CANADA

A STUDY OF SURFACE CARBIDES, DIFFERENTIAL STEEL ATTACK AND PORE FORMATION IN THE GALVANIZING PROCESS

by

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MINES BRANCH

RESEARCH REPORT
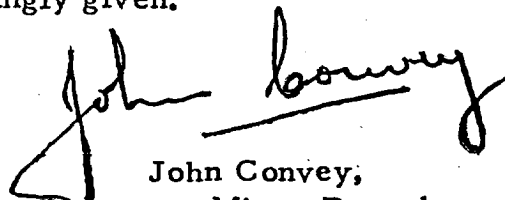
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PREFACE

The work described in this report forms part of a galvanizing project initiated in February, 1957, in co-operation with the Canadian Zinc Research and Development Committee. The Committee, which was formed in 1954, consists of members from the zinc producing and consuming industries and from interested research laboratories, including the Mines Branch.

The aims of the Committee are to develop new and improved zinc products, to improve existing techniques for the working and fabrication of zinc products, and to provide a centre for the discussion of mutual problems.

To further these aims, the galvanizing project, of which a part is described in this report, was undertaken at the Mines Branch with the assistance of the supporting companies. The Consolidated Mining and Smelting Company of Canada, Limited, Trail, British Columbia, the Hudson Bay Mining and Smelting Company, Limited, Flin Flon, Manitoba, and the Steel Company of Canada, Limited, Hamilton, Ontario, contributed towards the costs of additional staff required, and, also, supplied the special high grade zinc and steel sheet used in the project. The analytical facilities of the Consolidated Mining and Smelting Company were used to confirm some of the analyses completed at the Mines Branch, and this company also carried out the statistical work involved in the project. In order to establish the accelerated corrosion behaviour of the experimental coatings, the services of the Steel Company of Canada were utilized.

Throughout the project the guidance and assistance of the committee members were called on as required, and in all instances these were most willingly given.

John Convey,
Director, Mines Branch,
Chairman, Canadian Zinc Research
and Development Committee.

Mines Branch Research Report R 6

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ABSTRACT

An account is given of some metallographic observations made during an investigation on the influence of aluminium and lead additions on the structure and properties of laboratory-prepared galvanized coatings. The main investigation is described in a separate report.

It is shown that massive carbide inclusions present on the surface of steel sheet may have a pronounced effect on the structure of the galvanized coating. The behaviour of the carbides was found to be dependent on the temperature and aluminium content of the galvanizing bath.

Variation in galvanizing attack on two supposedly similar steels was found to be related to the type and degree of surface working. The surface of the more reactive sheet appeared to have been subjected to a rubbing or galling action during the final rolling operation.

Observations of pore defects on the surface of experimental coatings, and on commercial sheet prepared by the dry galvanizing technique, suggested that these were related to gas evolution accompanying the flux reaction.

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INTRODUCTION

A detailed study [1] on the influence of aluminium, lead, and iron on the structure and properties of galvanized coatings was undertaken in cooperation with the Canadian Zinc Research and Development Committee, a body comprising some of the major zinc producers, users, and research organizations in Canada.

In the course of this work, in which a large number of steel specimens were galvanized under different conditions in an experimental pot furnace, a number of side effects were noted which appeared to affect the quality of the galvanized coatings. The behaviour of surface carbides, differential steel attack and pore formation on the surface of experimental and commercial coatings were briefly examined.

INFLUENCE OF CARBIDES ON COATING STRUCTURE

Various investigators have stated that massive carbide particles which may occur on the surface of galvanizing grades of steel sheet are not attacked in the zinc bath. Some disagreement exists with regard to the wetting properties of such inclusions.

Observations in the detailed investigation [1] and in preliminary work leading up to it, indicated that the behaviour of carbide inclusions was markedly influenced by the galvanizing conditions. In an iron-saturated, aluminium-free bath, no apparent reaction was noted at a relatively low bath temperature (445°C, 833°F) and short immersion time. The typical behaviour is illustrated in Fig. 1 which shows a series of separated carbide particles at the steel surface. Negligible alloy formation is apparent above the carbides, which contrasts sharply with the vigorous attack of the surrounding steel surface. Under-cutting of the inclusions by the adjacent heavy attack was a characteristic feature of coating structures prepared under these galvanizing conditions.

The addition of 0.10 per cent aluminium to an iron-saturated bath effected a pronounced change in the behaviour of the carbides. The normal well-defined alloy layers which formed on a carbide-free surface in such baths were completely broken up into a loosely-packed colony of angular crystals embedded in zinc as shown in Fig. 2 (a). These exhibited pronounced columnar growth towards

the surface. Extension of such an outburst above the level of the adjacent normal alloy growth resulted in the formation of a raised pimple on the surface. Where many such pimples formed, solidification of the eta layer was apparently so affected that spangling did not take place.

Above the carbide the gamma and delta phases were replaced by a well-defined layer of a dark-etching phase. This was not identified but it was observed that the layer was formed by transformation of the carbide particle. With longer immersion times or higher bath temperatures the carbide was completely transformed. At this stage the transformation product was undermined by zinc attack of the surrounding steel, causing it to break up and float away. These effects are illustrated in Fig. 2(b).

The above observations were related to bath temperatures of 450°C (842°F) and higher. When the temperature was reduced to 435°C (815°F) in the aluminium-containing bath the carbides were again more or less inactive. The gamma and delta phases were absent and only a thin fringe of what appeared to be zeta formed next to the carbide, Fig. 2(c). On the steel surface at either side of the inclusion, well-defined iron-zinc layers were apparent.

In baths containing 0.15 and 0.20 per cent aluminium the carbides behaved in an erratic manner. In some cases the particles were not wetted by the zinc so that small bare spots or pinholes

were formed in the coating, Fig. 3(a). In others, some reaction was indicated by the presence of the typical dark-etching phase at the surface of the carbides, and the relatively large blocks of crystals above these, Fig. 3(b). Although the coatings were thin, the crystals were buried in the eta layer and did not cause pimple formation on the surface. Where a carbide was located at or near a local iron-zinc alloy growth in the coating, the structure of the growth did not appear to be appreciably affected, Fig. 3(c).

Based on these random observations it is apparent that massive carbide particles, when present on the surface of steel sheet, may or may not react with the zinc bath depending on the galvanizing conditions. In the absence of aluminium, the carbides are relatively inactive. When aluminium is added, their behaviour is dependent on the aluminium content. At a high aluminium level the carbides appear to be more or less inactive, but when the aluminium content is too low to prevent growth of the normal iron-zinc alloy layers on the steel, the activity of the carbides may or may not be extremely vigorous depending on the bath temperature. Under all conditions examined, a characteristic feature associated with the surface carbides was the complete absence of gamma and delta phases in the overlying alloy layer.

Further metallographic observations revealed the presence of massive isolated zeta crystals completely embedded in the alloy layers. These were reported by Haughton [2] and in discussion it was suggested that formation of such large crystals must be related either to the dipping time or to the degree of attack by the zinc bath. In the present work, massive isolated crystals of this type were only found in heavier coatings formed after 4 minutes immersion.

On closer study it was observed that some of the more prominent block crystals appeared to be related to the disrupted alloy structure associated with the carbide inclusions. To confirm this, various samples were lightly reground and repolished a number of times and photomicrographs taken at the different levels. A typical series is shown in Figs. 4(a), (b), (c). The isolated massive crystal formation in Fig. 4(c) is similar to that illustrated by Haughton [2]. As indicated by this series, the group of crystals shown in this latter photomicrograph appeared to be related primarily to the presence of a carbide inclusion on the steel surface, and this is supported by comparison of these photomicrographs with Fig. 2(a) (2 minute dip). In the various samples examined it could not be established that a long dipping time was solely re-sponsible for the formation of such crystals; on carbide-free sheet

subjected to similar galvanizing conditions, only a small number of isolated block crystals were observed and these were much smaller than that shown in Fig. 4(c).

VARIABLE STEEL ATTACK

In preliminary work, dipping tests on two different batches of steel revealed striking differences in galvanizing behaviour. These represented normal commercial stock of one mill processed at different times. The chemical composition of the two lots of material was almost identical, although they were not from the same heat. The No. 5 finish material from one batch was shown to be very active in the galvanizing bath. This abnormal behaviour was not evident with the No. 3 finish material from the same batch, nor with the No. 3 and No. 5 finish steels from the second batch. The chemical analyses of the various materials are given below:

	Analysis of Open Hearth Rimmed Steel Sheet		
	"Normal" Steel No. 3 finish	"Active" Steel No. 5 finish	"Normal" Steel No. 3 and No. 5 finishes
	%	%	%
Carbon	0.07	0.06	0.04
Phosphorus	0.013	0.015	0.010
Sulphur	0.030	0.033	0.026
Manganese	0.34	0.34	0.12
Silicon	-	-	0.002

Specimens of both No. 5 finish materials were galvanized under similar conditions in baths containing 0.15 per cent aluminium. Stripping tests revealed that coating weights on one lot of steel were more than twice those on the other. Micro-examination showed many separated patches of heavy alloy growth on the thickly-coated steel sheet despite the high aluminium level, Fig. 5(a). The eta layer was also very thick. The other steel represented more normal behaviour with a structure as illustrated in Fig. 5 (b). Only a thin uniform fringe of alloy was evident at the steel surface.

Macro-examination of the "as received" materials provided a probable explanation for these marked differences. In the case of the steel with normal coating structure, the surface profile imparted by temper rolling was moderately rough but uniform. On the other material the high spots on the roughened surface appeared to have been subjected to a rubbing or galling action indicating these areas had been heavily worked. It is suggested that the activity of the two steels in the zinc bath is related to the type and degree of surface working during temper rolling, assuming all other production conditions were similar. The actual physical roughness was not significant since comparison of the surface profiles with a Talysurf instrument revealed that the heavily-coated steel had a smoother surface.

PORE FORMATION

A common defect observed on experimentally galvanized panels was the occurrence of numerous small depressions or pores on the coating surface, Fig. 6(a). The most significant feature of these was their shape, and with few exceptions they resembled perfectly formed ball or oval-shaped impressions. At high magnification, one or more angular-shaped inclusions were seen to be embedded in each pore.

Micro-examination of cross-section samples confirmed that the pores were spherical or oval-shaped depressions which penetrated to various depths depending on the coating structure. In coatings where the various iron-zinc phases were present the pores seldom penetrated beyond 50 per cent of the thickness of the eta layer. Where alloy growth had been suppressed and the coating consisted essentially of zinc, the pores were of varying depth; in isolated cases, particularly when such coatings were very thin, the base of the pore was only slightly separated from the steel surface. The embedded inclusions were revealed to be particles of the zeta phase which had floated away from the alloy layer. As illustrated in Fig. 6(b), the size and shape of the inclusions corresponded to the fringed structure of the zeta layer, and the etching behaviour was also similar.

Specific dipping tests were not run to study the galvanizing factors which affected pore formation and distribution. However, examination of numerous specimens indicated that low density pre-fluxing solutions, fast withdrawal speed, long immersion times and agitation of specimens during immersion did effect a reduction in the number of pores formed. Time did not permit study of the particular influence and importance of each of these variables.

On the basis of the observations made, it is suggested that the pore defects must be related to gas bubbles originating from fusion of the flux layer on the steel. This is substantiated by the fact that pores were not evident on sheet galvanized by the Sendzimir process but could be found on commercial sheet processed by the pre-flux dry galvanizing technique.

It is not known by what mechanism the gas bubbles become attached to the coating surface. This might occur by pick-up from the bath which must become heavily contaminated with gaseous products from the flux fusion. Alternatively, attachment of gas bubbles to the steel during melting of the flux and eventual rejection of the bubbles to the coating surface could account for the depressions formed. Presumably loose particles of the zeta phase in the bath or liquid galvanizing layer attach themselves to the gas bubbles which accounts for their presence in the solid pores.

In a recent survey, Hughes [3] refers to two investigations which indicated that small uncoated spots or "pores" may not have much harmful effect on the corrosion behaviour of galvanized coatings. If this is correct, the shallow type depressions described above, which did not penetrate to the steel surface, may be of academic interest only. However, since the corrosion life of zinc coatings is directly related to their thickness and uniformity, the occurrence of such discontinuities cannot be entirely disregarded until their behaviour is clearly established.

SUMMARY

As an offshoot of a more detailed investigation, the effects of massive surface carbides on the structure of the galvanized coating, and the phenomena of differential steel attack and pore formation on the galvanized surface were examined with the following results:

In all cases where massive carbides were present on the surface of the steel sheet, there was no gamma or delta phase in the alloy overlying the carbide. In iron-saturated baths with nil or high aluminium, the carbides were relatively unreactive and in some cases with high aluminium, the carbides were not even wetted giving rise to bare spots in the coating. At intermediate aluminium

content (0.1 per cent) and at temperatures above 450°C (842°F) in iron-saturated baths, the carbides reacted vigorously with the zinc to give massive zeta crystals in the coating, and a transformation product on the surface of the carbide. At lower temperatures (435°C, 815°F) the carbides were again relatively unreactive.

The difference in coating weights, obtained under identical galvanizing conditions on two supposedly similar steel sheets, was related to excessive rolling and smearing of the high spots on the surface of the more reactive steel sheet.

Examination of pore defects on the surface of experimental and commercial, flux-galvanized material showed that the pores were shallow depressions associated with small particles of zeta phase. It is suggested that these pores were formed by gas evolution due to flux reaction either within the bath or on the surface of the steel during the galvanizing operation.

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(2) M. A. Haughton, The Effect of Aluminium and Iron on the Structure of Galvanized Coatings. Proc., Second International Galvanizing Conference, publ. by Zinc Development Association, London, 59-83 (1953).

(3) M. L. Hughes, Hot Dip Galvanizing 1946-1956. Paper MW/C/43/56, British Iron and Steel Research Association, London (1956).

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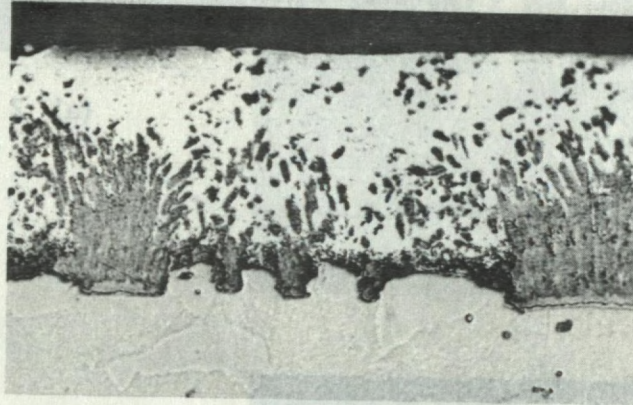
X750, nitramyl and picral etch.

Fig. 1. - Negligible reaction of carbides in aluminium-free bath. (Carbides are shown as structureless grey particles in steel matrix.) 0.5 minute dip at 445°C (833°F) in bath containing 0.5% Pb, 0.03% Fe.
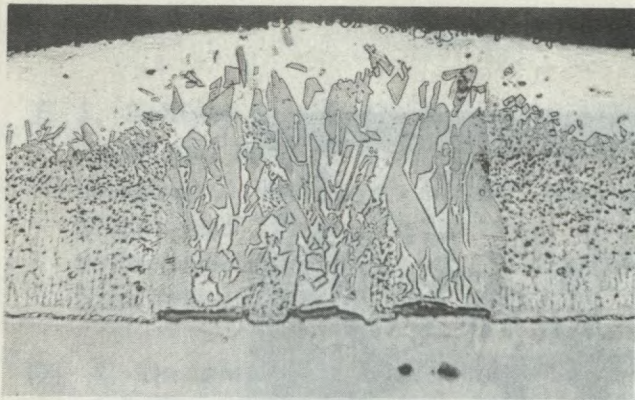
(a) 2 minute dip at
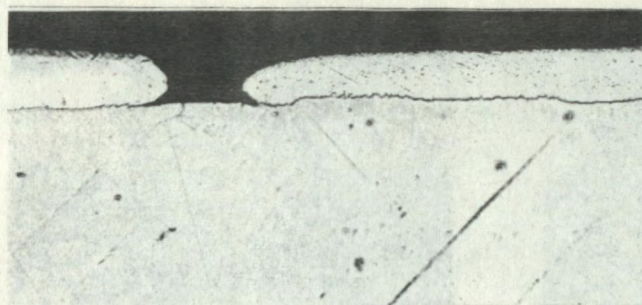   450°C (842°F)
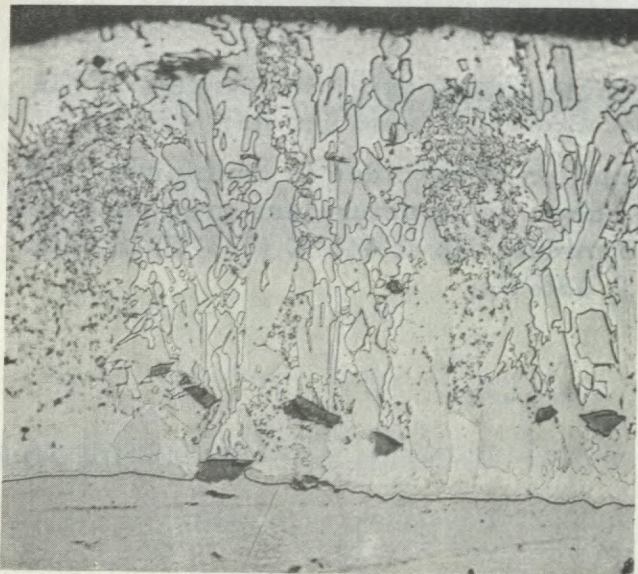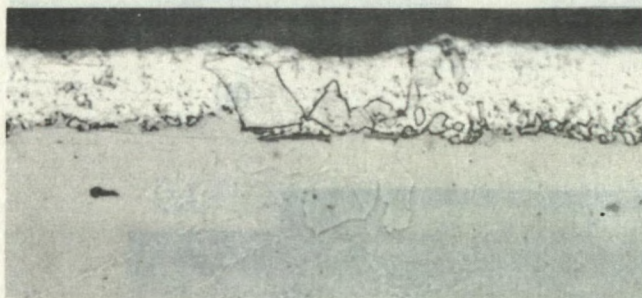
(b) 4 minute dip at
      455°C (851°F)
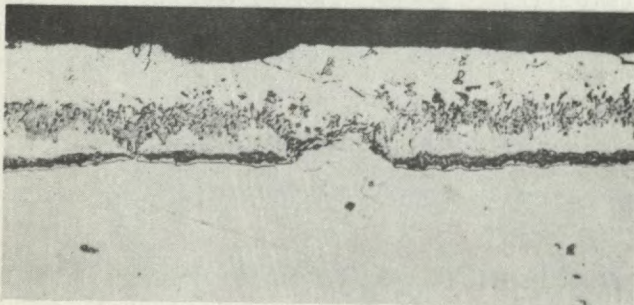
(c) 1 minute dip at
      435°C (815°F)

Fig. 2. - Behaviour of carbides in aluminium-containing bath (0.1% Al,
   0.5% Pb, 0.03% Fe). X500, nitramyl and picral etch.
   (a) Pronounced outburst of columnar crystals due to presence of
        carbides which have partially transformed.
   (b) An advanced stage of carbide transformation at long immersion
        time, showing break-up and floating away of dark-etching
        transformation products.
   (c) No apparent reaction of carbides at low bath temperature.

(a) X500, nitramyl etch.
1 minute dip at 455°C
(851°F).
Bath composition:
0.2% Al, 0.03% Fe.

(b) X750, nitramyl etch.
2 minute dip at 450°C
(842°F).
Bath composition:
0.15% Al, 0.75% Pb,
0.03% Fe.
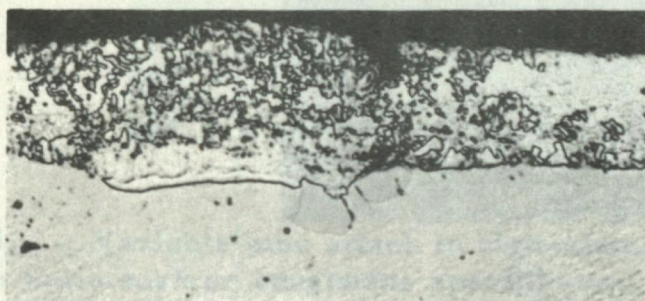
(c) X750, nitramyl etch.
2 minute dip at 450°C
(842°F).
Bath composition:
0.15% Al, 0.75% Pb,
0.03% Fe.
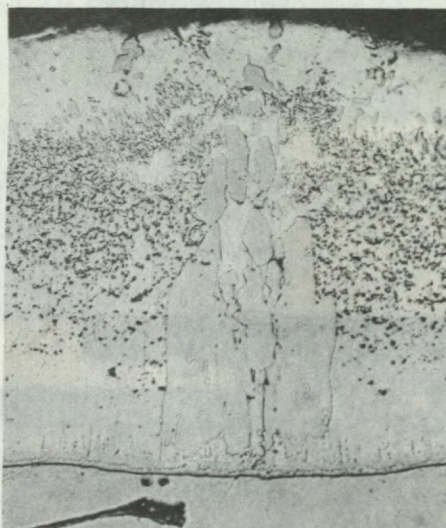
Fig. 3. - Behaviour of carbides in high-aluminium baths.
(a) Carbide not attacked or wetted, causing bare spot in coating.
(b) Block crystal growth in coating, indicating reaction between
carbide and zinc bath.
(c) Little or no effect of carbide adjacent to local iron-zinc
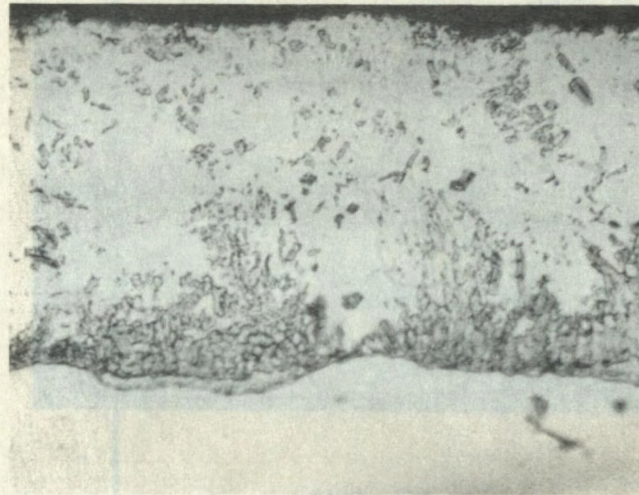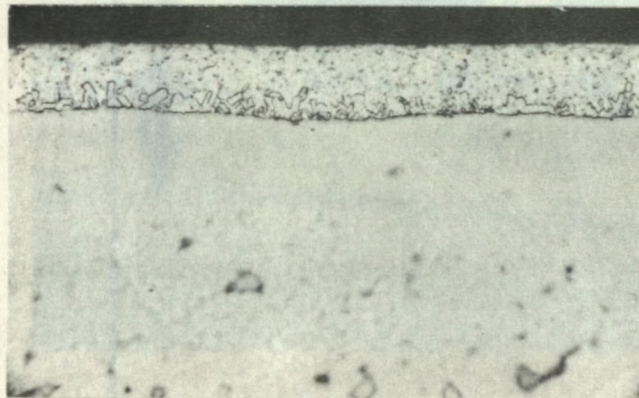growth.

(a)

(b)

(c)

Fig. 4. - Structures at different levels through single iron-zinc alloy
outburst, showing that the massive isolated crystals in (c) are
related to the presence of carbide particle on the steel surface.
4 minute dip at 455°C (851°F). Bath composition: 0.1% Al,
0.5% Pb, 0.03% Fe.

(X500; nitramyl and picral etch.)
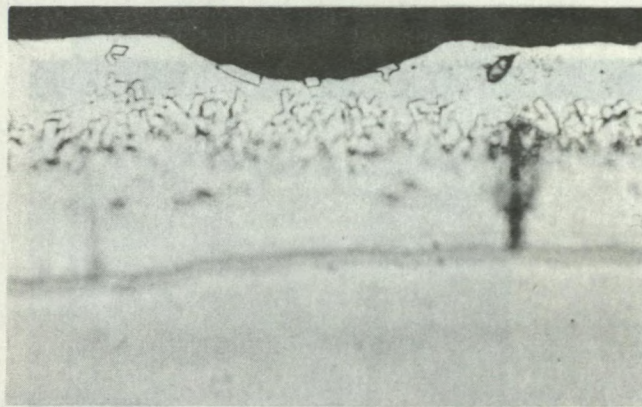
(a) X750; nitramyl
    and picral etch.

(b) X750; nitramyl etch.

Fig. 5. - Variable zinc attack in high-aluminium bath of steels processed
   to same surface roughness specification. 2 minute dip at 450°C
   (842°F). Bath composition: 0.15% Al, 0.75% Pb, 0.03% Fe.
        (a) Extensive iron-zinc alloy growth and very heavy coating on
            smoother but more reactive steel.
        (b) Normal coating on steel with rougher "as received" surface
            finish.
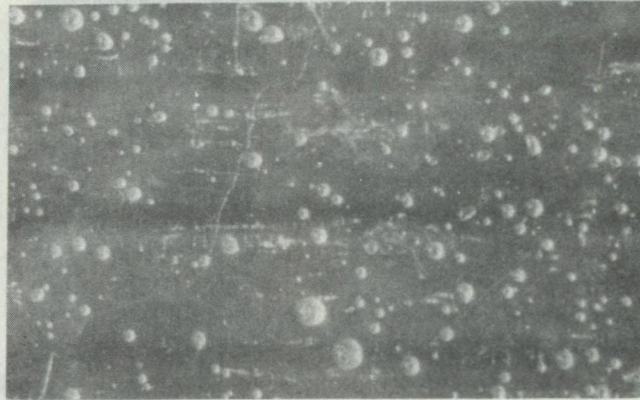
(a) X30.

(b) X1000, nitramyl etch.

Fig. 6. - (a) Typical pore depressions on coating surface.
(b) Structure through pore, showing penetration into eta
layer and embedded zeta crystals at the pore
periphery.

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