crystallographic orientations
are presented according to surface treatment in Figures 5 to 9.
For all treatments, a higher galvanizing reactivity was indicated
for the two Cambridge crystals. The difference in reactivity
between the Cambridge and Cleveland crystals was greatest for the
smoother surfaces, namely, electropolished, thermally faceted
and mechanically polished, and decreased as the surface
roughness increased. Reaction rates decreased in the order
- Cambridge (110), Cambridge (100), and Cleveland (111) - for
all surface treatments except the grit-blasted surface (Figure 9)
which indicated approximately the same rate for all orientations.
In the tabulation of reaction rates below, the underlined result
for the thermally faceted Cleveland (111) surface appears to be
anomalous. This behaviour may be related to the presence of a
surface contaminant such as carbon, as discussed previously.

	Reaction Rate (m)				
	Electro-polished	Thermally Faceted	Mechanically Polished	Chemically Etched	Grit-Blasted
Cambridge (110)	0.79	0.82	0.80	0.53	0.30
Cambridge (100)	0.51	0.60	0.66	0.39	0.30
Cleveland (111)	0.40	<u>0.22</u>	0.48	0.29	0.30

In Figures 10, 11 and 12, the iron losses are presented according to crystallographic orientation. For the Cambridge (110) and (100) orientations (Figures 10 and 11), reaction rates were similar for the smoother surfaces and decreased with increasing surface roughness. Figure 12 indicates that neither reactivity nor reaction rate varied appreciably with surface treatment for the Cleveland (111) crystal and, in contrast to the behaviour of the Cambridge crystals, the rougher surfaces appeared to have slightly higher reactivity. The Cleveland (111) reaction behaviour proceeded at less than a parabolic rate (m <0.5) for all surface treatments. With the Cambridge orientations, the reaction constant for the smoother surfaces was equivalent to, or higher than, the value of 0.5 for parabolic kinetics, and, as the surface roughness was increased, the magnitude of the reaction constant was reduced to less than 0.5.

The results for all three orientations indicated an absence of any correlation with surface strain. For example, in Figures 10 and 11, the reaction behaviour was similar for the thermally faceted and mechanically polished surfaces which had distinctly different hardnesses (Table 3), whereas significantly different reaction rates were exhibited by the thermally etched and chemically etched surfaces both of which were relatively unstrained.

Metallographic Observations

Photomicrographs of transverse sections of the galvanized coatings are presented in Figures 13 to 17. The microstructures of the coatings on the Cleveland (111) crystal, consisting of Γ, δ_1, and ζ iron-zinc alloy layers, as shown for the various surface treatments in Figure 13, are similar to those commonly formed on electrolytic iron and low-carbon steels. The thickness and compactness of the alloy layers were generally uniform for the smoother surfaces and more irregular for the grit-blasted surfaces. Thin Γ and δ_1 layers and a proportionately thicker ζ layer were formed during the shorter immersion periods and, as immersion time was increased, the proportions of δ_1 and ζ indicated the characteristic reciprocity of growth associated with these phases. The thickness of the ζ layer increased slightly with increase in surface roughness as shown for the chemically etched and grit-blasted surfaces. In the uniformly thick alloy-layer structures, the ζ crystallites adjoining the outer zinc layer were usually rounded off as is typical with a low-iron bath.

Completely different coating microstructures were observed on the Cambridge (100) and (110) crystals with the relatively smooth surfaces. Figures 14 and 15 show that the iron-zinc alloy in the coatings on the electropolished, thermally faceted, and mechanically polished surfaces consisted almost entirely of compact ζ. On each orientation, the ζ layers were of uniform and similar thickness for all three treatments. However, the ζ

thickness was up to twice as great on the (110) as on the (100) orientation. This difference was confirmed in edge sections of the Cambridge (110) crystal as shown by the example in Figure 16. Although the Cambridge crystals were found to contain only 0.019% Si (Table 1), the type of coating microstructure on these crystals, namely, the thick compact ζ layer and very thin δ_1 layer, is similar to that formed on semi-killed steels containing about 0.10% Si. A distinctive feature frequently apparent with the (100) orientation, particularly at the 2.5-min immersion time, was the occurrence of a layered ζ structure (Figure 14). A variable growth rate, periodically stifled or slowed down and then suddenly reactivated, is suggested.

Increase in roughness of the Cambridge crystal surfaces by chemical etching and grit blasting progressively changed the coating microstructure. The over-all alloy thickness was decreased and was more nearly equivalent on the two orientations after these pretreatments. Chemical etching produced a wave-like contouring of the ζ layer at longer immersion times, whereas all of the grit-blasted samples were characterized by much more irregular ζ growth. The structures on the grit-blasted surfaces exhibited more clearly the reciprocal growth of the ζ and δ_1 phases as well as the presence of the Γ phase.

For each of the three orientations, equivalent coatings were obtained on the smoother surfaces, namely electropolished, thermally faceted, and mechanically polished. Thus, the minor differences of topography on these surfaces had no apparent effect on the galvanizing reaction. Chemical etching, on the other hand, appeared to have sufficiently altered the surface to initiate some effect on the reaction. The greatest change in coating thickness and microstructure, as observed with the (110) surface, is possibly related to the coarser and more sharply stepped structure obtained by etching of this orientation. The topographic change produced by grit blasting resulted in more nearly similar galvanizing behaviour for all three orientations. A still closer similarity might have been achieved by using a coarser grit.

For all crystallographic orientations, there was no apparent correlation between the metallographic structures and the amount of surface strain produced by the various pretreatments. For example, the mechanically polished surfaces which had distinctly higher hardness (Table 3) exhibited similar reactivities to the electropolished and thermally faceted surfaces. Conversely, differences in reaction behaviour were observed between the chemically etched surfaces and those electropolished and thermally faceted, even though all were of relatively low hardness. An indication of the gross deformation produced by the grit-blasting treatment is illustrated in Figure 17 by the turned-over material at a sample edge. However, on the basis of the above evidence, the reaction effects on the grit-blasted surfaces are interpreted to be primarily related to topography.

SUMMARY AND DISCUSSION

Evidence was obtained of an interdependence between galvanizing reactivity and the experimental parameters of crystallographic orientation and surface pretreatment of the iron substrate. Consistent reaction differences were found on the orientations corresponding to the corner points in the basic stereographic triangle, namely the (110), (100), and (111) planes, when the substrate surface was pretreated by electropolishing, thermal faceting, and mechanical polishing. The level of reactivity on these relatively smooth surfaces decreased in the orientation order given, at least for immersion times beyond one minute. Increasing the roughness of the crystal surfaces by chemical etching and grit blasting gradually reduced the reactivity differences with crystallographic orientation so that, after grit blasting, more nearly similar reaction behaviour occurred on all three orientations. The strain conditions produced in the surfaces by the various pretreatments had no apparent effect on the galvanizing reaction in that no direct correlation was obtained between reactivity and surface hardness.

The differences in coating structure found on the smoothly finished Cambridge (110) and (100) surfaces must be related to crystallographic orientation and not to minor variations in topography of the substrate. This follows from the fact that these differences were consistently demonstrated on the mechanically polished samples, which had identical topographies for all orientations, as well as on the electropolished and thermally faceted samples. Other factors were presumably immaterial because both Cambridge crystals originated from the same source and should be identical in every way except orientation. Furthermore, as illustrated by the example in Figure 16, the same reaction differences were reproduced on the corresponding orientations represented by the top and side faces of a Cambridge (110) crystal after being pretreated by all three methods.

The Cleveland (111) crystal was of different composition and processing history, so its distinctly different galvanizing response compared to the Cambridge crystals could not be positively attributed to an orientation effect. As previously discussed (1), this difference in response may have been due to the more prominent physical and chemical inhomogeneities of the Cleveland material. Also, the substantially higher than trace content of silicon (0.019%) in the Cambridge material may have enhanced the sensitivity of the reaction to substrate orientation.

Increasing the roughness of the Cambridge (110) and (100) surfaces beyond a certain degree effectively reduced the iron-zinc alloy growth, gradually reduced the effect of crystallographic orientation, and tended to produce more equal proportions of the individual phase layers. This reduction in alloy growth is opposite to the increased attack on roughened polycrystalline surfaces between 440 and 460°C (820 and 860°F) reported for

mild [2,3,5] and semi-killed [6] steels. In other work [8], sand-blasting produced local reductions in the reactivity of a semi-killed steel. The tendency to increased attack on the roughened Cleveland (111) surfaces is more in accord with the generally accepted behaviour of polycrystalline mild steel surfaces.

The absence of a strain effect on the galvanizing reaction for the range of residual strains involved would seem to confirm similar results of previous work on polycrystalline surfaces (3,5,6). However, because of the different annealing treatment employed by each investigator, and without quantitative data on the conditions of strain in the reacting surfaces, meaningful comparisons cannot be made. To what extent the strain-relief of the pre-galvanizing reduction treatment in the present work may have influenced the coating reaction is unknown. In this regard, hardness tests on the mechanically polished Cambridge (110) crystals (Table 3) indicated that annealing in similar conditions reduced the hardness from 165 to 157, for example. These had the same galvanizing characteristics as the fully annealed thermally faceted crystals with a hardness of 92. Hence, in terms of surface hardness, it can be assumed that the strain-relief associated with the reduction treatment would have a negligible effect. Variable reaction effects have been associated with severe treatment of the surface in some cases. The highly disturbed surfaces resulting from both mechanical polishing and cold-rolling operations on mild steel have been found more reactive (2,7). On the other hand, decreased reactivity in the severely deformed rupture zone of a sheared edge of a semi-killed steel sample has been reported [8].

With regard to the deformation produced by mechanical polishing, the identical behaviour of this surface and those electropolished and thermally faceted may be explained when it is considered that, in the first 15 sec, reaction differences with orientation were not large and that 1 to 2 μ of the substrate material was consumed in this interval. It is possible that a sufficient amount of the deformed crystal was removed at this early stage to permit a subsequent crystallographic influence on the alloy growth. X-ray Laue diffraction of a mechanically polished surface after a typical pre-galvanizing hydrogen reduction treatment indicated a high degree of crystalline order within 2μ of the surface. Other X-ray diffraction analyses are being carried out on the mechanically polished surface to determine the relation of the conditions of strain and deformation to the observed reactivity.

In the previous investigation [1] rapid ζ-layer growth and negligible growth of δ_1 on electropolished Cambridge (110) and (100) surfaces was taken as an indication that the reaction proceeded according to the rate of zinc transport to the ζ-δ_1 interface, this rate being sufficient to sustain ζ growth in lieu of further δ_1 growth. The ease of zinc passage through the fine-grained ζ layer on the Cambridge crystals is presumed to be

principally related to the continuity and alignment of inter-granular paths formed in the growth of this phase. Following the premise that the ζ phase is the first alloy layer to be formed in the iron-zinc reaction (12,13,14) and considering that the Cambridge crystals are apparently identical in every respect except orientation, the difference in rates of ζ growth on the two orientations suggests a modification in the ζ-layer structure resulting from the way growth was crystallographically initiated and continued from the iron surfaces. The layered ζ structure apparent in most of the (100) coatings at 2.5-min immersion (Figure 14) provides further evidence of an orientation-related modification of the growth mechanism which was largely independent of surface pretreatment. Also, continued rapid growth of the very thick ζ layer in the (110) coatings (Figure 15) must be dependent on a high rate of mass transport through this layer, most likely via intergranular paths.

On the smoothly finished Cleveland (111) surfaces, ζ growth was presumably initiated in such a way that more compact layers were formed. A correspondingly lower rate of zinc diffusion to the ζ-δ_1 interface would be expected to result in ζ and δ_1 growth rates which would be lower and higher, respectively, than observed on the more reactive Cambridge crystals and in the formation of a visible Γ layer.

The contour effect of the substrate surface on the galvanizing reaction is well established by the characteristic growth of iron-zinc alloy in a direction normal to the iron surface (2). From the even ζ growth on the (110) and (100) surfaces pretreated by electropolishing, thermal faceting, and mechanical polishing, the surface irregularities present were apparently not large enough to disrupt the crystallographic effect on ζ growth. However, from the changes in growth characteristics of this phase caused by the surface roughening of chemical etching and much more so of grit blasting, the orientation dependence was correspondingly reduced but not entirely eliminated, particularly at the longest immersion time.

The reductions in iron-zinc alloy growth on these rougher surfaces is especially noteworthy because, as described earlier, increasing roughness is generally considered to cause increased alloy growth. From the evidence, the coating structures developed on the rougher (110) and (100) surfaces, particularly on the grit-blasted surface, can be explained in terms of the hypothesis that ζ growth is the result of intergranular passage of zinc through this phase.

1. Because of the highly irregular hill-and-valley contouring of the surface, the increased surface area of iron exposed to zinc would be expected to increase the amount of iron-zinc alloy growth in the initial reaction stages. In this period, any effect of substrate orientation would be overshadowed

and this is confirmed by the similarity of the
15-sec microstructures for all three orientations
in Figures 13 to 15.

2. In the valleys, the vertical growth habit of the
iron-zinc alloy phases would promote compacted
growth of the predominant ζ layer. As a result,
the reaction rate would be markedly reduced because
of the increased difficulty of intergranular
movement of zinc in the compacted ζ layer. With
the zinc availability reduced, and because of the
shortened diffusion path, growth of the higher iron-
zinc phases (δ_1 and Γ) would be favoured.

3. With alloy filling of the valleys, the area of iron
surface which is effectively exposed for reaction
is reduced.

4. Although ζ growth on the peaks is promoted because
the open granular structure of this phase allows
freer intergranular passage of zinc, the close spacing
and erratic contour of the peaks would be expected
to result in growth interference. A major restriction,
for example, could be interception by similar growth
from adjacent peaks. Thus, the rate of reaction at
the peaks eventually becomes less than that of
unrestricted growth on smooth surfaces. This reaction
stifling would develop in an early stage at the finely
serrated surface regions. The over-all reaction rate
is therefore suppressed, and the total alloy thickness
is less than that developed on smooth surfaces where
growth can proceed steadily on a plane front.

5. As the reaction proceeds, a levelling of the surface
peaks and dissolution of the disordered substrate
material occurs. Accepting that growth interference
between peaks restricts free formation of the outburst
type of ζ structure initially formed at these points
and considering the vertical alloy growth habit
combined with the surface levelling and dissolution
process, the substrate orientation would gradually
have increasing influence on ζ phase formation with
increasing immersion time. The irregular ζ growth
front established in the initial stages and, in part,
exaggerated by gross surface irregularities originally
present would be perpetuated until levelled out at
very long immersion times.

The fundamental mechanism by which iron-zinc alloy
formation is affected by the substrate crystallography is un-
resolved. The decreasing reactivity found on the (110), (100),
and (111) planes coincides with the atomic densities of these
planes. However, the corresponding surface energies would be

in increasing order, respectively, and therefore would not logically relate to the observed reactivities. Epitaxial alloy growth from the iron substrate is also discounted on the basis that the ζ layers on both Cambridge crystals appear to have a fine granular structure rather than a unique crystallographic relationship with the substrate. Further investigation by metallographic and electron diffraction analyses would be necessary to determine a textural relationship between the ζ layer and the substrate crystallography.

The significant differences in level and type of reactivity observed on the Cambridge crystals as compared with the lower reactivity of the Cleveland crystals might account for the type of sporadic outbursts in alloy growth found in coatings on commercial steels. Sufficiently large grains of (110) or other unknown orientations having similarly high reactivity might initiate and promote locally accelerated growth of the ζ phase. Such an orientation dependency is an alternative to the effect of a local impurity concentration in the reacting steel as advanced by Harvey [6]. To what extent orientation texture in mill-finished steel sheet surface does, in fact, influence galvanizing reactivity is a matter for further investigation.

CONCLUSIONS

Enhanced galvanizing reactivity consistently occurs on some crystallographic planes of commercial single crystals of iron after pretreatment by methods providing relatively smooth surfaces. The (110) crystallographic plane is most reactive and the (100) and (111) planes show decreasing effects in that order on surfaces produced by electropolishing, thermal faceting, and mechanical polishing. From the characteristics of the ζ iron-zinc phase which predominate in coatings formed at 450°C (840°F) on more reactive (110) and (100) surfaces, the orientation of the substrate affects the nucleation and growth mode of this phase and thereby modifies the galvanizing reaction rate and the coating microstructure.

Differences in reactivity with crystallographic orientation are gradually reduced by increasing the surface roughness of the iron substrate by chemical etching and grit blasting pretreatments. Evidence of the effects of both orientation and surface topography on the coating structures are well-defined on etched surfaces but the orientation dependency is significantly reduced on grit-blasted surfaces. The structure of the latter coatings is determined primarily by fine surface irregularities and larger-scale uneveness produced by grit blasting combined with the inherent vertical growth habit of the iron-zinc alloy layers.

Work hardening of the iron surface as induced by mechanical polishing and grit-blasting treatments has no apparent effect on the galvanizing reaction.

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TABLE 1

Chemical Composition of Iron Crystals

Element (%)	Cambridge Crystals (110),(100)	Cleveland Crystal (111)
C	.005	.012
Mn	.03	.017
Si	.03	Trace
	.019*	< .001*
P		.005
S		.025
Al		
Ni		
Cr	.03	
Sn		
Cu		
Mo		
Others	< .01	
Fe (by diff)	99.90	99.94

* By dc arc spectrography.

TABLE 2

Galvanizing Experiments

Run and Sample No.	Crystal Sample Data			Galvanizing ***	
	Material	Orientation	Surface Treatment **	Temp. $^{\circ}C$ ($^{\circ}F$)	Time (min)
93(1,2,3,4,5,6)	Cambridge	7° off (110)	cp(½ hr),ep(4 min),tf(3 hr,800°C)	448(840)	¼,1,2½,¼,1,2½
(7,8,9,10)	Cambridge	8° off (100)			¼,1,2½,2½
(13,16)	Cleveland	1 to 7° off (111)			2½,2½
94(11,12,14,15)	Cleveland	1 to 7° off (111)	cp(½ hr),ep(4 min),tf(3 hr,800°C)	449(840)	¼,1,¼,1
(13,16)	Cleveland	1 to 7° off (111)	ce(10 min)		2½,2½
95(1,2,3,4,5,6)	Cambridge	7° off (110)	ce(10 min)	448(840)	¼,1,2½,¼,1,2½
(7,8,9,10)	Cambridge	8° off (100)			¼,1,2½,2½
96(11,12,14,15)*	Cleveland	1 to 7° off (111)	ce(10 min)	449(840)	¼,1,¼,1
(13,16) *	Cleveland	1 to 7° off (111)	gb(5 sec)		2½,2½
97(1,2,3,4,5,6)	Cambridge	7° off (110)	gb(5 sec)	450(840)	¼,1,2½,¼,1,2½
(7,8,9,10)	Cambridge	8° off (100)			¼,1,2½,2½
(13,16)	Cleveland	1 to 7° off (111)			2½,2½
98(1,2,3,4,5,6)	Cambridge	7° off (110)	mp	450(840)	¼,1,2½,¼,1,2½
(7,8,9)	Cambridge	8° off (100)	mp		¼,1,2½
(11,12,14,15)	Cleveland	1 to 7° off (111)	ce(10 min)		¼,1,¼,1
99(10)	Cambridge	8° off (100)	mp	449(840)	2½
(11,12,14,15)	Cleveland	1 to 7° off (111)	gb(5 sec)		¼,1,¼,1
(13,16)	Cleveland	1 to 7° off (111)	mp		2½,2½
100(11,12,14,15,16)	Cleveland	1 to 7° off (111)	mp	450(840)	¼,1,¼,1,2½
(9)	Cambridge	8° off (100)			1

*   sample surfaces in Run 96 were incompletely reduced before galvanizing and tests were repeated in runs 97 and 98.

**   cp,ep,mp,tf,ce,gb – chemical, electrolytic, and mechanical polish, thermal faceting, chemical etch and grit blasting, respectively.

*** special high-grade (99.99%) zinc.

TABLE 3

Surface Micro-indentation Hardness Tests*

Substrate Surface Treatment	Knoop(H_K) and Vickers(H_V)Hardness (kg/mm^2)		
	Cambridge(110) H_K,H_V	Cambridge(100) H_K,H_V	Cleveland(111) H_K,H_V
electropolished	105,113	109, 93	99,124
thermally faceted	89, 92	83, 88	67, 86
chemically etched	98, 95	104, 93	76, 89
grit-blasted	206,257	294,211	218,217
mechanically polished	162,165	177,157	173,193
mechanically polished			
– before reduction	165	162	175
– after reduction	157	150	170

* Knoop indenter with 10-g load; indentation depth ranged from 0.7 to 1.5 μ (3 to 6 x 10^{-5} in.).

Vickers indenter with 15-g load; indentation depth ranged from 1.5 to 2.7 μ (6 to 11 x 10^{-5} in.).

TABLE 4

Iron Loss Results

Substrate Surface Treatment	Iron Loss (g/m^2)*		
	Cambridge(110)	Cambridge(100)	Cleveland(111)
Electropolished	10.4,28.5,55.5	10.6,21.5,33.1	2.9, 7.1, 10.6
Thermally faceted	10.5,26.9,57.3	33.8	14.7, 17.9, 16.3
Mechanically polished	9.8,28.7,57.0	40.3	6.6, 10.5, 16.0
Chemically etched	11.1,22.0,33.4	29.7	10.1, 17.9, 25.2 5.6** 8.1**
Grit-blasted	12.0,16.8,24.4	26.1	9.1, 12.8, 19.4 18.0**

*   For immersion times of ¼,1,2½ min, left to right, respectively.

**   Iron loss for incompletely reduced samples in Run 96 (Table 2).
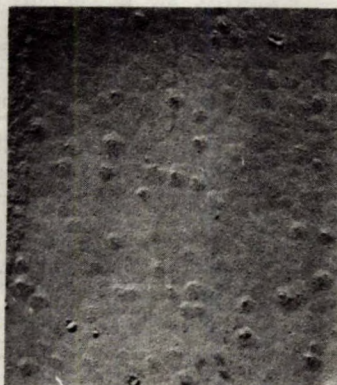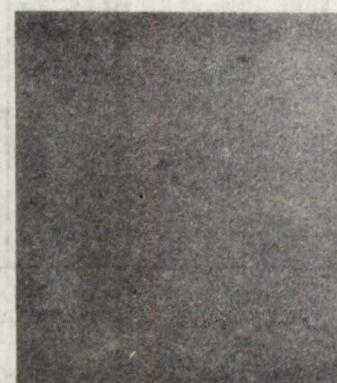
Figure 1. Surface replicas from crystals with surface treatment and crystallographic orientation as indicated. X15,000

Mechanically polished
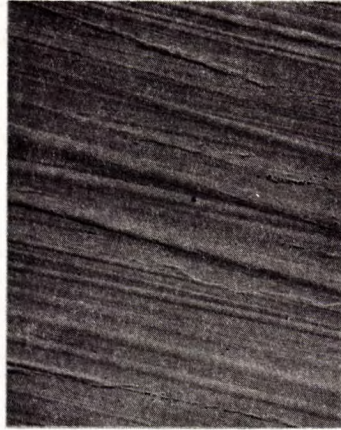
All orientations

Grit-blasted
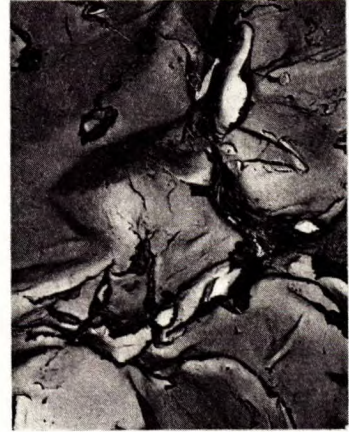
All orientations

Chemically etched

(110)   (100)   (111)

Figure 2. Surface replicas from crystals with surface
treatment and crystallographic orientation
as indicated. X5,000
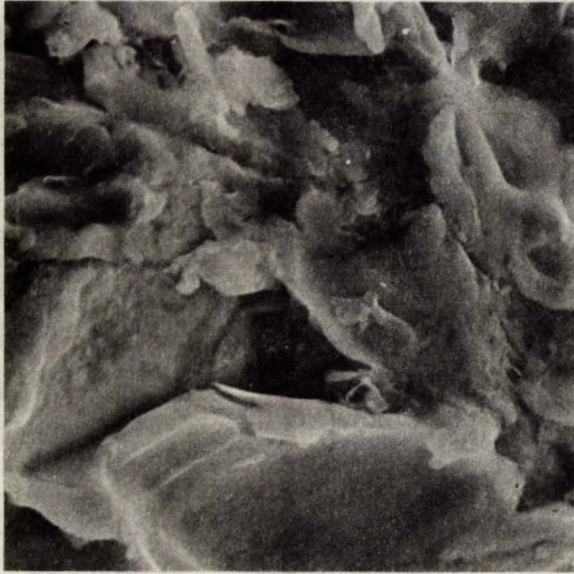
Grit-blasted (X 5,000)   Grit-blasted (X 1,000)
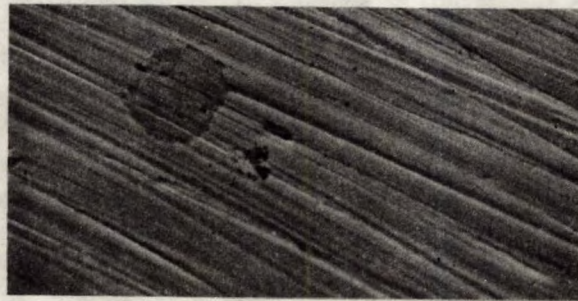
Mechanically polished (X 1,000)

Figure 3. Scanning electron micrographs of surfaces with treatment as indicated.
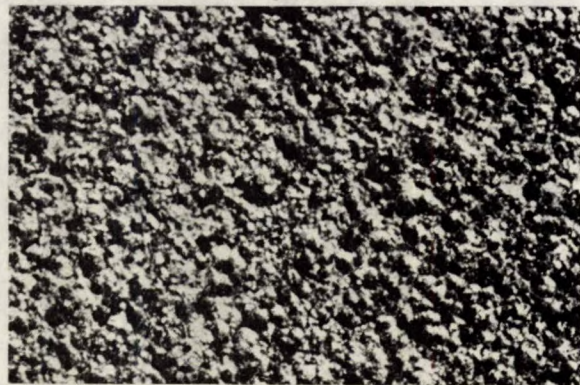
Mechanically polished   Grit-blasted

Figure 4. Optical photomicrographs of surfaces with treatment as indicated. X 50
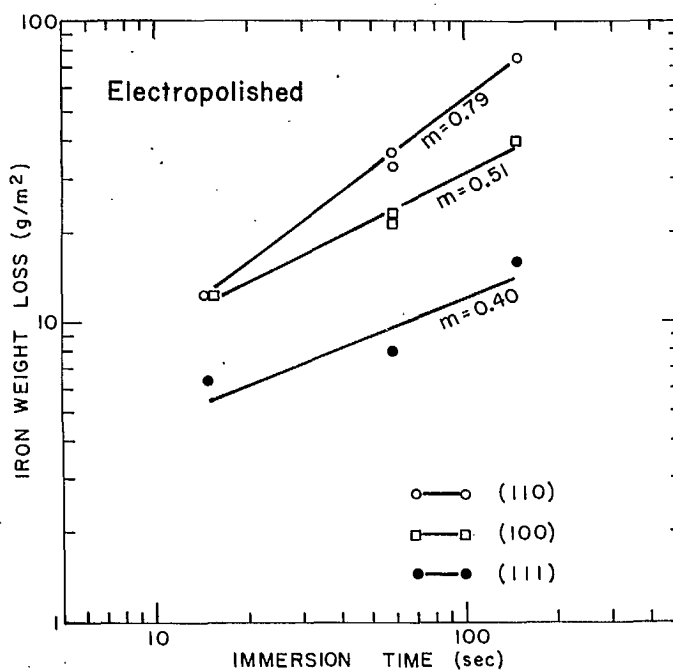
Figure 5. Iron loss vs. immersion time for Cleveland (111) and Cambridge (100) and (110) crystals with electropolished surfaces.
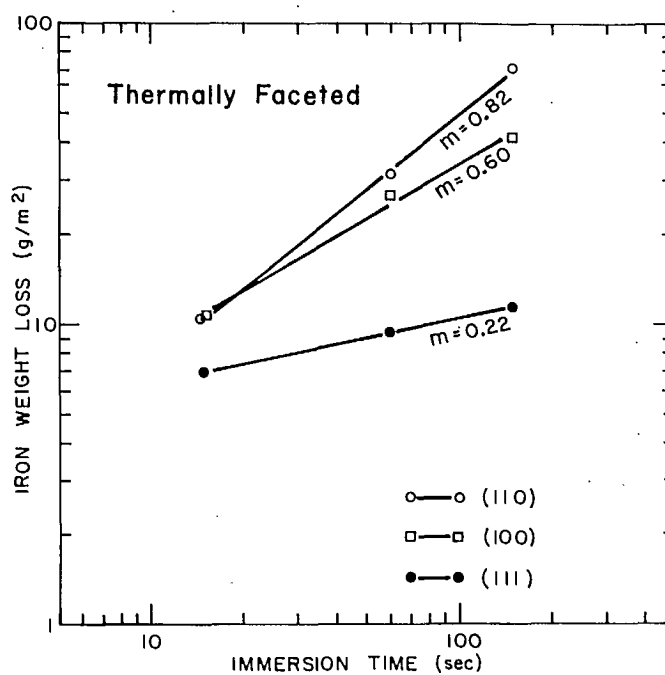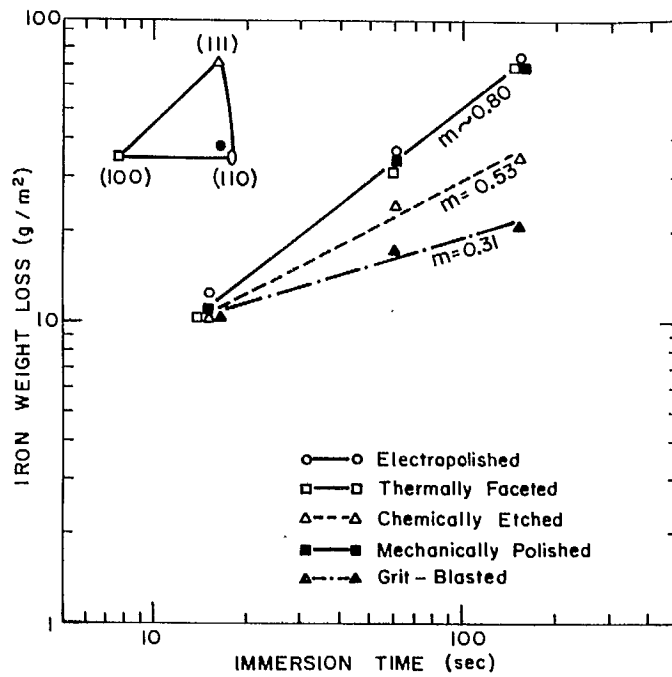

Figure 6. Iron loss vs. immersion time for Cleveland (111) and Cambridge (100) and (110) crystals with thermally faceted surfaces.
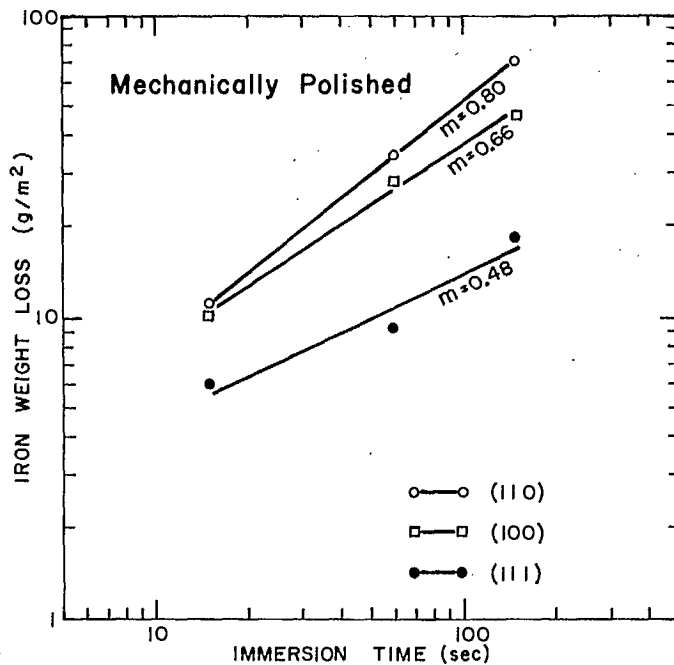
Figure 7.   Iron loss vs. immersion time for Cleveland (111) and
            Cambridge (100) and (110) crystals with mechanically
            polished surfaces.
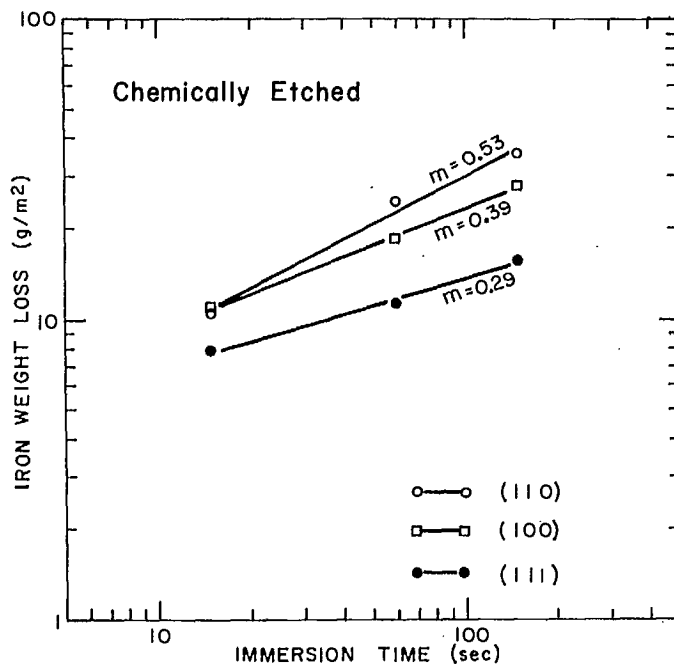
Figure 8.   Iron loss vs. immersion time for Cleveland (111) and
            Cambridge (100) and (110) crystals with chemically
            etched surfaces.
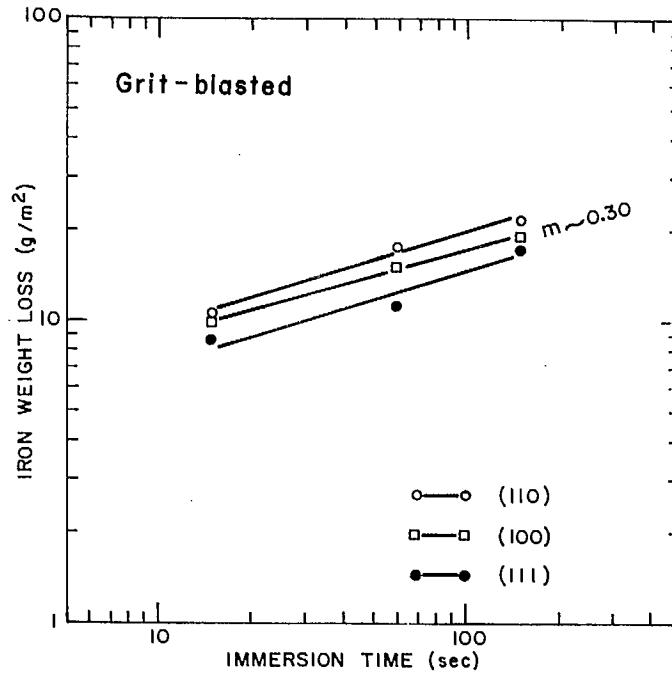
Figure 9. Iron loss vs. immersion time for Cleveland (111) and Cambridge (100) and (110) crystals with grit-blasted surfaces.

Figure 10. Iron loss vs. immersion time for Cambridge (110) crystals with surface treatments as indicated.
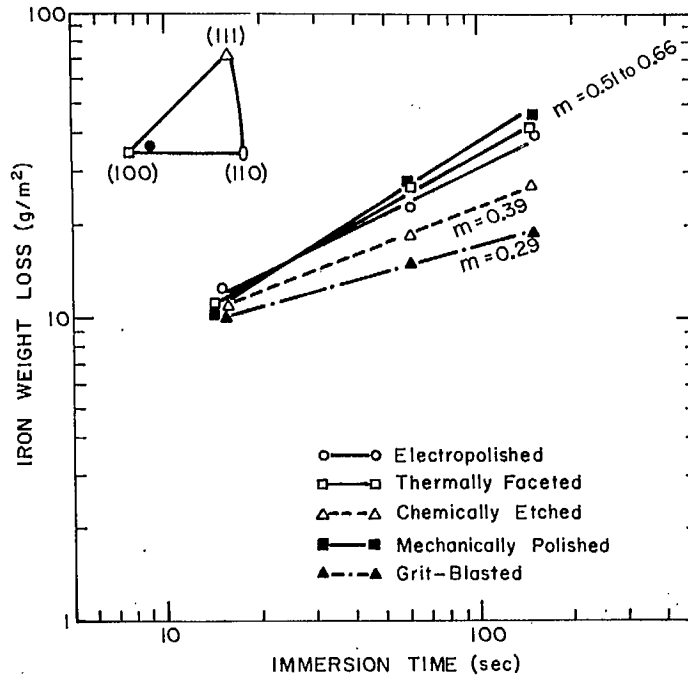
Figure 11. Iron loss vs. immersion time for Cambridge (100) crystals with surface treatments as indicated.
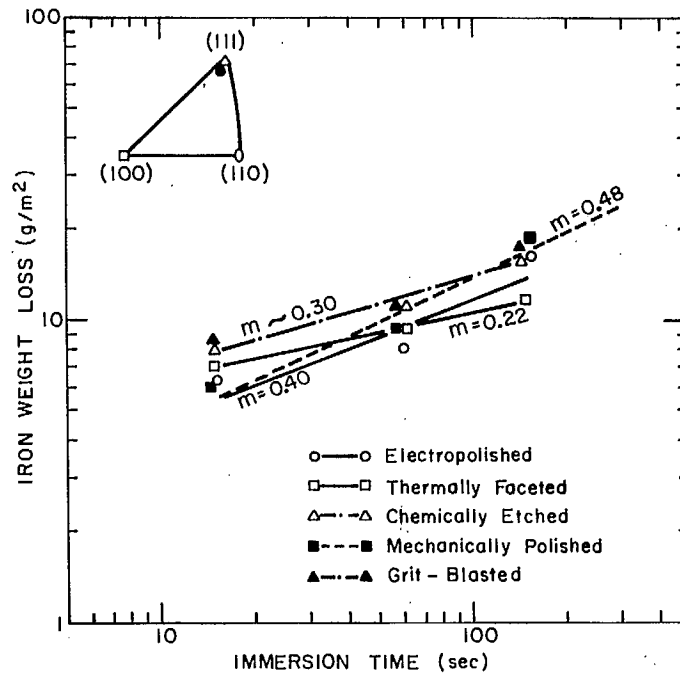
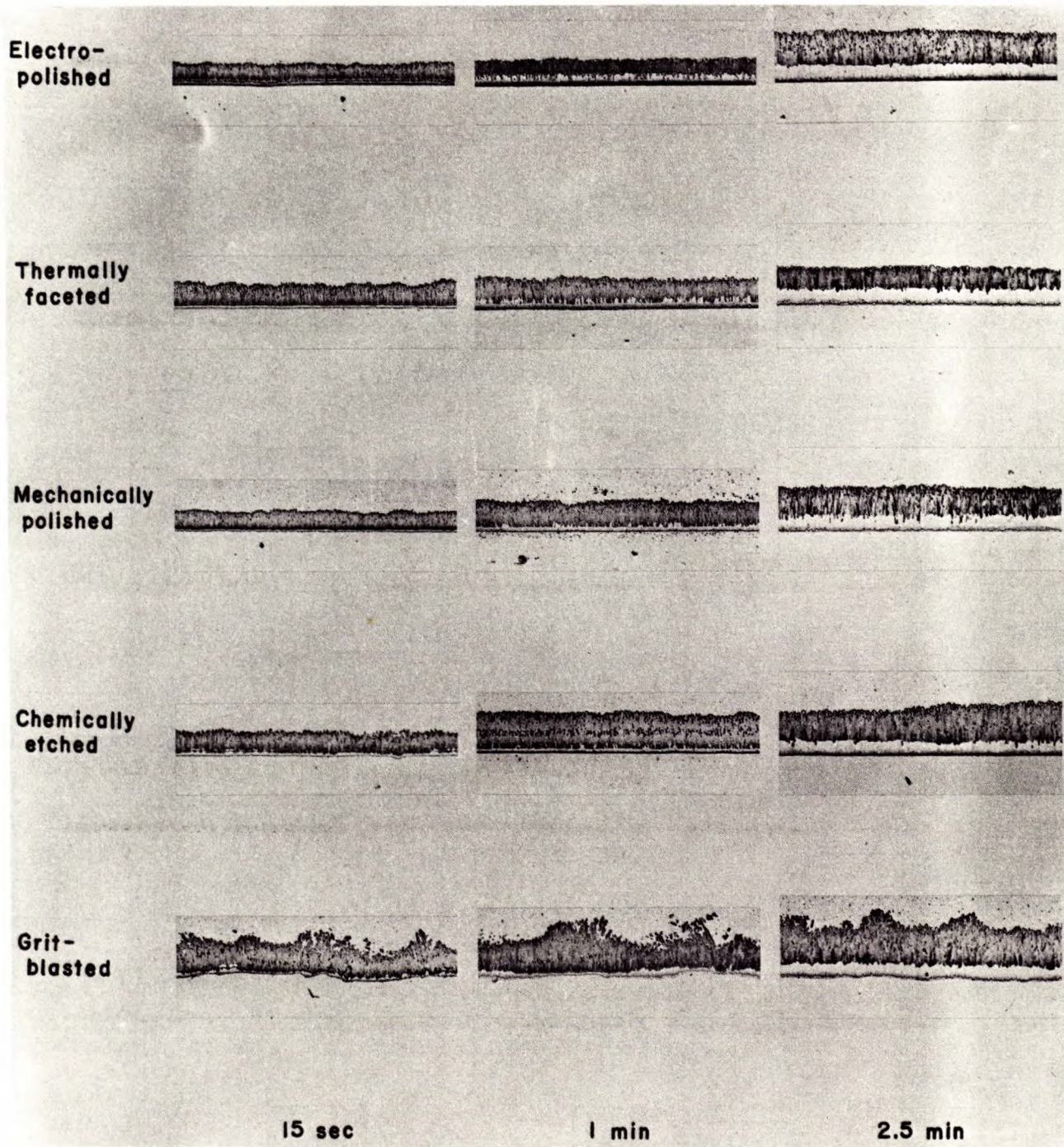Figure 12. Iron loss vs. immersion time for Cleveland (111) crystals with surface treatments as indicated.

Figure 13. Coatings on Cleveland (111) crystals at 450°C (840°F) for surface treatments and immersion times as indicated.   X 250
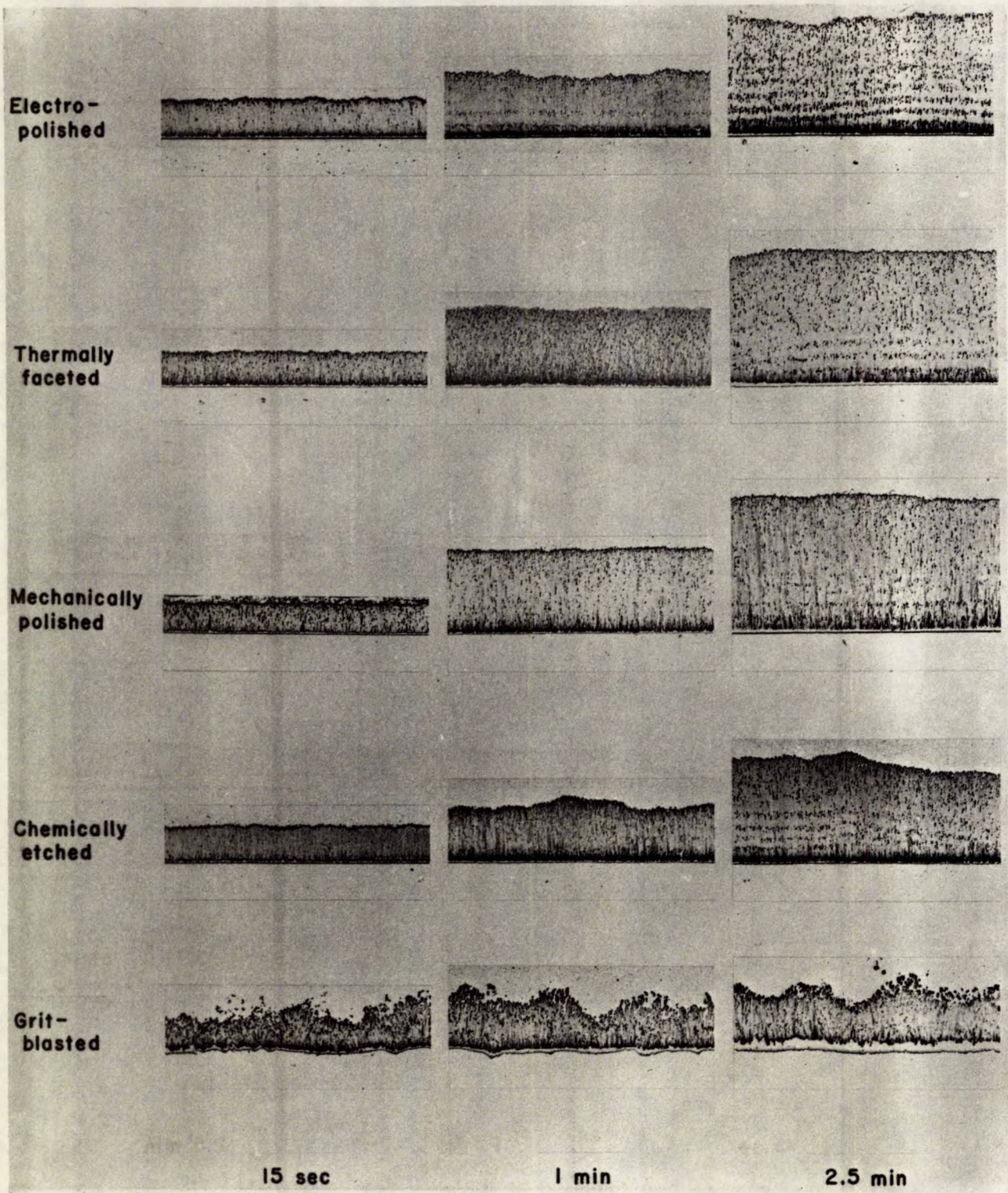
Figure 14. Coatings on Cambridge (100) crystals at 450°C (840°F)
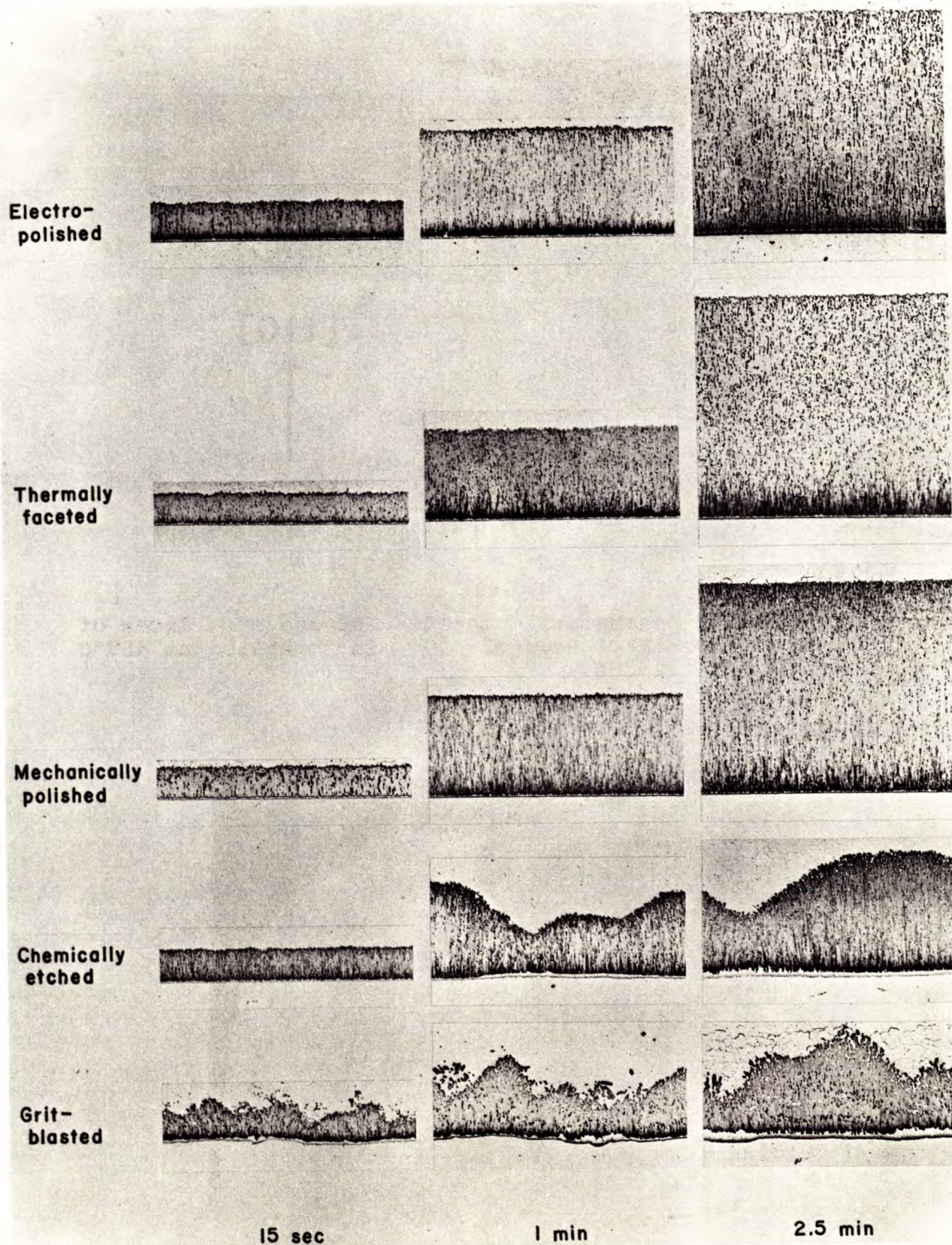for surface treatments and immersion times as indicated.
X 250

Figure 15. Coatings on Cambridge (110) crystals at 450°C (840°F) for surface treatments and immersion times as indicated. X 250
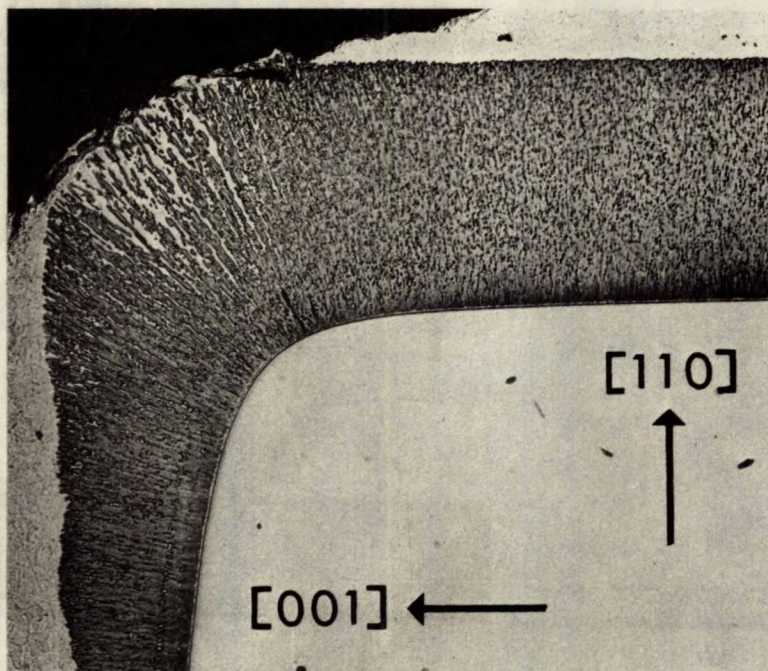
Figure 16. Coatings on thermally faceted top and side faces of Cambridge (110) crystal: 2.5-min immersion at 450°C (840°F). X 200
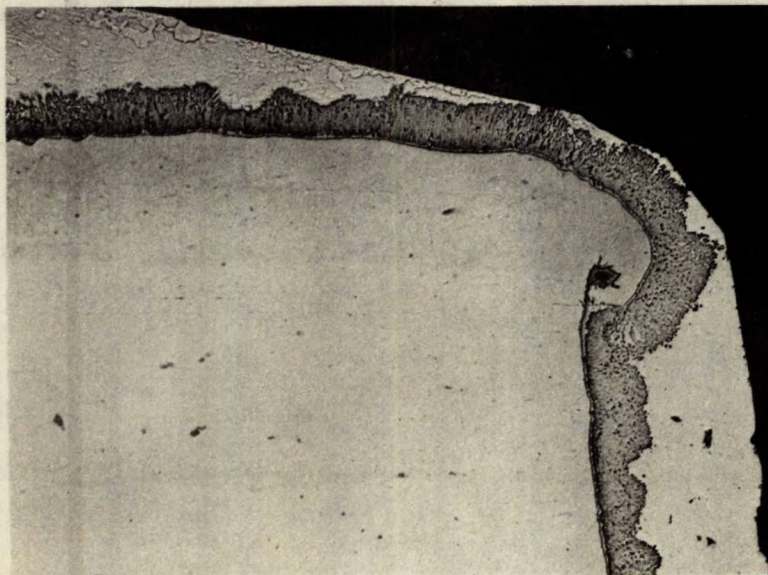

Figure 17. Coating on grit-blasted Cambridge (110) crystal showing deformation folding at edge of crystal: 15-sec immersion at 450°C (840°F). X 200