INDUSTRIAL CONFIDENTIAL

ELEVENTH GALFAN
SHEET LICENSEES MEETING
MINUTES

January 20-21, 1988

Reims, France

INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION, INC.

GALFAN TECHNICAL RESOURCE CENTER

2525 MERIDIAN PARKWAY
POST OFFICE BOX 12036
RESEARCH TRIANGLE PARK, N.C. 27709-2036
TELEPHONE 361-4647 (AREA CODE 919)
TELEX 261533
FACSIMILE (919) 361-1957

MINUTES OF THE ELEVENTH GALFAN SHEET LICENSEES MEETING

January 20-21, 1988

Altea Champagne Hotel
Reims, France

ATTENDANCE January 20, 1988

Name	Company
Anderson, D.	Laporte R & D
Arvidsson, E.	Plannja, SSAB
Ayoub, C.	C.R.M.
Barzoukas, H.	Galvanor Ziegler
Billiet, J.	Floridienne Chimie
Bourke, W.	New Zealand Steel
Brannstrom, B.	Plannja, SSAB
Brinsky, J.	Weirton Steel Corporation
Brugarolas, J.	Procoat
Celestin, A.	Weirton Steel Corporation
Colle, J.M.	Eurinter
Coutsouradis, D.	C.R.M.
D'Autilia, A.	ICMI
deWitte, M.	Bekaert
Durand, G.	F.F. Maubeuge
Ewing, R.	Weirton Steel Corporation
Franco, S.	Procoat
Frommann, K.	Mannesmann DeMag
Furken, L.	Hoesch - Stahl AG
Goodwin, F.	ILZRO, Inc.
Graham, E.	New Zealand Steel
Harrison, F.	Stelco, Inc.
Hatano, Y.	Nippon Denro Mfg. Co.
Hennechart, J.	Galvanor Ziegler
Hirose, Y.	Nisshin Steel
Hoboh, Y.	Sumitomo
Hostetler, J.	Hostetler & Decker
Howard, M.	Coil Steels Group
Hubert, R.	Arbed Research
Huvet, J.	Forger d'Haironville-Galvameuse
Jones, D.	British Steel Corporation
Jones, R.	University of Wales, Cardiff
Jossic, T.	Galvanor Ziegler
Kamimura, I.	Nisshin Steel
Kim, Y.	Inland Steel Co.
Kitada, M.	Kawatetsu Galvanizing Co., Ltd.

Name	Company
Klotzki, H.	Thyssen
Kosaka, K.	Nippon Kokan, K.K.
Kubiak, B.	Penarroya
Lindfors, T.	Rasmet Co.
Lindstroem, M.	Rautaruukki Oy
Maslet	Galvanor Ziegler
Massinon, D.	IRSID
Migliardi, M.	Aceros Revestidos
Molin, B.	SSAB
Naidu, R.	New Zealand Steel
Okamoto, N.	Kawasaki Steel
*Parkinson, R.	Falconbridge
Patil, R.	Inland Steel Co.
Pelerin, J.	Phenix Works
Petsch, N.	Salmax
Pierre, M.	Centre du Zinc
Polard, V.	Phenix Works
Pomp, R.	Mannesmann Demag
Renaux, B.	C.R.M.
Robertson, I.	Coil Steels Group
Roman, M.	ILZRO, Inc.
Schmitz, O.	Thyssen
Schoen, L.	SSAB
Schwarz, W.	Hoesch Stahl AG
*Sempels, R.	Vieille-Montagne/Belgium
Sippola, P.	Rasmet
*Sokolowski, R.	Vieille-Montagne/France
Solano, F.	Ensidesa
*Southern, J.	AM&S Europe
Sphener	Galvanor Ziegler
Splitt, M.	Thyssen
Stoneman, A.	Zinc Development Association
Suzuki, T.	Nippon Denro Mfg. Co.
Szydlik, A.	Salmax
Toomer, I.	Palmer Tube/Zinctek
Valdor, R.	Ensidesa
Veta, T.	Galvanor Ziegler

*ILZRO Member

INTRODUCTION

The meeting was convened at 9:30 a.m. by Mr. Roman, the Chairman, who also recorded the minutes. Mr. Roman first thanked Galvanor Ziegler for their hospitality and organization during the plant tour of their Mouzon Works the previous day. Mr. Roman noted that such a tour always contributes to the success of a conference such as this. Mr. Roman also then apologized for the apparent lack of space, although everyone was able to find a seat, there was approximately 72 people when only 55-60 were expected, and reflected the growing success of GALFAN and the GALFAN Licensee Meetings. Mr. Roman then showed a slide of all 37 process licensees and welcomed the three newest sheet licensees and their representatives to Reims. He first welcomed Coil Steels Group in Australia, represented by Mr. Ian Robertson and Mr. Merton Howard; he then welcomed Mr. Kosaka from Nippon Kokan K.K. in Japan. Mr. Roman also noted that An Mau Steel in Taiwan is now a licensee but could not send a representative to this meeting. Mr. Roman then noted that the third edition of the GALFAN manual, "GALFAN, Galvanizing Alloy & Technology" was now in the publication stage and would soon be available. Mr. Roman introduced Dr. Frank Goodwin, Vice President, ILZRO, at this point. Dr. Goodwin also welcomed all to Reims and echoed the sentiment of GALFAN's growth and the size of the meeting. Dr. Goodwin took the opportunity to welcome the ILZRO members to the GALFAN Licensees Meeting (those members are * in the attendance roster). Mr. Roman then asked all attendees to please introduce themselves to each other, one at a time, and then circulated the attendance roster.

OPERATIONS SESSION

Galvanor Ziegler

Mr. Roman introduced Mr. Hennechart from Galvanor Ziegler (the new name for Ziegler S.A., explained in a letter reprinted in appendix) who presented his report on operations at the Mouzon Plant. The entire text of Mr. Hennechart's presentation is reproduced in the appendix to these minutes. Some of the highlights of the presentation were: The Mouzon Plant was the first in the world to carry out an industrial pilot trial in July of 1981. Commercial production of GALFAN commenced in December of 1983. Ziegler also has capability to produce GALFAN via the Zinquench process.

Mr. Hennechart came to four main conclusions as listed below

1. Galvanor Ziegler has decided to use the Zinquench process to improve strip weldability and coating quality.

2. The low bath temperature used in the Zincquench process also makes strip minimization more easily achieved.

3. For light coatings, 100 to 120 grams per square meter, GALFAN surface quality is very good and may be skin passed on the temper mill and used for exposed parts after painting.

4. For heavier coating weights, 150 to 255 grams per square meter, surface quality is good for painting.

Mr. Ayoub questioned Mr. Hennechart about the dry process used for strip minimization. Mr. Hennechart replied that there was a need for very small water droplets for strip minimization in that they must avoid coalescence and free water which would drip into the pot itself. The dry process is desired to avoid any water problems. Dr. Hirose asked Mr. Hennechart what type of material was used for their heat exchanging equipment on the GALFAN bath pot. Mr. Hennechart replied that it was 316L stainless steel. Dr. Hirose also inquired as to the life expectancy of that equipment. Mr. Hennechart replied it should be two to three years in the bath. Dr. Hirose then asked if he had correctly heard that the dross generation was very low for the Mouzon Plant. Mr. Hennechart noted that he was correct but reminded him that Galvanor Ziegler runs short campaigns so there is not much chance for dross generation. He said the low bath temperature prevents iron from reacting to form very much zinc, however, the low iron content of the bath does tend to dissolve the stationary strip causing line stop problems. Mr. Patil of Inland Steel asked about the reason for only one deflector roll in the pot. Mr. Hennechart replied that the pot was just too full of equipment in and around the area and they could not fit another deflector roll in it.

ICMI Operations Report

Mr. Roman introduced Mr. A. D'Autilia from ICMI who presented the report on Cantieri's initial GALFAN trial in July of 1987. Mr. D'Autilia's report text is reproduced in its entirety in the appendix of these minutes. Highlights of the report were:

1. 2500 tons of GALFAN coated product were produced for prepainted applications. Coils were temper rolled and oiled for that application. The material was the thickness of 0.67 mm to 0.97 mm with strip widths of 895 mm to 1,265 mm. Mr. D'Autilia indicated that Cantieri felt that the first campaign was very satisfactory and ICMI would also like to pass on thanks to C.R.M. personnel who assisted in the start-up trial. Mr. D'Autilia said that there are several aims for future trials, two of them were to reduce the down time necessary to switch from galvanized to GALFAN and back to galvanized and also another aim was to produce GALFAN with an aluminum level of 4.4% for painted product.

Mr. Graham of New Zealand Steel asked what the actual down time for switching products was. Mr. D'Autilia noted it was a total of fifty hours; twenty-five hours to convert to GALFAN, twenty-five hours to convert back to galvanized. Dr. Goodwin asked if the time involved in that switch was limited by the pump capacity or was it limited by the melt time of the GALFAN alloy. Mr. D'Autilia replied that it was the pump capacity that was responsible for the long switch time. Currently they can only pump 200 liters per minute of alloy and would desire a larger capacity pump. Mr. Toomer asked if the coating weights (see appendix) were for one side or two side. Mr. D'Autilia replied it was two side coating weight. Mr. Stoneman asked about possible visual differences between product produced at 4.4% and 4.8% during the campaign.

Mr. D'Autilia replied that there was some visual difference which they are still investigating. Mr. Pelerin asked if Cantieri used the same minimizing device for GALFAN as used for galvanizing. Mr. D'Autilia replied that it was the same minimizing device (air and water) however ICMI encountered a problem with water drops and had to temper roll the material. Mr. Hennechart inquired as to the iron content in their alloy bath. Mr. D'Autilia replied that it ranged from 0.1 to 0.18%.

Hoesch Stahl Operations Report

Mr. Roman introduced Dr. Lutz Furken of Hoesch Stahl who presented the operations report for Hoesch Stahl.

Dr. Furken began by showing the total tonnages of GALFAN produced by Hoesch Stahl from 1983 through the present date. In 1983 Hoesch had two campaigns producing a total of 550 tons. In 1984 there were two campaigns producing a total of 4,060 tons. In 1985 three campaigns produced 8,120 tons. Four campaigns in 1986 produced 14,170 tons, and four campaigns in 1987 produced 15,580 tons. One campaign so far in January 1988 has produced almost 6,000 tons of material. Dr. Furken indicated that Hoesch Stahl may expect to produce at least 20,000 tons of GALFAN product in 1988.

Dr. Furken went into detail about that January 1988 campaign of GALFAN. Hoesch Stahl produced almost 6,000 tons of GALFAN between January 4th and January 13th of 1988, with a 31.7 tons per hour production rate. Hoesch produced steel qualities of that of lock forming quality, drawing quality, special drawing quality drawing, and structural qualities. Of those 6,000 tons, approximately 2400 tons were temper rolled on line and the balance produced was temper rolled off line. Gauges produced were in the range from 0.5 to 2.0 mm. Bath temperature for the trial ranged from 430° to $470^{\circ}C$. The strip temperature in the heating section of the furnace ranged from 500° to $560^{\circ}C$. Average bath analysis was 4.4% aluminum with 0.04% cerium and lanthanum. Coating weights produced were in the range of 95 to 300 grams per square meter. Dr. Furken noted that one of the more important aspects of production realized so far at Hoesch was the relationship of wiping with air and wiping with nitrogen (Hoesch Stahl utilizes a Mannesmann Demag wiping system). Dr. Furken showed a slide of a relationship between the wiping pressure in millibars versus the line speed achieved for GALFAN with various isobars of specific coating weights. He noted that at approximately 60 millibars pressure was the cut-off line for using air wipe and nitrogen wipe. That is at pressures under 60 millibars, air wiping is acceptable. At pressures over 60 millibars, nitrogen wipe is necessary to avoid wiping related surface defects such as ripples and tears.

Dr. Furken noted that the main defect seen at Hoesch Stahl for GALFAN are:

1. deep grain boundaries (i.e. grain boundary dents);
2. ripples and tears ;
3. bare spots.

Some of the things that Hoesch Stahl is working on to avoid those defects are:

1. to avoid grain boundary dents, Hoesch is lowering the bath and ingot aluminum to achieve a hypo-eutectic structure. They find this as a good surface for painting and have less GALFAN alloy pickup on their skin pass rolls. Dr. Furken then showed several samples of varying aluminum content.

2. to avoid ripples and tears, Hoesch is wiping with air at high pressure and moving on to a nitrogen wipe, however they do have problems achieving heavy coating weights or reducing the line speed when using nitrogen wipe. Dr. Furken again showed some samples of these defects.

3. to avoid bare spots, which is caused by poor wettability, Hoesch can reduce line speed, however Dr. Furken noted that the best way to avoid bare spots is to have a clean incoming steel surface and to use proper furnace practice, that is: good atmosphere and proper (dry) dewpoints. Again Dr. Furken showed samples of these defects.

Dr. Furken then reported on oncoming improvements at Hoesch Stahl. In August of 1988, they will use a quick change two-pot system. It is noted that Hoesch will be at that time, producing GALFAN, galvanize, and Galvalume. The changeover time from galvanize to GALFAN is now sixty hours. With the new system, they expect to reduce that switch time to three hours when switching from GALFAN from Galvalume (in which case they would just switch two portable pots). The switch from GALFAN to galvanize would be approximately 4.5 to 5 hours (same pot would be used - the GALFAN would have to be removed and pure zinc would have to be pumped in). Dr. Furken also noted that later in 1988 Hoesch would install a new wiping system which would utilize two stabilizing rolls in the pot. Also Hoesch intends to improve their pot cooling capabilities. Dr. Furken noted that GALFAN is now produced at their Eichen #2 hot dip galvanizing line. Production at Eichen commenced in 1986. That line has a capacity of maximum width of 65 inches. Dr. Furken concluded by noting that one of the biggest aims of Hoesch Stahl was to improve in-house quality in that they desire to improve the strip cleanliness as well as improve their in-line temper rolling process.

Dr. Patil asked Dr. Furken if Hoesch Stahl currently had in-line chem-treat (chromating) capability. Dr. Furken replied that there was not. A question was raised if Dr. Furken could re-explain the new pot exchange system. Dr. Furken indicated by showing his slide that there were two main pots, each of which could be moved on or off line in a short amount of time. One pot would be for high zinc products, galvanized and GALFAN; the other pot would be strictly for Galvalume only. The high zinc pot sharing GALFAN and galvanize would be supported by two pre-melt pots, one for pure GALFAN and one for pure zinc which would then serve as transfer pots when switching from two and from GALFAN and galvanized. The Galvalume pot is strictly independent of the high zinc products. Dr. Furken was asked if there was any difference seen between mechanical properties of the steels produced for GALFAN and galvanized, referring to SQ, LFQ, FLQ, CQ, DQ. Dr. Furken replied that there was no apparent mechanical property difference. Dr. Furken was asked if there was any lead used in their galvanizing. Dr. Furken replied that Hoesch Stahl uses low lead zinc for their GALFAN, galvanizing pot and always maintains a low lead level. Dr. Furken was asked if in addition to nitrogen wiping, if they had a nitrogen shroud, similar to that seen at the Mouzon Works the previous day. Dr. Furken replied that only nitrogen is used in the air knives. Dr. Furken was then asked how Hoesch Stahl maintained the low bath temperature. Dr. Furken replied that a strip is cooled at much as practically possible in their jet cooling system. However, currently Hoesch Stahl can not cool the bath. Mr. Hostetler asked if Dr. Furken could repeat the critical air pressure as shown previously. Dr. Furken repeated if was approximately 50 to 60 millibars where the transition from air to nitrogen wiping was made. Mr. D'Autilia asked what the pot for the standby GALFAN was made of. Dr. Furken replied it was Armco iron coated with stellite. When a GALFAN campaign is complete, the GALFAN alloy is pumped into its standby pot and kept warm. If there is an extended time period between GALFAN campaigns, the GALFAN alloy is allowed to solidify in the standby pot and remelted when necessary. If necessary, the alloy in the standby pot can be cast into ingots. Mr. Hennechart asked if Hoesch Stahl measured the temperature of the air or the nitrogen which was used for wiping. Dr. Furken replied that they did not. Dr. Patil asked what the knife profile was. Dr. Furken replied that the gaps for the knives were 2.5 mm at the edges and 1.5 mm in the center. A question was asked of Dr. Furken if Hoesch Stahl could run full hard material. Dr. Furken replied they do not currently produce full hard, however they don't expect to encounter any problems should they decide to do so. Dr. Furken was asked to repeat the dross production and he said that it was 1 Kg/ton of product produced.

Weirton Steel Corporation Operations Report

Mr. Roman introduced Mr. James Brinsky of Weirton Steel who presented the Weirton Steel production report. Mr. Brinsky noted that Weirton Steel was at the time of the meeting in Reims, producing GALFAN and expected that campaign to produce 2,000 tons. Mr. Brinsky noted that later in 1988, Weirton Steel would begin operations with increased size capability. Currently their maximum width is 42 inches (1067 mm). They expect to expand that to 48 inches (1219 mm). Currently the heaviest gauge produced at Weirton for GALFAN is 0.07 inches (1.78 mm). Weirton expects to increase that capability to as high as .168 inches (4.27 mm). Mr. Brinsky noted that in the near future, Weirton Steel desires to experiment with lower aluminum levels. Currently they produce GALFAN with aluminum levels of 4.7 to 5.2% and they would like to try varying aluminum levels down to 4.0%. Mr. Brinsky also noted that Weirton Steel will be working to reduce their switch time for galvanized to GALFAN and back. It is now 48 hours total for the switch from galvanized to GALFAN they feel they can reduce that time to 16 hours and the current time for the switch from GALFAN to galvanized is now 24 hours. Mr. Brinsky felt that time could be reduced to 16 or even 8 hours. A large part of this improvement will come from the installation of a pre-melting pot for the GALFAN alloy.

RESEARCH SESSION

The research session chaired by Dr. Frank E. Goodwin, commenced with the C.R.M. research reports first on grain boundary dents and then corrosion studies.

Grain Boundary Dents

Dr. Goodwin introduced Mr. Bruno Renaux of C.R.M. who presented his results on the study of grain boundary dents. The entire text and slides presented by Mr. Renaux are reproduced in the appendix of these minutes for accuracy. In the text of the report, each slide is referred to as "D1 through 40." The work presented was extremely technical and was thoroughly explained in detail by Mr. Renaux. He concluded by noting that grain boundary dents are a problem of eutectic solidification shrinkage. The grain boundary dents increase in number as the aluminum content increases and approaches the eutectic composition. Formation of dents may be reduced by: 1)decreasing the aluminum content, yielding a greater percentage of zinc rich globules; 2)increasing the cooling rate which in turn allows distribution of other globules at the coating surface, therefore decreasing the amount of eutectic phase present at the surface. However Mr. Renaux noted that even at 4% aluminum, the problem is not completely solved. Mr. Renaux cautioned that the corrosion resistance tends to decrease in effectiveness as the aluminum content decreases.

Dr. Harrison asked if the cooling rate (slow or fast) had any difference in the formation of grain boundary dents at 4% aluminum. Mr. Renaux replied that there appeared to be no differences. There was also a question raised as to the effect of magnesium on grain boundary dents. Mr. Renaux replied that currently the effect of magnesium on grain boundary dent formation was not being studied. At this point C.R.M. and the Research Steering Committee had not considered it a significant parameter for study, however it can be considered for future study.

Corrosion Studies

Dr. Goodwin then introduced Mr. Ayoub of C.R.M. who presented his report on corrosion studies. That presentation is also reproduced in its entirety in the appendix of these minutes for the purposes of accuracy. Highlights of the presentation were the presentation of the data on the atmospheric corrosion of GALFAN, galvanized, and Galvalume coated sheets after five years. This data included thickness loss data, data on cathodic protection, the surface appearance of the exposed panels, cross section of microstructures from the exposed panels, and mechanisms of atmospheric corrosion of GALFAN, galvanized, and Galvalume via scanning electron microscopy. Mr. Ayoub also detailed the mechanisms of atmospheric corrosion of galvanized coatings. There were several specific points as listed below:

1. Corrosion in marine and industrial sites;

2. Influence of the orientation of aluminum rich lamellae;

3. Corrosion through dents and grain boundaries;

4. Corrosion induced by the presence of zinc rich globules.

Mr. Ayoub finished by listing conclusions on the atmospheric ... first GALFAN coatings and then Galvalume coatings. His conclusions were:

1. From first observations, corrosion seems to be conditioned by:

   a. the orientation of aluminum rich lamellae, the horizontal direction providing the lowest corrosion rate;

   b. the concentration of zinc rich globules, thus the aluminum content;

   c. the dents and boundary shrinkage densities to a lesser extent; and

   d. the lead content.

2. The orientations of these lamellae could be influenced by:

   a. the heat flow during solidification of the coating i.e. the cooling rate;

   b. the presence of zinc rich globules, i.e. the aluminum content.

3. Also, grain boundary dents and boundary shrinkage seems to occur ...

   a. the aluminum rich lamellae between two adjacent cells are differently oriented; and

   b. these lamellae tend to be vertical at cell boundaries.

Mr. Ayoub's conclusions for Galvalume coatings are:

1. Normal corrosion occurs in two steps:

   a. corrosion of inter-dendritic zinc rich phases;

   b. corrosion extends to the aluminum rich dendrite. This second step is slower than the first one.

2. Local failure phenomenon due to:

    a. the insolubility and the increased volume of the inter-dendritic corrosion products, leading to stresses in the coating;

    b. presence of a brittle secondary intermetallic phase as a discontinuous layer between the primary intermetallic and the coating and also as sharp shaped phases within the coating; and

    c. low formability of the Galvalume coatings which can not accommodate the internal stresses generated.

Dr. R. D. Jones asked if the migration of Al_2O_3 was related to chromation on these coatings of GALFAN. Mr. Ayoub noted that chromation may delay this migration (conversion to an aluminum chromate). Mr. Ayoub also noted that there is much rainfall in Belgium and the surfaces of the tested samples are frequency washed clean of corrosion products. Dr. Harrison asked Mr. Ayoub what the pH of rainwater in Belgium was. Mr. Ayoub did not know the exact pH but he indicated that should be somewhat acidic due to the presence of heavy industry in the site. Dr. Harrison indicated that in the Toronto area of Canada, whether it be industrial or rural, the pH of the rainwater is 4 which is very acidic. Dr. Harrison then noted that he had seen some variation in the Ziegler five-year exposure panels with respect to the coating weights noted. Mr. Ayoub noted that each panel was specifically measured and there were some normal coating weight variations, however the coating weights listed were an average value. Dr. Kim of Inland Steel asked if any salt spray tests had been conducted on the vertical lamellae as indicated in the research report. Mr. Ayoub noted that there had not been, that the study was still very new and they had not yet had the chance to do so. Dr. Hoboh asked if there was any correspondence study relating corrosion rates to lamellae orientation versus the overall bulk corrosion rate. Mr. Ayoub indicated that had not been done and he would like to do so. Mr. Massinon asked if the aluminum enrichment had been measured quantitatively. Mr. Ayoub noted that had not been done so and the results were more qualitative. Dr. Hirose then questioned the corrosion rates for galvanized and GALFAN. Mr. Ayoub drew a graph of the corrosion rate versus time noting that he has observed a galvanized corrosion rate to be non-linear and increasing with time. He also noted that he has observed GALFAN corrosion rate to begin as linear but leveling off or slowing down as time increases. Dr. Hirose noted that he expects the galvanized corrosion rate to be a linear 45^{o} line. Dr. Goodwin interjected, noting that Mr. Ayoub had revealed very interesting data, especially the section about the localized corrosion of grain boundary dents depending upon the orientation of lamellae. He would like to assemble all the facts presented for some kind of recommendation. Mr. Ayoub noted that he was very concerned about the reduction in aluminum levels as a temporary solution

Dr. deWitte began by noting he believed the galvanized corrosion rate would be linear, referring back to Mr. Ayoub's presentation. Dr. deWitte noted that Bekaert can coat wire and produce a fully eutectic composition on their product. So they have no problem with grain boundary dents. Bekaert does use a water quench after coating, achieving a cooling rate of greater than 100°C per second. Dr. deWitte agreed with Mr. Ayoub's previous comment that the coating should be cooled faster to achieve the proper microstructure rather than reducing aluminum levels to maintain high corrosion resistance. Dr. deWitte also noted the adherence of GALFAN to the steel substrate was as good or better than for galvanized coatings. He noted that Bekaert achieves a very controlled alloy layer in their double dip product of three to five microns. Dr. deWitte also noted that there soon will be published a University of Ghent corrosion study on GALFAN and galvanized material, using salt spray, Kesternich, and diversion tests. He noted that another test performed by Bekaert is a slurry test which is relevant for wire product involving a slurry mixture of fungicides, herbicides, and pesticides, which are commonly seen in the vineyard industry. He noted that GALFAN has been performing at least twice as well as galvanized product. Another test performed also involves a slurry of 5% sodium chloride, and calcium chloride. Again GALFAN's performance is twice that of galvanized. Dr. deWitte noted also that, however in an industrial atmosphere he has some preliminary results showing GALFAN has a faster corrosion rate that galvanized, but it was his opinion that the GALFAN corrosion would level off to a flat rate, while the galvanized corrosion rate would remain linear. Dr. deWitte noted that GALFAN was definitely superior to galvanized in rural and marine environments in his experience. Dr. deWitte noted that in 1975 Bekaert has begun trials with Galvalume wire in coordination with Bethlehem Steel. He noted that in comparison with galvanized product the Galvalume product looked initially better than galvanized, however microscopically it was seen that Galvalume wire exhibited a tremendous amount of pitting and red rust. Dr. deWitte then passed around two Galvalume fence posts from a vineyard. The first fence post had one year's exposure and was severely red rusted at the cut edges and exhibited red rust at the pitting areas. The other fence post was a control and was not yet exposed.

Research Results of Hoesch Stahl

Dr. Goodwin introduced Dr. Schwarz from Hoesch Stahl who presented his research report. The full text of his report is reproduced in the appendix. Dr. Schwarz began by noting that there are currently investigations ongoing at Hoesch to prove that the use of a low coating weight GALFAN will substitute for a higher galvanized coating weight to provide the same amount of corrosion resistance. Hoesch Stahl has four exposure sites. They are Olpe (rural), Kreuztal-Eichen Stahl (industrial), Dortmund (industrial), and Baltrum (severe marine). After two years of exposure, some difference has been observed between GALFAN and galvanized (GALFAN, galvanized have the same coating thickness) however GALFAN performance seemed to be better than galvanized in all cases. The tests will be concluded in one or two years.

Dr. Schwarz then reviewed the formability tests conducted by Hoesch, noting that only qualitative differences between GALFAN and galvanized were noted.

Dr. Schwarz then reviewed some results on weld tests conducted by Hoesch, noting that the spot weldability and seam weldability of GALFAN is not as good as that of galvanized. Dr. Schwarz then reviewed some findings on the influence of annealing on the structure of GALFAN, concluding that the formability of GALFAN can be detrimentally effected by subsequent heat treating.

Sumitomo Metals Research

Dr. Goodwin introduced Dr. Hoboh from Sumitomo who presented his report on the formation of intermetallic layer in the GALFAN coating process. Dr. Hoboh's report is reproduced in its entirety in the appendix to these minutes.

Dr. Hoboh first reviewed the general composition of the bath and the chemical composition of the steel substrate along with the hot dip coating conditions. Figure 1A showed examples of the intermetallic layer with relation to the amount of iron in the coating film. His figure 1B showed an EPMA image of aluminum zinc and iron. Figure 2 shows the relation of alloy bath temperature and strip inlet temperature for the formation of an intermetallic layer. Figure 3 shows a linear relationship between the iron content and the aluminum content film. Figure 4 shows that the corrosion resistance of GALFAN will tend to decrease as the iron content in the intermetallic is increased. Figure 5 is a photo-micrographs of Zero-T bends with respect to iron content. The 4.9% iron content shows a severely cracked edge. Figure 6 shows the effect of the intermetallic layer formation on ductility. At approximately 1% iron the ductility worsens dramatically.

Dr. Goodwin then closed the research session for the day, noting that the next day's session would begin with the research report by Dr. Hirose of Nisshin Steel.

MINUTES OF THE GALFAN SHEET LICENSEES MEETING CONTINUED

ATTENDANCE January 21, 1988

Name	Company
Anderson, D.	Laporte R&D
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Barzoukas, H.	Galvanor Ziegler
Bourke, W.	New Zealand Steel Ltd.
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Celestin, A.	Weirton Steel
Colle, J.M.	Eurinter
Coutsouradis, D.	CRM
D'Autilia, A.	ICMI
deCodt, P.	CIMNF
Ewing, R.	Weirton Steel
Fraisse, P.	Galvanor Ziegler
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Hoboh, Y.	Sumitomo Metals
Howard, M.	Coil Steels Group
Hubert, R.	Arbed Research
Jones, D.	British Steel Corporation
Kamimura, I.	Nisshin Steel
Kim, Y.	Inland Steel
Kitada, M.	Kawatetsu Galvanizing Co., Ltd.
Klotzki, H.	Thyssen
Kosaka, K.	Nippon Kokan K.K.
Lindfors, T.	Rasmet Co.
Lindstroem, M.	Rautaruukki-Oy
Mercier	Galvanor Ziegler
Migliardi, M.	Aceros Revestidos
Molin, B.	SSAB
Naidu, R.	New Zealand Steel
Okamoto, N.	Kawasaki Steel
*Parkinson, R.	Falconbridge
Patil, R.	Inland Steel Co.
Petsch, N.	SALMAX
Pierre, M.	Centre du Zinc
Renaux, B.	CRM
Robertson, I.	Coil Steels Group
*Rollez, D.	Metallurgie Hoboken-Overpelt
Schoen, L.	SSAB
Schwarz, W.	Hoesch Stahl
*Sempels, R.	Vieille-Montagne/Belgium
Sippola, P.	Rasmet

Name	Company
*Sokolowski, R.	Vieille-Montagne/France
Solano, F.	Ensidesa
*Southern, J.	AM&S Europe Ltd.
Stoneman, A.	Zinc Development Association
Szydlik, A.	SALMAX
Toomer, I.	Palmer Tube/Zinctek
Valdor, R.	Ensidesa

*ILZRO Member

MEETING CONVENED

Dr. Goodwin welcomed everyone back to the second day of the GALFAN Sheet Licensees Meeting and as previously indicated, resumed the reports with Dr. Hirose.

Nisshin Steel Research Report

Dr. Goodwin introduced Dr. Hirose who presented his report on the effects of magnesium addition on the properties of GALFAN coatings. Dr. Hirose's report is reproduced in its entirety in the appendix of these minutes. Dr. Hirose noted that this study was conducted on the effects of magnesium addition to GALFAN coatings, on their performance of GALFAN coated steel sheets, with and without organic paint coatings. Highlights of the report were as listed below. Dr. Hirose noted that his aluminum levels range from 4.25% to 4.28%. His magnesium levels range from 0.002% to .305%. The coating weights tested range from 86 grams per meter to 193 grams per square meter. The summary of Dr. Hirose's results is as follows:

1. Magnesium in GALFAN precipitates on to the aluminum rich phase in the GALFAN eutectic structure. This means that the addition of magnesium has an effect of shifting the eutectic point to a higher aluminum content composition.

2. Magnesium addition to GALFAN coatings improved their corrosion resistance. The improved corrosion resistance effect becomes saturated at the magnesium content of 0.1%; therefore, the optimum content of magnesium is from 0.05% to 0.01%.

3. The addition of magnesium reduces coating ductility of GALFAN, however it is not seen to be harmful in a practical manner.

4. In accelerated cyclic corrosion tests, magnesium containing GALFAN coatings have a better performance with respect to blister growth on painted panels. This same effect has been confirmed in three year atmospheric exposure tests. Therefore the addition of magnesium retards blister formation i.e. yields better sacrificial protection.

5. At 2T bend portions of painted GALFAN panels, red rusting is not observed after three years of exposure.

Dr. Goodwin noted that Dr. Hirose's tests had used a paint system with a chromate pretreatment. Dr. Goodwin noted that Kawasaki Steel had showed GALFAN to have better performance than galvanized (painted product) with a phosphate pretreatment. Dr. Kim also added that the paint is a protective coating. One should not categorically rate GALFAN, Galvalume, and galvanized using only one system. Dr. Patil asked if any microstructural studies similar to those conducted at CRM had been conducted. Dr. Hirose indicated that some had been performed. Mr. Sokolowski questioned the deleterious effect of magnesium on GALFAN ductility. Dr. Hirose replied that there is some loss of coating ductility but he has heard on complaints from customers, noting that Nisshin has produced large amount of this type of GALFAN and to their experience the effect is not considered severe. Dr. Goodwin noted that the ASTM allowance for magnesium is 0.1%. Dr. Klotzki asked if any Superzinc from Nippon Steel had been tested. He felt that it was very similar to the Nisshin GALFAN but with no mischmetal. Dr. Hirose noted that he agreed it was similar, however there were no tests performed. Dr. R.D. Jones noted that he has seen that you have more primary zinc with the addition of magnesium as well as its apparent better corrosion resistance. Dr. Jones was interested how he could relate those results of more free zinc yielding better corrosion resistance to the studies at CRM where the corrosion resistance declined with more primary free zinc. Dr. Hirose noted that the beneficial effect of magnesium on corrosion resistance is well known and that was responsible for the improvement.

Stelco Research Report

Dr. Goodwin introduced Dr. Frank W. Harrison who presented his research report from Stelco. Dr. Harrison noted that there are three primary areas of concern to Stelco. They are: 1) grain boundary dents; 2) formability i.e. there are no quantitative numbers to backup the formability claims of GALFAN; 3)Stelco feels that the edge creep results for painted GALFAN are not superior to those of galvanized. Dr. Harrison noted that there are six exposure sites in Canada. He also noted that so far GALFAN thickness loss is 30% lower than that for galvanized. He noted that the corrosion rate for GALFAN has leveled off similar to that graph presented earlier by CRM and that galvanized corrosion rate has not leveled off. However, he still feels that it is early and would like to continue his observations. Dr. Harrison noted that the first concern, grain boundary dents, is being addressed very adequately by CRM and had no further data on that aspect. He continued on with the edge creep concern and presented data showing GALFAN's inferior performance to painted galvanized. (See Figure in appendix). Dr. Harrison noted that the paint system used in this testing program was not optimized. Dr. Harrison then moved on to the last concern of Stelco which is quantifying the ductility of GALFAN versus other hot dip coatings. He noted that the Stelco procedure for quantifying tension bend cracking utilizes the image analysis of high contrast back scattered electron micrograph on Hitachi S-570SEM with Link Systems AN10000 Digipad image analysis program (see attached figures in appendix). In this matter Dr. Harrison noted that Stelco has been able to quantify the ductility of GALFAN, Galvalume, and galvanized.

Dr. Kim asked Dr. Harrison if he had done any simple tension tests. Dr. Harrison replied that he had not yet looked at that aspect of formability. Dr. Patil asked what was the composition of the galvanized sample. Dr. Harrison noted that he didn't have exact chemistry available, but he did say that there was some presence of lead and antimony. Dr. R.D. Jones asked about the correlation of number of cracks in the unit area and their sizes and the crack area being the site of localized corrosion attack. Dr. Harrison replied that it was an important factor involving galvanic protection of the steel. Dr. Goodwin noted that the number of cracks was greater for Galvalume and galvanize. It would be important to account for crack density and differentiate small and large cracks per unit area. A question was raised as to what size the samples tested were. Dr. Harrison replied that samples were all similar of 0.6 mm thickness. The question was raised to Dr. Harrison if he had attempted these formability tests on electrogalvanized and Dr. Harrison replied that he had not.

Coating Weight Capability

Dr. Goodwin introduced Mr. Roman who presented the results on a questionnaire on coating weight capabilities. Mr. Roman gave a short report on the results of the coating weight questionnaire issued several months prior to the meeting. Mr. Roman noted that on the basis of the results, he had concluded that the questionnaire (due to poor wording) had been misinterpreted, and therefore, the results were not meaningful. The questionnaire will be reissued and distributed to all Licensees. The questionnaire had been circulated to ascertain what licensees could fill the specific coating weight windows as per the General Motors Specification GM-6185M. Specific windows were 70 to 120 grams per square meter, 90 to 150 grams per square meter, and 98 to 160 grams per square meter. These "windows" are for single spot one side test results. It is felt that it would be important for the automotive market to know of the capabilities of GALFAN producers.

Formability Questionnaire

Mr. Roman continued by presenting the response to an earlier circulated formability questionnaire. The questionnaire had been circulated to determine the number of licensees performing quantitative formability tests on GALFAN. The main conclusion is that five out of eleven responses indicated that their companies are conducting quantitative performance tests. It would be hoped t maximum width. Rautaruukki is scheduled a trial run in March of 1988 and Mr. Lindstrom noted that Rautaruukki is also licensed to use the Zinquench system. Rautaruukki will be pursuing the painted domestic market in Finland with applications requiring severe forming. Mr. Lindstrom also noted that there should be some applications in the appliance industry. Mr. Lindstrom noted that after their initial trial an evaluation will be made and further production will be determined at that time.

Thyssen Market Report

Mr. Roman introduced Dr. Klotzki who presented Thyssen market report. Dr. Klotzki noted that Thyssen had produced 550 tons of GALFAN in 1982 but had not produced any since. Thyssen is looking at the improved formability and corrosion resistance of GALFAN, however the commercial department of Thyssen is not yet convinced that GALFAN is a marketable product. However Dr. Klotzki noted that due to the increased amount of GALFAN by Hoesch Stahl and the potential by SALMAX, the commercial department may have to resume GALFAN production. Dr. Klotzki noted that he thinks they will run in the summer of 1988 at their Finnentrop Works.

SALMAX Market Report

Although the representatives from SALMAX had previously departed, Mr. Roman noted that SALMAX had produced approximately 700 tons of GALFAN in their initial product trial in June 1987 and they were still evaluating material for further production trials in 1988. No other details were available.

Galvanor Ziegler Market Report

Mrs. Barzoukas of Galvanor Ziegler confirmed that Ziegler had produced approximately 3,600 tons in 1987, most to be applied for the prepainted market. It was indicated in 1988 that there was a forecast of 5,000 tons.

FFM Market Report

Mr. Durand, the FFM representative, had departed, so Mr. Roman noted that FFM had produced no GALFAN in 1987 (later discussions revealed there are no plans to produce GALFAN in 1988). Mr. Roman also noted that FFM was undergoing major reconstruction on their galvanize line.

Phenix Works Market Report

Mr. J.M. Colle of Eurinter, marketing representative for Phenix Works, made a presentation for Phenix Works. He noted that Phenix Works was not currently making GALFAN. Phenix Works had produced GALFAN in two trials in 1984 but there were no plans for 1988, however Mr. Cole also noted that the GALFAN Data Sheet (as presented in the minutes of the Pittsburgh Licensee Meeting) was a useful tool and saw it as helpful for GALFAN.

Ensidesa Market Report

Mr. Valdor noted that currently Ensidesa has not made GALFAN, however they intend to produce GALFAN sometime later in 1988 and hope to produce 2,000 tons at that time. Mr. Valdor also noted that Ensidesa has one galvanizing line which produces galvanized product and Galvalume product and the GALFAN product will be in the same line.

ICMI Market Report

Mr. D'Autilia noted that in 1987 Cantieri produced 2,500 tons. Currently there are no concrete plans for tonnage figures in 1988 because the market for galvanized product is very strong, however Mr. D'Autilia said there will be another production campaign in 1988.

SSAB Market Report

Mr. Lars Schon noted that Svenskt Stal has not yet had any GALFAN production and there are no current plans for GALFAN production, however he and his colleagues were present at the meeting to further evaluate GALFAN for future production.

European Zinc Institute Market Report

Mr. Roman introduced Mr. Sempels of Vieille-Montagne who was representing the European Zinc Institute. Mr. Sempels noted that EZI supported GALFAN from the start. EZI has concluded that GALFAN is a good product worth its promotional efforts. Mr. Sempels noted that at INTERGALVA '85 in Munich EZI received encouragement to a test market approach for GALFAN and then conceived the three step plan for GALFAN promotion. The three steps are: 1)provide general information on GALFAN to interested parties; 2)provide general promotion and establish a positive image for GALFAN and; 3)provide GALFAN promotion to market development associations and producers. Mr. Sempels concluded that EZI promotes the "four G's" (galvanize, GALFAN, Galvalume, and electrogalvanized) and he uses the "four G's" to expand the total market for zinc.

Zinc Development Association - London Market Report

Mr. Roman introduced Mr. Alan Stoneman of ZDA of London who presented his market report. Mr. Stoneman noted that he would like to update his 1987 activities and review his plans for 1988. He noted that he had hoped to announce a new GALFAN wire licensee in the U.K. but at this point in time the deal has not yet worked out.

Mr. Stoneman noted that ZDA has mailed 600 of the EZI GALFAN brochures to selected recipients and is currently receiving responses at a 9% rate. He noted that this mailing was done to inform the marketplace of possibilities for GALFAN. He noted that the mailing was aimed to highlight the ductility aspect of GALFAN to markets such as agriculture, construction, and automotive, and had also distributed some GALFAN samples when available.

For 1988 the ZDA has produced its own GALFAN brochure. Again it is the aim of this brochure to promote GALFAN ductility as the major advantage. It also promotes GALFAN as an improved galvanizing alloy. This approach is aimed at the automotive and building markets. Mr. Stoneman noted that GALFAN has a great potential with the automotive industry in the U.K., especially for Peugeot and Landrover. Mr. Stoneman concluded by noting that the ZDA is sponsoring INTERGALVA '88 in Rome from June 6 through June 10.

Inland Steel Market Report

Dr. Kim noted that Inland had not yet produced GALFAN on a commercial basis. They have had 40 tons of their material coated at Weirton Steel in 1987 and another 120 tons to be coated at Weirton Steel in 1988. All of this product will be shipped to customers for evaluation.

Stelco Market Report

Dr. Harrison noted that there has been no GALFAN production at Stelco and there are currently no plans to produce GALFAN, pending further evaluation.

USX Market Report

Mr. Roman indicated that to the best of his knowledge there were no plans to produce GALFAN in 1988 by USX. To date, there has been no GALFAN production through 1987.

Weirton Steel Market Report

Mr. Andy Celestin of Weirton Steel noted that in 1987 Weirton Steel had produced 6,000 tons of GALFAN. For 1988 they are currently running a campaign aimed to produce 2,000 tons and for nine campaigns planned for 1988 they expect to produce any where from between 15,000 to 18,000 tons.

Mr. Celestin continued by noting that GALFAN is slowly growing in the United States with applications in the appliance, automotive, construction, and electrical equipment industries. Weirton Steel has approached GALFAN with a heavy promotion and advertising campaign. Mr. Celestin showed copies of one of the ads used for the construction market. Also noted the use of the GALFAN Data Sheet which was compiled with the cooperation between the Zinc Institute and Weirton Steel. Mr. Celestin noted that one of the problems in the United States is that Weirton Steel is the only producer of GALFAN. He noted that they are currently working with Inland to assist their trials.

Mr. Celestin noted that Weirton Steel is not a volume producer of GALFAN but is oriented for profit and considers GALFAN to be applied in small niches. Some of the applications in those niches are storage buildings, prepainted appliance wrappers, walk-in coolers, air conditioners, heaters, prepainted roofing. Mr. Celestin noted that the prepainted roofing market has a tremendous market for growth, especially in the standing seam and architectural roofing applications. Mr. Celestin noted that Galvalume is the coating of choice for low slope bare roof, but indicated as slope increases and the product is painted that GALFAN is the product of the future and that is the applications that Weirton Steel will be pursuing.

Mr. Celestin noted that Weirton Steel is looking for applications where the customer is not currently satisfied with galvanize product. He also noted that as previously mentioned by Mr. Brinsky, Weirton Steel will soon have capability to produce wider and thicker GALFAN which will be applied for the unpainted market. Mr. Celestin also noted that Weirton Steel is also looking at substituting lower coating weight and GALFAN for higher coating weight galvanized. It was noted that Weirton Steel will experiment with differentially coated GALFAN.

Mr. Celestin noted that for painted GALFAN, Weirton Steel has seen that a zinc phosphate pretreatment is the best treatment for GALFAN. They have also noted that a dry-in-place pretreatment works well. They have noted that epoxy primers and water base primers are giving good results and the topcoats include polyesters, silicon modified polyesters, plastisols, and PVDF systems.

Mr. Celestin concluded by noting that the application of a paint system depends on the environment in which the final product will be applied.

Dr. Klotzki noted that aluminized product has a 25-year warranty and Galvalume product has a 20-year warranty. He questioned Mr. Celestin as to what kind of warranty will Weirton Steel offer on GALFAN. Mr. Celestin replied that with the proper paint system, Weirton Steel will match any warranty. Dr. Hirose questioned Mr. Celestin about his plans for differentially coated GALFAN. Mr. Celestin replied that it would be applied for one side painted product with only a wash coat on the reverse side. Mr. Roman asked Mr. Celestin what were examples of the heavy gauge wider product that could be made when Weirton Steel expands its capabilities. Mr. Celestin replied that such parts would be deep drawn auto underbody parts, and electrical appliance applications, unexposed appliance parts, and some unspecified agricultural applications.

<u>Nisshin Steel Market Report</u>

Dr. Hirose noted that in 1987 Nisshin Steel had produced 14,000 tons of GALFAN of which 10,000 tons were painted. In 1988 Nisshin Steel plans to produce approximately 23,000 tons of which 18,000 tons would be painted. Dr. Hirose noted that 80 to 90% of total production would probably be applied to the pre-engineered housing market. Process parameters for Nisshin Steel are 0.35 to 0.4 mm thickness for the painted product, with coating weights of 120 grams per square meter per side. For the 5,000 tons of bare product, both cold rolled and hot rolled material will be used in thickness of 1 to 2.3 mm with a potential increasing up to 4.5 mm. Coating weights would 150 to 190 grams per square meter per side. The uses for the painted product would be for roofing and siding market, and for the bare market for the pre-engineered housing market, along with some agricultural (farming) applications. Dr. Hirose noted that heavily chromated GALFAN is accepted as an alternative to galvanized for housing. Dr. Hirose concluded by noting that the ratio of bare production to painted production should increase in the future for Nisshin Steel.

Kawasaki Market Report

Kawasaki Steel produced 11,000 tons of GALFAN in 1987 and planned on producing 12,000 to 13,000 tons in 1988. Almost all of their product is supplied in painted form for the roofing and siding industries.

Sumitomo Market Report

Dr. Hoboh indicated that in 1987 Sumitomo produced 12,000 tons of GALFAN of which 7,000 tons were bare, 5,000 tons were painted. Dr. Hoboh continued by indicating in 1988 Sumitomo would hope to produce at least 12,000 tons or more depending upon market conditions. Dr. Hoboh noted that the uses and applications for GALFAN at Sumitomo were similar to those as presented by Nisshin, that is roofing and siding markets, and the pre-engineered building market.

Yodogowa Market Report

(These figures were reported to Mr. Roman via FAX message after the meeting courtesy of Mr. Nishiguchi). Yodogowa has produced the following tonnages of GALFAN:

1982-1987	51,940 MT
1987 Only	10,400 MT
1986 Only	9,800 MT
1988 Forecast	12,000 MT

Yodogowa produces GALFAN for both bare and prepainted applications.

New Zealand Steel Market Report

Mr. Bourke of New Zealand Steel indicated that in 1988 they intend to run their first trial of GALFAN. They hope to produce approximately 500 tons at that time. They expect the end use to be for roofing material and most would be produced as full hard.

Mr. Bourke then continued by showing some slides he had brought with him. The first three slides showed stain pattern that New Zealand Steel had observed and Mr. Bourke asked if anyone had seen similar stains in their experience. It was the consensus opinion of the group that what was being shown was a humid storage stain from the outer racks of stored GALFAN coils. A possibility was also raised that those panels represented the transition area from a no chemtreat campaign to chemtreat campaign. It is thought that this may be possible since the erection of stained GALFAN was not likely and the stain appeared at a later date. (rapidly on the non treated panels, whereas the treated panels remained stable.)

Mr. Bourke continued with more slides showing exposure panels of GALFAN, galvanized, and Galvalume with varying exposure periods of 2 1/2 to 6 1/2 years. The environment in all of New Zealand can be considered to be a marine environment and the GALFAN panels, both bare and prepainted did perform extremely well.

<u>Coil Steels Group Market Report</u>

Mr. Merton Howard of Coil Steels Group noted that as a new licensee they had not yet produced GALFAN but are in the process of building a dedicated line for the production of GALFAN with a potential for 150,000 tons per year. Of that, 40% would be applied in the painted market. Coil Steels Group has looked at GALFAN since mid-1986 and noted they needed a superior product to compete with Galvalume which holds 90% of the hot dip market in Australia. Coil Steels Group feels that large growth market is in the prepainted area and would also pursue niche markets - areas where galvanize or Galvalume are inappropriate. If necessary, Coil Steels would produce full hard steel by importing the full hard substrate.

<u>Palmer Tube Market Report</u>

Mr. Ian Toomer noted that Palmer Tube produces ERW tubing and they had not yet produced any GALFAN tube nor did they have any plans to produce any soon. Mr. Toomer indicated that Palmer Tube is waiting for the flux process for GALFAN to be perfected. He noted that the potential for pipe in Australia is 30,000 to 40,000 tons per year. Mr. Toomer also noted that Zinctek, the parent company for Palmer Tube is also involved with a roof tiling product and they intend to use GALFAN sheet for that process.

<u>Gregory Galvanizing Market Report</u>

Dr. Goodwin noted that Gregory Galvanizing in Canton, Ohio, had made 300 tons of heavy gauge GALFAN in December and planned to run approximately 300 more in 1988. Their market was for the fence posts as used by Cyclone Fence where the narrow strip is formed, utilizing total coverages on edges.

Dr. Goodwin also noted the makeup of the flux consortium referring back to Mr. Toomer's comments, noting that companies, Wheeling-Pittsburgh, LTV Steel, Empire-Detroit, Southwestern Pipe, H.H. Robertson, and Nippon Denro Mfg. were supporting the research work on flux trials and the purpose of the flux work was to determine useful limits of process variables.

Patent and Trademark Report

Mr. Roman displayed two slides detailing the present patent and trademark estate of ILZRO on GALFAN. Those slides are reproduced in the appendix of these minutes. Mr. Roman noted that with respect to the trademark estate, he had previously circulated a memo to all licensees asking for promotional material in GALFAN. Such material is useful in maintaining a GALFAN trademark maintenance file to protect the trademark of GALFAN. Mr. Roman noted that he does have many promotional brochures but would appreciate receiving the newest and latest promotional brochures when licensees make them available. Mr. Roman also noted that providing such brochures to ILZRO is part of the contract outlined in the GALFAN License Agreement. Dr. Hirose raised the issue that the patent application in Japan was soon to expire and that ILZRO should be very concerned about that. Dr. Goodwin noted that ILZRO was aware of that and the patent attorneys for ILZRO were acting on that issue at that moment.

GALFAN Alloy and Product Consumption Report

Mr. Roman indicated that he had solicited responses from all licensees regarding GALFAN alloy consumption and production as required in Section 7. in the GALFAN License Agreement, however the response has not yet been significant and the report could not yet be formulated. Mr. Roman noted that these reports as required by the GALFAN License Agreement were useful for determining worldwide zinc and GALFAN consumption. Mr. Roman noted he would make up a uniform reporting form for licensee use for this subject.

Discussion

Mr. Roman initiated discussion of a review of marketplace trends that effect GALFAN production. (coating weight, thickness, physical properties, etc.). A questions was raised as to how such trends would effect GALFAN in the automotive, appliance, construction, and agricultural markets. A question of weldability arose as thought to be a problem for GALFAN. Mr. Roman reminded the group that Weirton Steel's work with the upsloping technique had provided weldability that surpassed minimum standards as specified by Ford Motor Company. Those results were thoroughly reviewed in the minutes of the Pittsburgh meeting and have also been published for general distribution by Weirton Steel. It is now felt that GALFAN is a weldable product.

Mr. Roman also noted that lighter coating weights for GALFAN product could open up areas for substitution for heavy coat galvanized as noted by both Hoesch Stahl and Weirton Steel. Mr. Roman referred to Underwriters' Laboratory who has approved GALFAN for corrosion equivalence as noted below:

GF 60 = G90
GF 45 = G60

GALFAN is being applied to that UL specification in the United States.

Mr. Roman also noted that the properties of steel substrates coated by GALFAN are applicable to all markets and there is interest in the automotive market. There was mention made of the Zinquench process for the production of all types of steel grades. There was a mention for the production of dual phase steels. Mr. Celestin noted that in the United States, there is really no interest in dual phase steels now that electrogalvanized product has taken over the market for automotive.

Mr. Toomer asked all in attendance what were some commonly seen GALFAN problems. Mr. Roman replied that in his work with potential licensees, there are several commonly asked questions about GALFAN. Some of those questions are:

1. Concern about gray patina;

2. A concern about the actual corrosion resistance.

Mr. Roman noted that now that the five year results of the commercial Ziegler material are public, it has helped give credibility to all the promotions that GALFAN has so far received. Mr. Roman continued by noting that there are many questions about the composition of GALFAN and the proper microstructure desired. Mr. Roman noted that one of the biggest obstacles he encounters is that customers do not know about GALFAN. Although a steel company may know about GALFAN, they would have a tremendous marketing effort in order to promote GALFAN. Mr. Roman then referred to Mr. Celestin's remarks on the major marketing effort of Weirton Steel to promote GALFAN.

Dr. Goodwin wondered if it would be worthwhile to produce a commercial directory of GALFAN producers, and noted that such a questionnaire would be distributed. Such a directory would indicate who is producing GALFAN and what type of GALFAN is produced. Included would be product parameters such as gauge, width, coating weight, and typical end use products. Mr. Roman noted that he would send out a questionnaire as soon as possible.

Mr. Roman addressed the group of the question: Where do the ideas for new uses come from for GALFAN? Mr. Celestin replied that in most cases, such an application will arise when a customer is not satisfied with the old material be it galvanized, cold rolled, or Galvalume. In most cases, the marketing people just have to go out and look for these types of new products.

GALFAN Standards Activities

Dr. Goodwin reviewed the GALFAN standards activities beginning with ASTM B750-85. Dr. Goodwin noted that there is now underway a revision of that standard to drop the aluminum level from 4.7% minimum to 4.2% minimum. The maximum level of 6.2% will remain unchanged.

Dr. Goodwin also noted the ASTM sheet specification for GALFAN which is ASTM A875 and A875M. Dr. Goodwin noted that Nippon Steel wanted a Type 2 specification for this standard that would include Superzinc and reviewed the possibility for a Type 3 standard for GALFAN plus magnesium as per Dr. Hirose's report in the research session.

Dr. Harrison asked if a Type 3 5% aluminum zinc was necessary. He noted that the ASTM standard currently includes a specification for up to 0.1% magnesium. Dr. Goodwin replied that it still may be necessary for such a standard since Dr. Hirose's studies included magnesium levels up to 0.3%.

Dr. Goodwin then reviewed the previously mentioned Underwriters' Laboratory standard of corrosion equivalence of light GALFAN coated coatings to heavier galvanized coatings. Dr. Goodwin also mentioned there are other private industrial specifications such as the Ford welding specification, the GM coating weight specification, and noted that in Germany a building standard for the construction industry should be issued within a very short time.

Summary and Review

Mr. Roman reviewed the activities of the last three days. Mr. Roman again thanked the personnel from Galvanor Ziegler for their cooperation in hosting the tour of the Mouzon Works, noting that it is always part of a successful meeting for GALFAN licensees.

Mr. Roman also reviewed the initial attendance as the most attendance ever for a GALFAN licensees meeting and reflected the growth of GALFAN as a commercial product.

Mr. Roman also reviewed the operating session where reports were heard from Galvanor Ziegler, ICMI, Hoesch Stahl, and Weirton Steel.

Mr. Roman then reviewed quickly the research reports, noting that the only way to make the product better was to investigate the negative aspects of a product in order to eliminate them. Mr. Roman made it clear that although some of the research may sound negative, it is just the classic approach to solving a problem - to eliminate one's weaknesses. Mr. Roman thanked CRM for their detailed work on grain boundary dents and the ongoing corrosion studies. He also noted that Professor Jones' attendance was his first at a GALFAN licensee meeting and thanked him for his contribution. Mr. Roman also noted the contributions by Procoat, Hoesch Stahl, Sumitomo, Nisshin Steel, and Stelco in the research sessions.

Mr. Roman also reviewed the outcome of the marketing session, noting the increase in tonnage for most of the licensees present, along with the increase in forecast tonnage. He also noted that companies such as Ensidesa and Rautaruukki, Coil Steels Group, New Zealand Steel, and Thyssen were all about to initiate new GALFAN trials in the near future. Mr. Roman concluded with a review of the GALFAN standards as given by Dr. Goodwin, noting that in order for a product to grow standards and specifications must be established for marketplace acceptance.

MEETING ADJOURNED

As there were no further questions and discussion, Mr. Roman adjourned the meeting at 4:00 p.m.

GALFAN PROCESS LICENSEES

Company Name	*Location*
An Mau Steel Company, Ltd.	Kaohsiung, Taiwan (R.O.C.)
Arbed Research	Esch/Alzette, Luxembourg
Arc Tube Inc.	Sault Ste. Marie, Canada
N.V. Bekaert S.A.,	Zwevegem, Belgium
British Steel Corporation	Deeside/Clwyd, Wales, United Kingdom
Bundy Corporation (Bundy Tubing)	Warren, Michigan, U.S.A.
Empresa Nacional Siderurgica S.A. (ENSIDESA)	Aviles, Spain
Coil Steels Group Pty., Ltd.	Granville, Australia
Fabrique de Fer de Maubeuge (FFM)	Louvroil, France
Fils et Cables d'Acier de Lens (FICAL)	Loison-Sous-Lens, France
Florida Wire & Cable Company	Jacksonville, Florida, U.S.A.
Galvanor/Coloracier S.A. (USINOR)	Montataire, France
Gregory Galvanizing & Metal Processing Inc.	Canton, Ohio, U.S.A.
Hari Krishnan Coated Sheets, Ltd.	Kanpur, India
Hoesch Stahl AG	Dortmund, West Germany
Indiana Steel & Wire	Muncie, Indiana, U.S.A.
Industrie Cantieri Metallurgici Italiani (ICMI)	Naples, Italy
Inland Steel Company	East Chicago, Indiana, U.S.A.
Iscor, Ltd.	Pretoria, South Africa
Kawasaki Steel Corporation	Tokyo, Japan
New Zealand Steel Limited	Glenbrook, South Auckland, New Zealand
Nippon Denro Ispat, Ltd.	Calcutta, India
Nippon Kokan K.K.	Kanagawa, Japan
Nisshin Steel Company, Ltd.	Tokyo, Japan
Palmer Tube Mills (Pty) Ltd.	Acacia Ridge, Australia
Galvameuse S.A. (Phenix Works)	Flemalle, Belgium
Rautaruukki Oy	Hameenlinna, Finland
RMHK Trepca	Kosovska Mitrovica, Yugoslavia
SALMAX	Saltzgitter, West Germany
Steel Company of Canada, Ltd.(STELCO)	Hamilton, Ontario, Canada
Sumitomo Metal Industries, Ltd.	Tokyo, Japan
Svenskt Stal, AB (SSAB)	Borlange, Sweden
Thyssen Aktiengesellschaft	Duisburg, West Germany
US Steel/USX Corporation	Pittsburgh, Pennsylvania, U.S.A.
Weirton Steel Corporation	Weirton, West Virginia, U.S.A.
Yodogawa Steel Works, Ltd.	Osaka, Japan
Ziegler, S.A.	Paris, France

GALVANOR
ZIEGLER

Ladies and Gentlemen,

Welcome to the MOUZON plant for the GALFAN Conference.

In 1987, USINOR and SACILOR have merged their flat rolled products activities into a new company SOLLAC. SOLLAC'S ambitious goal in continuously to improve the quality of its products and services in order to promote a strong and dynamic image.

With a turnover of 28 billion francs (5 billion dollars) with 53 % of sales exported to 130 countries, SOLLAC has become the leading European flat rolled producer and the second largest in the world.

VALOR in France, SAARLUX in West Germany and DAVAL for other countries distribute these products among a very diversified range of markets. The Tin Mill Products are sold to all markets, except West Germany, by LE FER BLANC.

The coated products activity is managed by a specialized department which controls a wide range of brand names, as well as hot dip galvanized, electrogalvanized, aluminized and organic coated products.

GALVANOR ZIEGLER, a new company resulting from the merger of GALVANOR and ZIEGLER at the end of 1987, is the largest coated product subsidiary of SOLLAC. GALVANOR ZIEGLER capacity is made up of 1.100 KT of metallic coated products and 270 KT of organic coated products.

Most of the production of coated products comes from 4 plants, DESVRES (62), MONTATAIRE (60), MOUZON (08), ONNAING (59). The ELSA electrogalvanizing line in Lorraine and a hot dip galvanizing line in LAMINOIRS DE STRASBOURG (67) complete the total SOLLAC capacity.

The MOUZON plant specialises in the production of aluminized, galvannealed steel and GALFAN. This plant includes some slitting and cut-to-length equipment. The MOUZON plant's 200 KT yearly output mainly serves the automotive (and its subontractors) industry as well as the appliance manufacturers. Close to 60 % of the production is exported towards the European Community, the USA and Scandinavia.

The first GALFAN industrial trial runs took place in MOUZON in 1981. Other developments were made later on, including such important ones as the ZINQUENCH process.

We would like to wish you a very pleasant visit of the MOUZON plant and we hope that the Rheims GALFAN Conference will afford you an enjoyable opportunity to discover the lovely CHAMPAGNE ARDENNES Province.

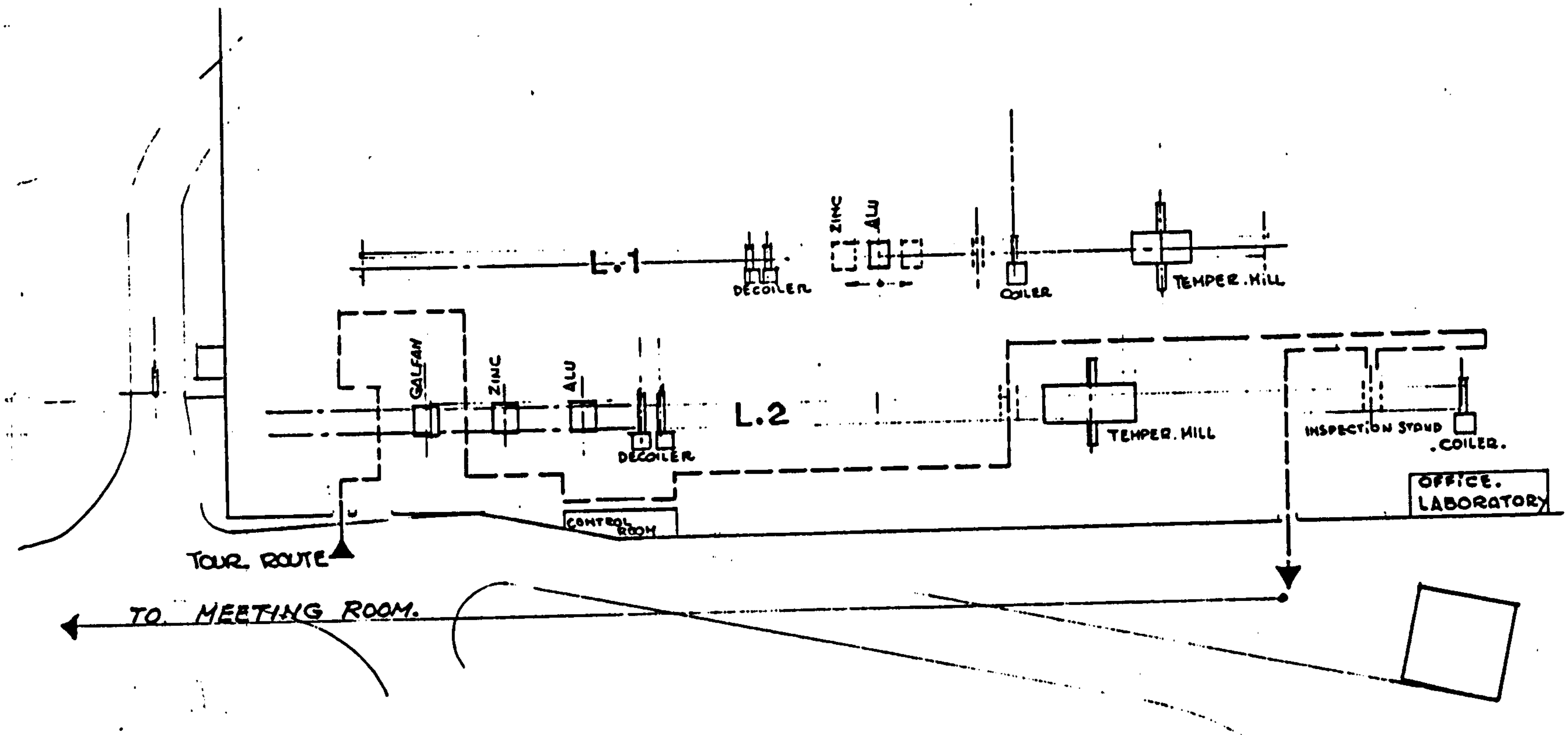
Have a pleasant stay with us.

Adresser la correspondance à :
Immeuble Elysées - La Défense - Cédex 35
92072 PARIS - LA DEFENSE
Télex : 612552 - Tél. (1) 47.67.90.00
Télécopie : (1) 47.67.85.85

Société Anonyme au capital de F 154303000
R.C.S. Nanterre b 572066835
Code APE 2103
Siège social : 29 Le Parvis La Défense 4
Puteaux (Hauts de Seine)

GALVANOR ZIEGLER

MOUZON PLANT

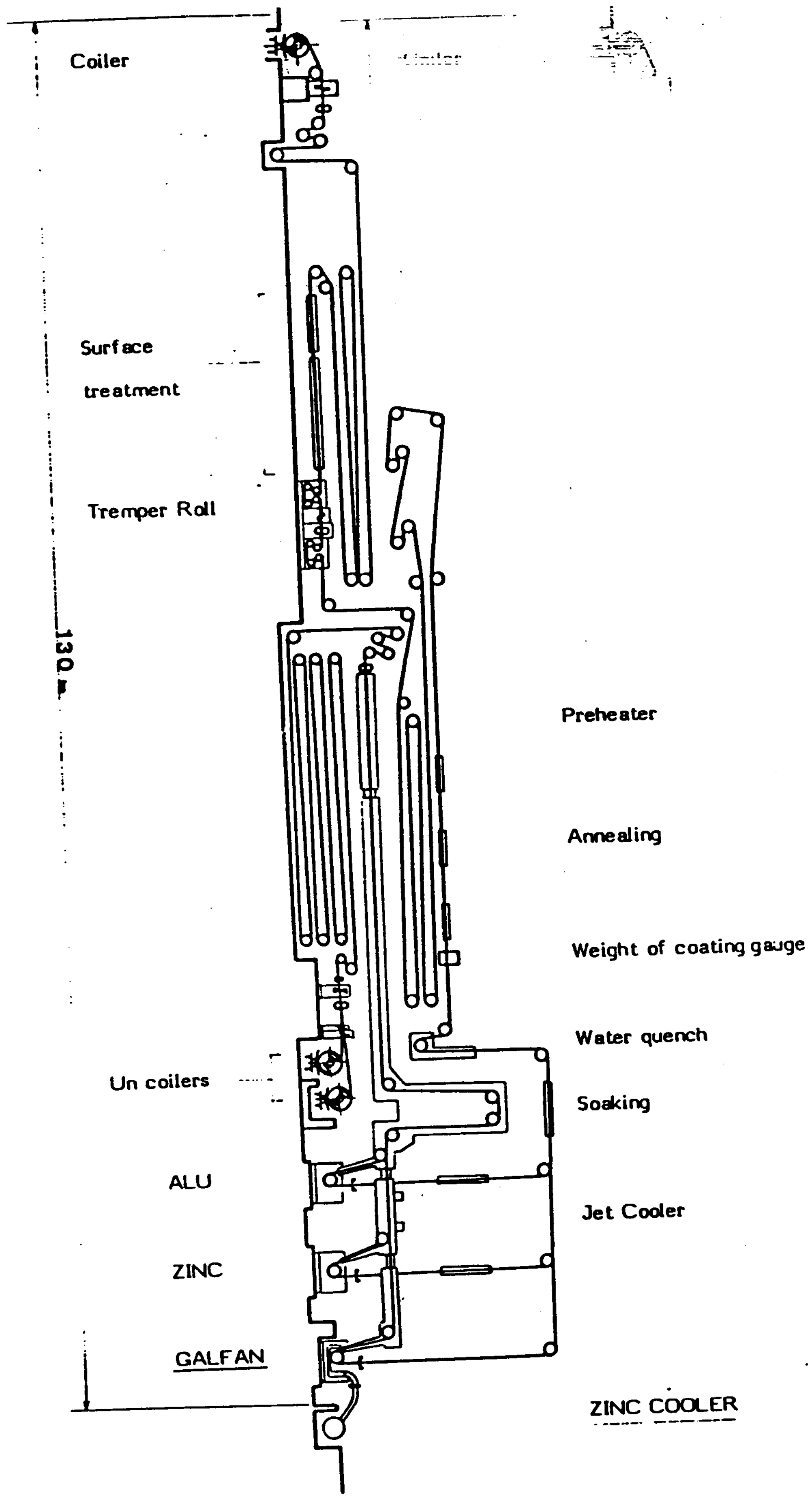


11th GALFAN MEETING

19 JAN 1988

GALVANOR ZIEGLER

LINE N° 2



THICKNESS 0,3 - 3,0 mm

WIDTH 600 - 1540 mm

SPEED 80 m/mn (Process)

ZIEGLER'S EXPERIENCES IN THE GALFAN PRODUCTION 1981 - 1987

J.P. HENNECHART, GALVANOR ZIEGLER, MOUZON

INTRODUCTION

On our N° 1 line in the Mouzon plant, we carried out two production trials :
- July 1981 (the first industrial trial of Galfan in the world)
- Oct. 1982

After the evaluation of the product, Ziegler made the decision to produce GALFAN and to start a commercial production on :
- Dec. 1983

In order to reach a larger scale of the coated sheets market, we decided to modify our N° 2 line in Mouzon to produce GALFAN. The maximum strip width is :
- 1070 mm on N° 1 line
- 1540 mm on N° 2 line

The strip width on N° 1 line was too limited to ensure the proper development, specially for prepainted applications.

To preserve our flexibility we installed a third pot in the line and this pot is reserved totally for GALFAN.

The main characteristics of our N° 2 line are :

- three pots to produce hot dip coated sheets with aluminium, zinc and GALFAN
- maximum speed 80 M/Mn
- air or recirculated nitrogen wiping

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- strip dimensions : 0,3 to 3 mm thickness, maximum width 1540 mm
- furnace built and rebuilt by Heurtey, with horizontal preheater and annealing zones followed by a vertical soaking zone and jet cooling equipment in front of the pots
- the GALFAN pot equipped with the Zinquench process to cool the bath
- fast cooling device to cool the GALFAN coating

1 - RESEARCH

We would like to describe the study of the systems, which have been built and tested to reach the best quality of GALFAN in production campaigns.

After the first trial on the N° 1 line, the investigations on the microstructure of the coating were targeted to find solutions for a better coating aspect in order to minimize grain size.

The solution was to cool the coating as fast as possible - i.e. to quench the coating - in order to achieve uniform eutectic structure. Some laboratory experiments and simulations on the galvanizing line were carried out and during the second trial on N° 1 line we cooled the strip after the bath with a mix spray of water and steam. We tried also with diammonium phosphate additions. The results were consistent but very heterogenious and we didn't completely succeed in that path.

It is very difficult to spray without any formation of larger droplets of water, which produce craters in the coating. To eliminate such defects we tried to reduce the volume of water in mix spray. We found that in order to produce a coating without any craters, the conditions are very close to using dry steam. That is why we came to the conclusion that it will be better to cool with air.

During the trial, we also tried air cooling with Heurtey minimum spangle equipment with or without zinc powder. The conclusions after that trial were that :

- the cooling device must be very efficient in order to reach a uniform eutectic structure in the coating.

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There are two ways of exploration for that cooling device :

- mix spray ; water and steam or water and air
- high speed jet cooling with air.

We also found that diammonium phosphate additions in water or zinc powder additions in dry air do not significantly change the grain size.

2 - N° 2 LINE

When we started to produce GALFAN on the N° 2 line, the choice for the cooling device was not made. We developed in the beginning both systems : spray and air cooling.

Spray systems : we tried the box of the minimized spangle unit with :

- wet steam
- water and diammonium-phosphate
- superheated water sprayed at high pressure

For each trial, we were obliged to use a less and less efficient cooling system to avoid craters. The wet steam after adjustement of the water flow was near dry, and the superheated water was so hot that a big amount was changed into dry steam at the exit of the nozzles.

Air cooling systems :

We found that the results were good with air jet cooling equipment and we developed one equipment inside of the nitrogen wiping box and another one outside.

WETTABILITY PROBLEMS

When we started to produce GALFAN on N° 2 line, we also had some wettability problems. In December 1983, the chamber between the pot and the GALFAN pot was not equipped with heating elements and thus it was wet.

The galfan bath with 5 % Al is easily oxidized in the snout, so that the dew point has to be low, in order to reach an acceptable wettability. -30°C is considered to be the maximum value allowed. To reach that dew-point level, we ran some coils in unnormal conditions ; some minutes with a very hot strip, to heat and dry that chamber, and thereafter we stopped the line to eliminate the water with nitrogen and hydrogen. We found that with a high strip temperature the GALFAN wettability was better, but very quickly - when the chamber was heated - the dew-point became very high and bare spots appeared again.

For the other runs in 1984 and 1985, we equipped the chamber with heating elements, and we dried it, on its stand-by position - before assembling to the line with a nitrogen and hydrogen atmosphere.

Nevertheless that experience gave us a good solution to obtain a better wettability. We ran the strip as hot as possible, and controlled the bath temperature around 430°C without heating it with light gages. It was possible to immerse the strip at a temperature of 480 to 500°C if the coating weight was sufficient to pick out the heat from the bath (cooling by melting ingots and natural losses).

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INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION, INC.

GALFAN TECHNICAL RESOURCE CENTER

2525 MERIDIAN PARKWAY
POST OFFICE BOX 12036
RESEARCH TRIANGLE PARK, N.C. 27709-2036
TELEPHONE 361-4647 (AREA CODE 919)
TELEX: 261533
FACSIMILE. (919) 361-1957

MEMORANDUM

TO: GALFAN Process Licensees
GALFAN Alloy Licensees
GALFAN Technical Resource Center Sponsors
GALFAN Sheet Licensee Meeting Attendees
GALFAN Suppliers

FROM: Marshall P. Roman, Director
GALFAN Technical Resource Center MPR

DATE: March 30, 1988

SUBJECT: Minutes of the Eleventh GALFAN Sheet Licensees Meeting
Reims, France, 20-21 January, 1988

Enclosed are the subject minutes. For your information, the latest (as of this date) GALFAN Sheet Tonnages are as follows:

1987 Total: 76,000 MT
1982-1987 Cumulative Total: 200,000 MT
1988 Forecast: 108,000 MT

The cumulative total is slightly lower than earlier published, due to corrected actual tonnage figures received from Yodogawa (previously estimated). Still, the 1988 forecast predicts a better than 50% one year increase. The 1988 forecast could be significantly increased depending on Rautaruukki's performance. Rautaruukki will soon commence industrial trials on their GALFAN dedicated line (100,000 MTPY capacity), and actual production can not be predicted at this time.

As mentioned during the meeting, the next GALFAN Sheet Licensees Meeting will be in Naples, (following INTERGALVA '88 in Rome, preceding the E.C.C.A. Annual Meeting 20-22 June in Sorrento), 13-15 June 1988.

Tentatively, the January 1989 meeting will take place the week of Monday, 9 January in Japan. The Japanese GALFAN Licensees have already been contacted to assist in coordinating that meeting. The summer (June or July) 1989 meeting will be hosted by Rautaruukki, either in Helsinki or Hameenlinna, Finland.

MPR/ja

Encl.

TRIAL FOR GRAIN REFINING WITH BATH ADDITIONS

During the run on September 84, we have tried both mix spray and air cooling equipment, to improve the coating.

We also tried, together with the CRM zirconium additions in the GALFAN bath, to reach the fine eutectic structure. We observed an influence on the grain size, and we reached minimized aspect equivalent to the aspect we obtain with the jet air cooling device on a 0.75 mm thick strip. The conclusions of that trial were, that it would be interesting to know, if zirconium is also effective with heavy gages, 2 mm or more, but we never tried again.

MORE IMPROVEMENTS

On October 1984, we continued the production improvements. We decided :

- to develop the high speed gas-jet cooling equipment after the bath
- in the same time also to continue the evaluation of the high pressure superheated water
- to run the strip as hot as possible at the bath entrance.

On September 1984, we ran one coil at 600°C. The result was good for the wettability.

In 1985, we produced GALFAN with the following parameters ; the bath temperature was maintained between 420 and 430°C and the strip as hot as possible, up to 500°C on light gages and 450°C on heavy gages.

After two more trials with superheated water spray, we only decided to use air cooling equipment inside and outside of the jet-wiping equipment box.

We made reports after each run and found that the wettability defects are very sensitive to black or uncoated spots, specially on heavier gages.

THE ZINQUENCH PROCESS

All these observations, joined to the proposition of Rasmet to try a cooler in the bath, conducted Ziegler to accept to carry out industrial trials of the zinquench process in the production scale.

We made the first trial on January 1986 and made the decision to buy the licence in the middle of 1987. During the one and a half year we made, together with Rasmet, experiments in all aspects concerning GALFAN coating, produced by the Zinquench-process.

The first trial :

- gave an evaluation of mechanical properties of processed coils
- gave an evaluation of the bath cooling equipment
- confirmed, that high entry temperature of the strip in the bath is a major condition to improve the coating quality.

Further, the second trial confirmed the good mechanical properties of low carbon steels processed with Zinquench and post-annealed before temper rolling and gave an evaluation of the quenching effect on steel with carbon and manganese. We obtained a dual-phase structure very easily. During that trial we appreciated the flexibility of the process concerning the free choice of the strip entry temperature and the bath temperature.

To utilize the quenching advantage, we use a high strip temperature in the range of 600 to 700°C, the bath is maintained between 415-420°C.

Since March 1986, we have produced GALFAN with the above mentioned conditions. We have also made some other experiments, for example : we produced with a conventional galvanizing bath, dual-phase steel with 4,2 % elongation in the skin-passing and we reach 500 N/mm^2 yield strength with 20 % elongation of steel.

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The properties are near full-hard but with highly better formability. Such a product is obtained directly on the line.

From the production point of view, the original application of Zinquench is to quench the strip. The main reasons, why Ziegler had decided to buy the Zinquench process, are its contributions to improve the quality of the GALFAN coating.

The bath cooler and the circulation of the melt in the pot give stable conditions for the melt. Typical analysis of the bath at a temperature of 415 - 420°C :

- Al 4.7 to 5 %
- Fe 0.023 to 0.028, no more
- Zn rest

The iron content is practically independent of the strip entrance temperature.

The corrosion of the immersed parts in the bath is minimum.

CONCLUSIONS

When using the Zinquench-process, the strip entrance temperature from 530°C to 570°C will provide a good wettability and coating quality suited to our development target of the product. That is the main reason, why we decided to choose the Zinquench-process.

It is easy to minimize the grain size with a low bath temperature, because we have less energy to loose in the rapid cooling after the bath. The stability of the bath temperature and some adjustments in the bath on strip temperatures can help to reach a minimized grain size for the coating.

For light coatings, 100 to 120 grs/m^2, the surface quality is comparable to zingrip (conv. Zn) after skin pass and can be used for exposed parts after painting.

For coating weights of 150 to 255 grs/m^2, the surface quality is good for the painting line.

INDUSTRIE CANTIERI METALLURGICI ITALIANI S.p.a.
NAPLES - ITALY -

FIRST "GALFAN" CAMPAIGN

JULY 1987

1. Introduction

The first Galfan campaign made at I.C.M.I. was intended to prove the suitability of the installation for the production of Galfan coated sheets (quality of atmosphere, procedure for conversion from normal galvanized to Galfan and vice-versa, wiping and cooling devices, etc.) . It was also important to understand the effect of some process parameters on the coating surface quality in order to solve eventual coating defects. On the same time "Cantieri" decided to do it with the main object of preliminary survey of Italian market.

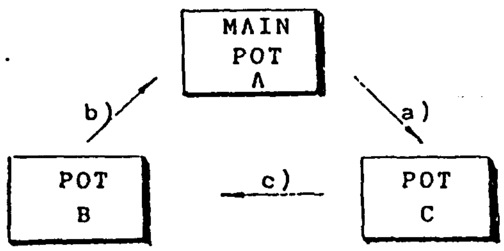
2. Description of the trial

2.1 Specifications of "Cantieri" Continuous Galvanizing Line

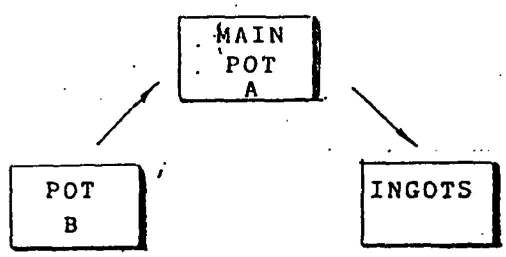
Type of process	Sendzimir (N.O.F.)
Strip thickness	0,25 + 2,90 mm
Strip width	650 + 1250 mm
Line speed	110 m/min
Productivity	26 T/h

2.2 Bath exchange

"Cantieri" has performed to convert the line from galvanized to Galfan and vice-versa a 3-pot system as follows :



From "G" to "GF"



From "GF" to "G"

-Operations :

a) pumping out of conventional molten zinc into insulated pot C (preheated by gas burners);

b) filling of pot A by transferring liquid metal previously melted in pot B (iron pot electrally heated) ;

c) pumping out from pot C of liquid zinc to the heated pot B at the end of operation b). The zinc was maintained in the liquid condition in pot B until the trial was completed.

After completion of the campaign, Galfan was poured to ingots, cooled and set aside for the next campaign. The overall time of change of the sistem was ∼50 hours,half of which from galvanized to Galfan.

2.3 Steel coils

During the whole campaign were used coils of hot rolled continuous cast steel produced by ITALSIDER and cold rolled at "Cantieri" . The thickness of strip was 0,67 + 0,97 mm and its width was 895 + 1265 mm.
Among the 2500 tons galfanized, about the half was intended for coil coating (skin-passed material, unchromated and lightly oiled).

2.4 Conditions of production

- Chemical composition of ingots :

Al	Ce	La	Pb	Fe
4,4 + 4,8 %	0,01 + 0,03	0,01 + 0,03	below 0,005	below 0,005

- Bath temperature	460 + 485 °C
- Strip temperature at snout	470 + 500 °C
- Annealing temperature	∼750 °C
- Nozzle-to-strip distance	10 + 20 mm
- Coating weight	100 + 200 g/m^2
- Line speed	50 + 80 m/min

During production craked ammonia (75 % H_2 - 25 % N_2) was injected in the snout with a flow rate of 100 Nm^3/h ; moreover, especially for this Galfan campaign, nitrogen with a flow rate of 50 Nm^3/h was injected in the furnace section to let down Dew Points.

The Dew-Point measurement in the furnace gave the following results :

Snout	– 32 °C
Soaking section	– 25 °C
Jet cooling section	– 15 °C

3. Production results and conclusions

This first Galfan campaign has been quite satisfactory and proved the suitability of the installations for the production of galfan coated sheets. The surface aspect of the product showed the typical Galfan spangle and no major defect was observed (fish bones, dents, horse-shoe defect, etc.) even when the bath temperature was reduced to 460 °C . No wetting problem was observed (bare spots or craters) and coating adherence was excellent .
During the production, the analysis of the bath showed the tendency of aluminum content towards lower values, may-be, because of some drosses still remaining on the bottom of the pot after the pumping of zinc.
In the next trial the aim of "Cantieri" will be :

1) to reduce time of conversion from galvanized to Galfan and vice-versa;

2) to produce Galfan coated sheets with maximum value 4% to give best surface aspects and coating aderence, both considered as main advantages of Galfan by Italian customers .
"Cantieri" ascribe to low aluminum content the absence of characterics Galfan's defects and is oriented to emphasize specially two points of this product that is better formability and painting compared to Galvanized.

"Cantieri takes here the opportunity to thank C.R.M. personnel for their useful cooperation during this first trial .

11th Galfan Sheet Licensee Meeting
19 - 21 January 1988
Reims, France
Operations Session

Operating Report from Hoesch Stahl AG by Dr. Lutz Furken

In former times we often have reported about our testruns, developments and commercial production of Galfan at Hoesch Stahl. The last report was given by Mr. Zwingmann at the Galfan Meeting in Siegen, November 1986.

Today I'll give you a brief summary about

1. The Galfan production since 1983
2. The 16th campaign, January 1988
3. The main defects typical for Galfan
4. Further developments

1. Galfan production since 1983

Fig. 1 shows the frequency of campaigns and production since 1983.
After two test-runs at the galvanizing line in Ferndorf Work Hoesch Stahl started the commercial production in 1984 at the line in Eichen Work. In each of the last two years we produced in four campaigns.
In 1987 the production was lower than planned because of the occurence of a defect typical for Galfan.
We think to know the reason why and we hope to have found a way to avoid this fault.

For the year 1988 we plan to produce 25000 tons. In the first campaign in January 1988 we were able to produce about 8000 tons but we had to limit the production time in consideration of the beginning of the building up of the quick-change two-pot system at the galvanizing line in Eichen Work.

I'll tell you more about this new equipment in chapter 4.

2. The 16th Galfan campaign, January 1988

Fig. 2 shows some dates about the last campaign.

Now the main production parameters are:

- adjusting the aluminium concentration in the bath in the hypo-eutectic region
- various bath-temperatures depending on thickness
  Fig. 3: Relation Gauge/Temperature
- proportionate high strip temperatures when dipping
- wiping with air by low pressures,
  wiping with nitrogen in special cases
  Fig. 4: Relation between wiping pressures (air) and line speed
- skin-passed surfaces are produced mainly by on-line temper-rolling

3. The main defects typical for Galfan (Fig. 5)

We still have to get along with some defects typical for Galfan appearing numerously and being very disturbing:

- deep grain boundaries
- ripples and tears
- bare spots

We have discussed reasons of those faults in former times.

Let me tell you now how to avoid those faults or how to decrease their frequency and size.

- deep grain boundaries

  We have lowered the aluminium concentration in the ingots to achieve a hypo-eutectic region in the bath.

  We now find proportionate smooth surface that is suitable for colour coating after on-line temper-rolling. We have observed a lower buildup of Galfan on the rolls of the tempermill and on the bending rolls of the stretcher leveller, too (sample: wiped with air, on-line temper-rolled).

- ripples and tears

  These typical faults are caused by wiping with air at higher pressures. In order to avoid ripples and tears it's required to use nitrogen instead of air, in case that it's not possible to raise the coating weight or to reduce speed.
  Fig. 4: Relation between wiping pressures (air) and line speed

 - 3 -

(Samples: wiped with air (170 g/m^2, 70 m/min) and wiped with nitrogen (120 g/m^2, 92 m/min)).

- bare spots

  We have a lot of trouble with faults caused by restrained wetability of the strips. Samples: bare spots, wiped with nitrogen.

  These faults often will disappear by reducing speed; the better wayis to take clean surfaces with the cold rolled material.

  We later will report about results of some experiments and investigations which show a relation between the cleanness of the strip surface and the appearance of this fault.

4. Further Developments

Beginning in August 1988 we'll use a quickchange two-pot system in the galvanizing line in Eichen Work. We'll replace the stationary steel pot by two ceramic pots which are heated by induction and which can be moved and lifted (Fig. 6: Changing system).

We'll build up two additional Stelite-plated steel pots used for zinc and Galfan. One of the both ceramic pots will be used for galvalume continuous, the other one will be used for changing zinc and Galfan in connection with the additional pots (Fig. 7 and Fig. 8: Multipurpose Hot-Dip Galvanizing line). At the same time we'll get an new wiping system improved by a three-rolls system in the pot. The cooling system after coating will also be extended.

This new equipment will

- reduce the time of changing the coating system
- improve the wiping condition
- raise the cooling rate
- improve the cleanness of the bath

Furthermore we'll make efforts to improve

- the quality of the Galfan surface
- the cleanness of the cold rolled strip
- the condition of on-line temper-rolling

A lot of work has still to be done.

Galfan sheet production at Hoesch Stahl, F.R.G.

Year	No. of campaigns	Total production, metric tons
1983	2 (trials)	550
1984	2	4,060
1985	3	8,120
1986	4	14,170
1987	4	15,580
1988	(first)	5,920

Cumulative output, 48,400 tons

Fig. 1

HOESCH CAMPAIGN Nr. 16

Eichen work

January 4 - 13, 1988

Production		: 5917 t
Operation rate		: 31,7 t/h
Quality		: Lockformer Quality Drawing Quality Special Drawing Quality Structural Quality
Skinpassed		:
	on line	2390 t
	off line	1870 t
Thickness		: 0,50 - 2,00 mm
Speed		: 23 - 120 m/min
Temperature		:
	bath	430 - 470 ^{o}C
	strip	500 - 560 ^{o}C
Analysis		:
	Ingots	4,4 % Al, 0,04 % Ce + La
	bath	4,1 - 4,5 % Al
Coating		: 95 - 300 g/m^2
Consumption		: 221 t
Dross		: 1,0 kg/t production

Fig. 2

Relation Gauge / Temperature

Gauge	Temperature
≤ 0,80 mm	450 °C - 470 °C
≤ 1,50 mm	440 °C
> 1,50 mm	430 °C

Fig. 3

Relation between wiping pressure (air) and line speed

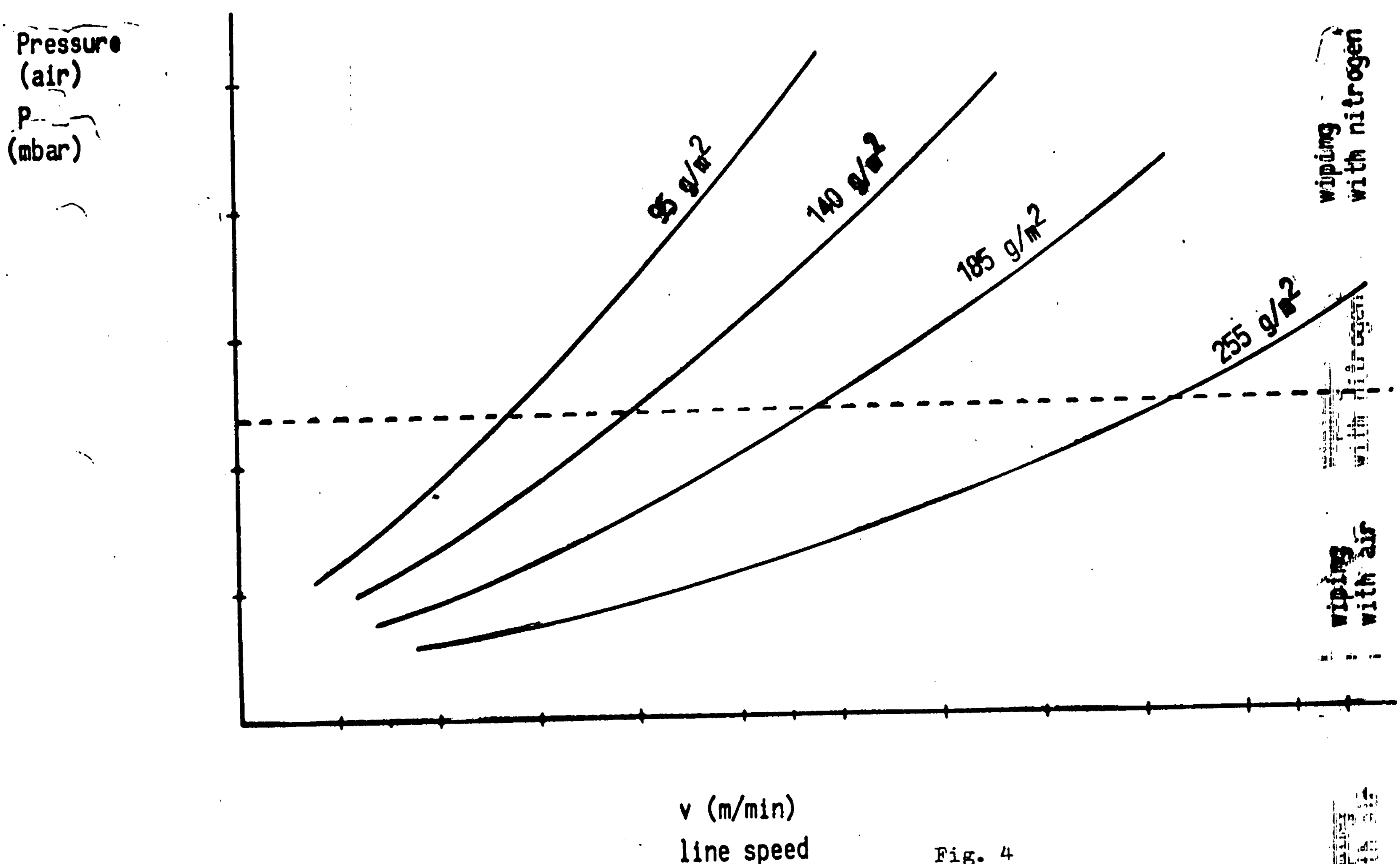


Fig. 4

The main defects typical for Galfan

- deep grain boundaries
- ripples and tears
- bare spots

Fig. 5

Changing system

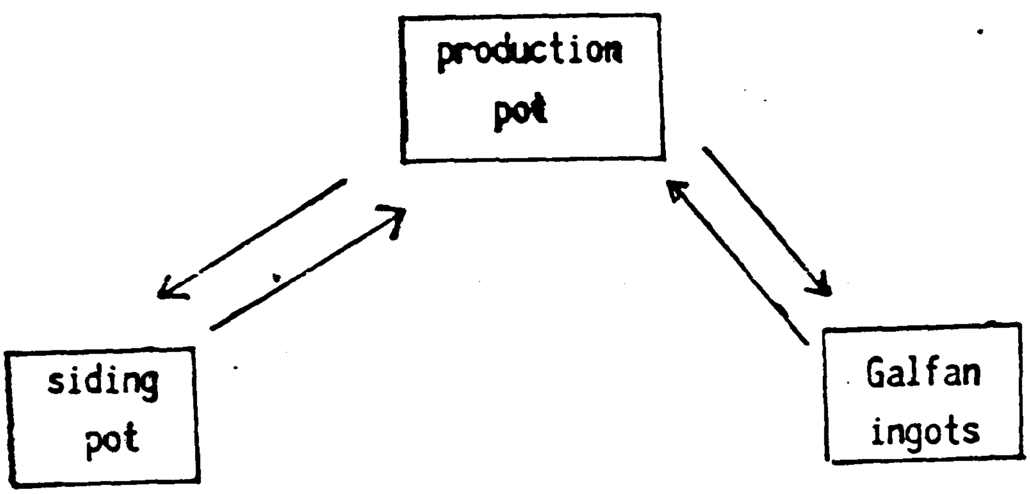


Fig. 6

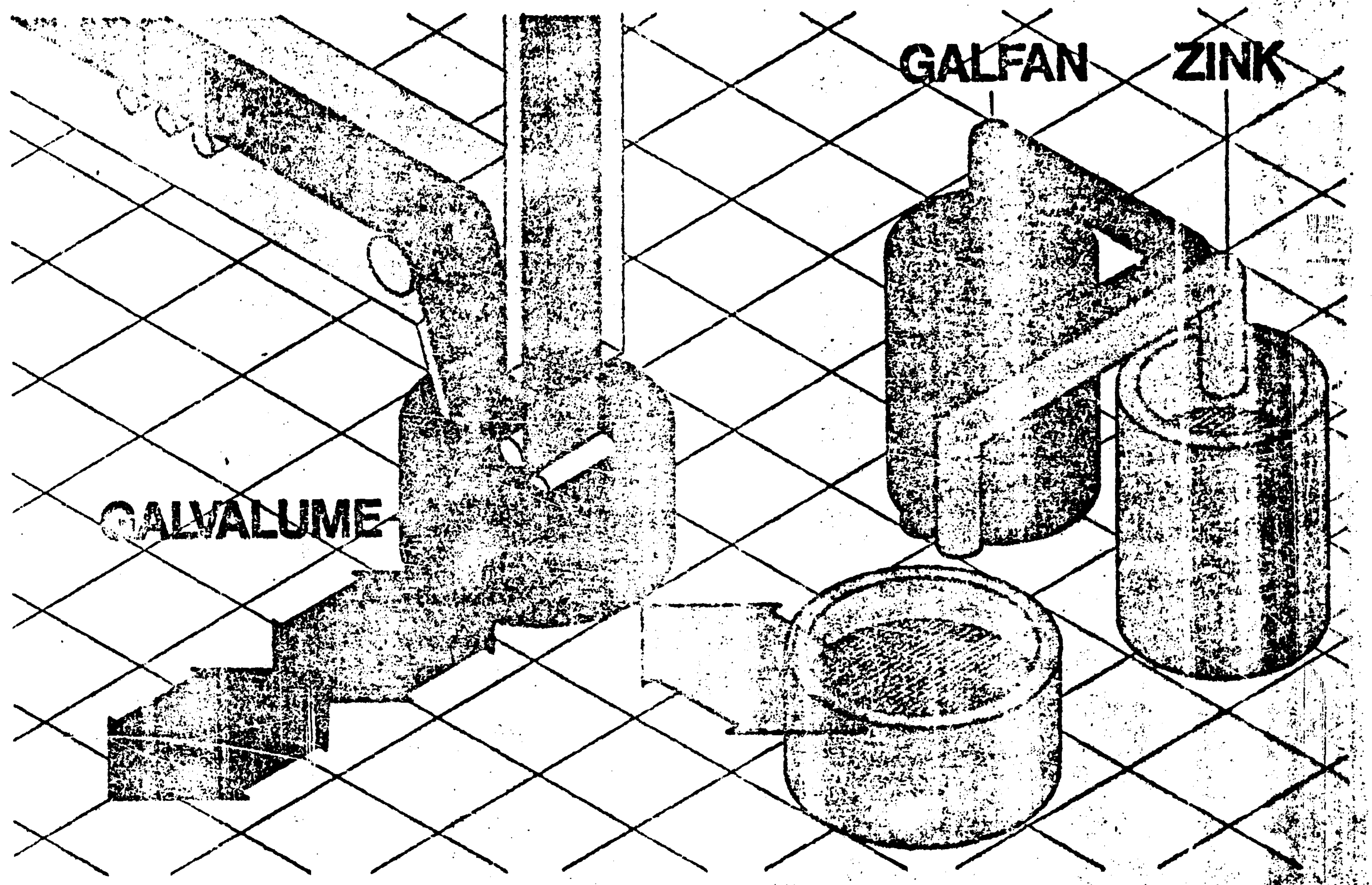


Fig.7

Multipurpose Hot-Dip Galvanizing Line

No. 2 Hoesch Stahl, Kreuztal-Eichen plant

● Started:	1966
● Width:	65 in. (1,650 mm) maximum
● Speed:	430 fpm (130 m/min) maximum
● Capacity:	26,000 tons per month (36 tons an hour)

● Equipped with Heurtey minimized spangle unit

To be rebuilt in 1988

● To include two interchangeable ceramic pots plus two stand-by pots

● Products:	Hot-dip galvanized GALFAN GALVALUME

Fig. 8

GRAIN BOUNDARY DENTS

I am going to talk to you about the influence of the aluminum content of the bath and the cooling rate on the appearance of a surface defect of GALFAN coated sheets which is called "grain boundary dents." Following the studies made by Dr. Fuchs from Hoesch and Dr. Hirose from Nisshin, the dents are mainly observed with an eutectic structure and appear as a solidification shrinkage. They cannot be completely removed by a skin-pass treatment even with higher reductions; the dents are very detrimental when the sheets must be coil coated. Following the experience of different licensees the decrease of Al content can reduce the dents formation but the corrosion resistance has to be checked. The eutectic structure which is harmful for the coating appearance can be obtained by different means: adjustment of Al content, very high cooling rates (higher than 100° to 200° C/sec) and grain refining by zirconium additions.

On the following slides, we can see the grain boundary dents observed with the scanning electron microscope in the case of industrial GALFAN sheets. That defect is a depression along the grain boundaries whose depth is the most important at the ternary joints. Sometimes, there is a clustering of zinc-rich globules at ternary joints whose presence could be explained by a local Al depletion of the liquid metal.

- Sheets from Fabrique de Fer de Maubeuge - normal spangle and minimum spangle:

D3 - samples from Weirton Steel; the dents appear clearly at a low magnification.

D4 - GALFAN from Hoesch and Weirton for which the depth at tenary joints is between 3 and 5 microns. It was measured by a focusing technique with a light microscope.

D5 - Samples from an industrial campaign at Ziegler with zirconium additions as a grain refiner. The structure is fully eutectic but the surface roughness is too high due to depressions at grain boundaries. The dents are very deep (about 10 to 15 microns).

D6 - During 1987, a series of trials were carried out at CRM with the simulation equipment. These trials were intended to complete information concerning the lowering of Al content in the ASTM specification by covering a wide range of Aluminum between 4.0 and 5.2%. The effect of magnesium has been studied for the bath containing 4.0% Al. The entry temperature 500°C and the bath temperature (470°C) correspond with the present industrial practice. A convection cooling or slow cooling (2° to 5°C/sec.) giving big spangles and a gas jet cooling or rapid cooling (20° to 30°C/sec.) have been used for each bath.

D7 - You can see here the scheme of our simulation equipment which can achieve the whole treatment (annealing and galvanizing) under protective atmosphere (mixture of nitrogen with 5% of hydrogen).

D8 - The bath analysis are listed on this slide; a magnesium addition (0.03%) has been tested for the bath containing 4.0% Al. Lanthanum and cerium ranged each between 30 and 500ppm.

D9 - The samples were evaluated with respect to:
- coating analysis
- adherence and ductility (Zero T bend and impact test)
- surface aspect (visual - roughness measurements using a three dimensional surface topography)
- metallographic study - cross-sectional and surface investigation.

Moreover, a corrosion study has been initiated with accelerated tests, polarisation measurements and atmospheric exposure.

Coating Analysis

D10 - On this graph, the X-axis is the Al content of the bath; there is a regular increase of the Al content of the coating which is almost equal to the Al content of the bath; the cooling rate has no influence.

D11 - As can be seen on this slide, the increase of cooling rate can reduce the iron content of the coating and thus the thickness of the intermetallic layer which mainly results from the diffusion of Aluminum towards the steel during the cooling. The Al content of the bath has an influence on the Fe-Al reaction especially for the slow cooling (it is the dotted line on this slide); the maximum thickness of the intermetallic layer (about 0.2 μ) is obtained at 4.6% Al.

D12 - The adherence trials using O-T bend and impact test were very good for the whole range of Al content; only a very slight cracking was observed.

D13 - Concerning the visual aspect of the samples, we can say that the grain boundary dents become deeper with the increase of Al content mainly above 4.6% Al; the dents are deeper and wider with the slow cooling rate. (You will see the samples in a few minutes).

To evaluate the surface aspect for each bath composition, roughness measurements were made using a powerful technique which provides a three dimensional surface topography and which is called "Mechanical Scanning Microscope"; I express here my thanks to Dr. Hirose from Nisshin Steel for the very useful and important work he has made with his equipment to characterize our samples. The tracing speed is very low (0.3 mm/sec.) and it takes about 2 hours to get the topography of the whole surface of a square sample of 20 mm.

D14 - The following slides show some examples of three-dimensional topography. This slide corresponds to 4.02% Al and slow cooling rate. We can see the boundaries between different grains as well as the ternary joints. Three typical dents are surrounded with a red circle and the way to measure the depth along the Z-axis is indicated by the red line. The magnification is one thousand times along the Z-axis and 10 times along the two other axes.

In that case, the average depth of dents is 5.7 μ.

D15 - For 4.6% Al the average depth is more important (10.8 microns)

D16 - At 5% Al, the problem is very serious because the depth of some dents can read 20 microns, the average depth being 15.7 microns.

D17 - With the rapid cooling, the grains are smaller of course; the dents are more numerous but they are less deep and less wide than for the slow cooling.

D18 - Nevertheless, the depth is increased with higher Al contents - 7.5 microns at 4.6% Al.

D19 - up to 9.3 μ at 5% Al.

D20 - The grain size does not seem to be influenced by the Al content or by the presence of magnesium. The number of grains per square decimeter is about 2,000 for the rapid cooling and 300 for the slow cooling.

D21 - The number of dents per unit area is strongly influenced by the Al content of the bath for the rapid cooling with a maximum of about 2000 dents per square decimeter at 5.0% Al; at 4.0% Al, the density of dents is low even for the rapid cooling. (Mg has no significant effect.)

D22 - As shown on this slide, the average depth of dents increases with the Al content up to 5.0% Al and is higher for the slow cooled samples.

D23 - But it is necessary to normalize these values by dividing the average depth (D) by the coating thickness (T) in microns since the grain boundary dents are affected by the coating weight for the same bath composition.

The normalized average depth is minimum at 4.0% Al (20 to 30% of the coating thickness); it remains almost constant between 4.2 and 4.6% Al and is very high between 4.9 and 5.1% Al with a maximum value at 5.0% Al (about 70% of the coating thickness for the slow cooled samples and 45% for the rapid cooled samples). The tendency is very similar for the two types of cooling and the presence of magnesium has no remarkable influence.

D24 - The number of dents per grain is a parameter which takes account of the density of dents as well as the grain size. The tendency is similar to that observed for the normalized average depth. For the rapid cooled samples with 4.0% Al, the number of dents per grain is very low; Mg has no significant influence.

D25 - The susceptibility to dents formation can be defined by the product of the two parameters: the number of dents per grain and the normalized average depth.

D26 - Using this new parameter, the difference between slow cooling and rapid cooling is very strong especially for higher Al contents; moreover a bath composition of 4.0% Al seems to be necessary to minimize the dents formation.

D27 - The cross-sectional microstructures show the distribution of the zinc-rich globules which is influenced by the cooling scale and the Aluminum content.

The globules are big and parallel to the steel substrate for the slow cooling and they are smaller, more numerous and often perpendicular to the steel in the case of the rapid cooling; moreover, some of them reach the coating surface.

D28 - When the Al content is increased, the presence of primary phase is less important. On the lower part of the slide which corresponds to 4.9% Al and slow cooling rate, we can see a cross-section just through a ternary joint with a depth of about 12 microns. You can observe that the area of eutectic structure is very important between the coating surface and the zinc globules which are close by the steel. This type of microstructure must be put in relation with the dents formation.

D29 - As can be seen on this slide, some primary phase is still observed at the aluminum content of 5.13%.

The two following slides show the coating surface as observed with the scanning electron microscope:

D30 - 4.3% Al - slow cooling

D31 - 4.6% Al - slow cooling.

D32 - The grain boundary dents defect is a problem of eutectic solidification. To understand the mechanism of their formation, we must consider at first the solidification at the scale of the eutectic lamellae. This slide shows the Zn-Al phase diagram; Alpha-phase is the zinc-rich phase and Beta-phase is the Al-rich phase. A regular lamellae two-phase eutectic is growing unidirectionally and the solid/liquid interface is moving upwards at a rate V. The distance between two lamellae is called "interphase spacing." The alloy of eutectic composition is growing with its isothermal interface at a small temperature difference ΔT below the equilibrium eutectic temperature T_c (in our case 382°C). The alpha and beta lamellae grow side by side and are perpendicular to the solid/liquid interface. The form of the junctions where the three phases (alpha, beta, liquid) are present is determined by the condition of mechanical equilibrium. The eutectic growth is largely a question of diffusive mass transport. In order to drive the interface at a given rate V, an undercooling ΔT is necessary. This total undercooling is the result of two undercoolings: a solute undercooling and a curvature undercooling.

D33 - The solute undercooling is explained on this slide. At the rear of the drawing, we can see two lamellae Alpha and Beta (solid phases) which are growing at a speed V towards the front of the showing. C_{Zn} which is measured in the direction of the vertical arrow, is the zinc concentration of the liquid phase; during growth, the solid phases reject solute into the liquid; the solute which is rejected by one phase is incorporated into the other phase; it is the <u>diffusion coupling</u>. Therefore, lateral diffusion along the solid/liquid interface will become dominant and a periodic diffusion field will be established; the liquid becomes richer in zinc close by the Beta lamella (C_L^{β} on the slide) which is the Al-rich phase and poorer close by the Alpha lamella (C_L^{α}) which is the zinc rich phase. The thickness of the boundary layer is approximately equal to the interphase spacing λ. The interface composition on the boundary layer oscillates a very small amount, about the eutectic composition C_E and the amplitude of the oscillation decreases when the interphase spacing λ is smaller, for a given growth rate V. The lateral concentration gradients exert a "compressive" force perpendicular to the alpha/beta interface and tend to decrease λ. The Zn-Al phase diagram has been placed to determine the local phase equilibria; as can be seen, the amplitude of the concentration variation (C_L^{β} minus C_L^{α}) is proportional to a solute undercooling ΔT_s; the liquidus temperature varies along the solid/liquid interface.

The solute undercooling is a linear function of λ and V.

Where λ is the interphase spacing, V is the growth rate.

D34 - The proximity of the lamellae (the value of λ), while making diffusion easier and reducing the solute undercooling, also causes a departure from the equilibrium described by the phase diagram, due to capillarity effects. It is an opposing effect which arises from the increased surface energy associated with the increased curvature of the solid/liquid interface as λ decreases; this effect is called "curvature undercooling" and it depresses the liquidus lines of the equilibrium phase diagram as shown on this slide. The positive curvature of the solid phases in contact with the liquid results from the condition of mechanical equilibrium of the interface at the three-phase junction. The curvature undercooling ΔT_r is inversely proportional to the interphase spacing λ .

D35 - On this slide, the solute undercooling (diffusion effect) and the curvature undercooling (capillarity effect) are considered together. At the upper part of the slide, the diffusion paths of aluminum from alpha-phase to beta-phase are shown schematically; they rapidly become less significant as the distance from the interface increases. We can see here some depression or microdents at the scale of the alpha and beta lamellae.

The zinc concentration in the liquid at the interface is shown in the middle of the slide. Note that the eutectic composition C_E is not necessarily found at the junction of the two phases.

According to the Zn-Al phase diagram, the sinusoidal concentration variation and the solid/liquid interface leads to a change in the liquidus temperature of the melt in contact with the phases. It is the continuous curve at the lower part of this slide; the points where the liquid composition C_{Zn} is equal to the eutectic composition C_E are exactly at the eutectic temperature T_E. The difference between this curve and the eutectic temperature is ΔT_s, the solute undercooling.

The growing interface can be considered as being in a state of local thermodynamic equilibrium. That means that the measurable or actual temperature T_q of the interface which is constant along the solid/liquid interface corresponds to equilibrium at all points of the interface; thus, the interface undercooling ΔT which is the difference between T_E (the eutectic temperature) and T_q is constant along the interface; therefore, the difference between T_q and the continuous curve (the hatched region of the slide) has to be compensated by the local curvature in order to maintain local equilibrium at the interface. This hatched region represents the curvature undercooling ΔT_r which varies along the interface. (A negative curvature depression can appear at the center of a lamella in order to compensate for a very high local solute concentration which is often associated with a large interphase spacing λ .)

D36 - As we have just observed, the solute undercooling and the curvature undercooling vary in opposite senses as a function of the interphase spacing λ. ΔT_s increases linearly while ΔT_r decreases very rapidly with increasing spacing. The equilibrium between an attractive force arising from the diffusion field and a repulsive force between the lamellae arising from capillarity effects at small λ determines the eutectic spacing.

For a given growth rate V, the sum of the contributions, ΔT, which is measured downwards with respect to the eutectic temperature T_E exhibits a minimum for a certain value λ_M of the interphase spacing. At smaller spacings, eutectic growth is controlled by capillarity effects; at larger spacings, diffusion is the limiting process. Generally, it is assumed that growth would occur at the extremum λ_M An increase in the growth rate increases the absolute value of the slope of the ΔT_s line without influencing the ΔT_r curve; then, the extremum will be displaced to smaller spacings and the total undercooling ΔT is higher.

D37 - As shown on this slide, binary eutectics can undergo two types of morphological instability.

a. is the single phase instability which leads to the appearance of dendrites of one phase with interdendritic eutectic; this type of instability appears when a third alloying element is incorporated preferentially into one phase.

b. is the two phase instability with the appearance of eutectic cells and which occurs when a third alloying element is similarly distributed between both solid phases. This type of instability leads to depressions or grain boundary dents, at the junction of two eutectic cells for which the lamellae are differently oriented.

Then, the microdents observed between two adjacent lamellae become macrodents when the eutectic structure becomes unstable and gives rise to the formation of eutectic cells as it is always the case for the Galfanized sheets.

D38 - The coupled zone (hatched region on this slide) represents the temperature/composition region where the eutectic grows more rapidly (or at a lower undercooling) than dendrites of the alpha and beta phases. In the case of continous Galfanizing, we are always in the central part of the hatched area (cellular coupled eutectic) because the growth rate V and then the interface undercooling ΔT is too high to keep a planar eutectic which are typical of very low growth rates near equilibrium conditions.

D39 - With a slow cooling at the exit of the Galfan bath and a high Al content (for example 5.0% Al), the percentage of zinc rich particles is low and they are concentrated close by the steel substrate leaving a large pure eutectic area at the top of the coating; this type of structure is more sensitive to dents formation as we observed during our trials, because depressions or dents can easily appear at the intersection of two eutectic cells with differently oriented lamellae. (It seems that there are no dents between two cells in which the lamellae are parallel to the substrate).

On the opposite, with a rapid cooling and a low Al content (4.0% Al), the susceptibility to dents formation is much lower because the zinc rich globules are very numerous and they are distributed across the whole coating; many of them reach the coating surface which reduces the portion of eutectic phase at the surface.

D40 - In conclusion, we can say that the grain boundary dents... (per the actual writting conclusions).

GRAIN BOUNDARY DENTS

1986 :

STUDIES MADE BY DR. FUCHS AND DR. HIROSE (9TH GALFAN MEETING-SIEGEN, NOVEMBER 1986)

- SORT OF SHRINKAGE MAINLY OBSERVED WITH AN EUTECTIC STRUCTURE
  NOT COMPLETELY REMOVED BY SKIN-PASS
  DETRIMENTAL FOR COIL COATED SHEETS

- DECREASE OF AL CONTENT

  —> GREATER PERCENTAGE OF ZN-RICH GLOBULES
  —> EFFECTIVE TO REDUCE THE DENTS FORMATION
  —> CORROSION RESISTANCE MUST BE CKECKED

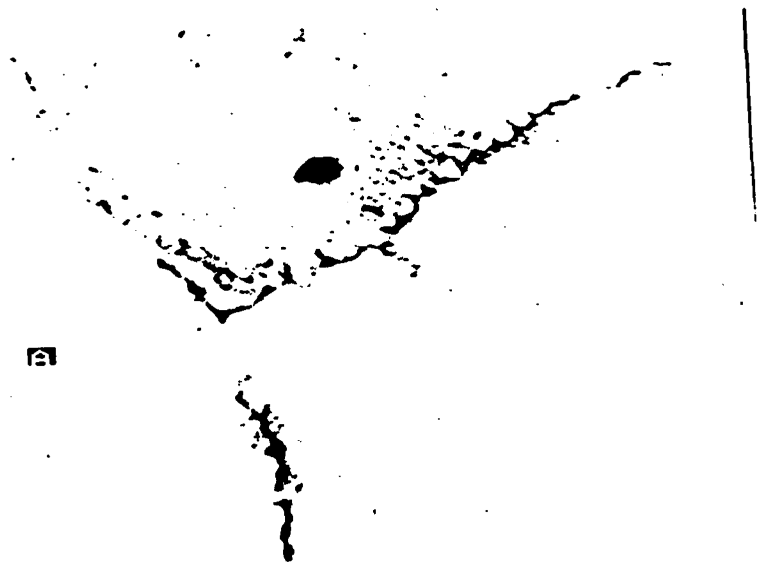
- THE EUTECTIC STRUCTURE IS HARMFUL WHEN IT IS ACHIEVED BY :

  - ADJUSTEMENT OF AL CONTENT (5.2 TO 5.3%AL)
  - VERY HIGH COOLING RATES (> 100-200°C/SEC)
  - GRAIN REFINING BY ZR ADDITION

D2

INDUSTRIAL SAMPLES - FFM (4.9% Al)

87/251/1 NORMAL SPANGLE 1000x

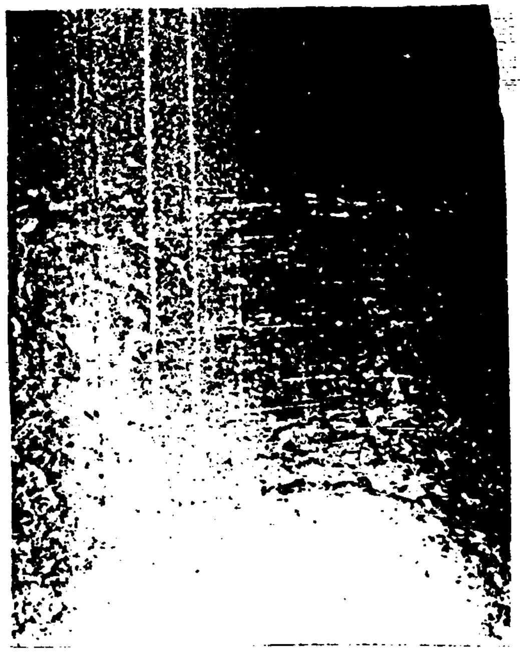


87/251/5 MINIMUM SPANGLE 3500x

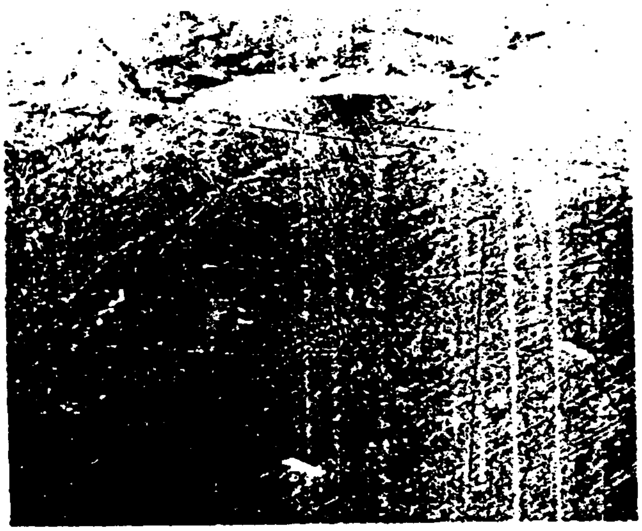
GALFAN SHEET WITH GRAIN BOUNDARY DENTS. EXAMINATION WITH THE SCANNING ELECTRON MICROSCOPE

INDUSTRIAL SAMPLES

WEIRTON



MACROGRAPH 5 x



86/295/5 80 x

86/295/6 2000 x

FIG. 5.23 - GALFAN SHEET WITH GRAIN BOUNDARY DENTS - EXAMINATION WITH THE SCANNING ELECTRON MICROSCOPE

GRAIN BOUNDARY DENTS

INDUSTRIAL SAMPLES

HOESCH

≃ 5,4

87/138/3 750 x

WEIRTON

≃ 3,4

86/29 2000 x

DENTS – ZIEGLER TRIAL WITH ZIRCONIUM

DEPTH
$\simeq$ 10-15 μ
R_A = 1.1 μ
R_T = 7.8 μ

87/81. 200 x

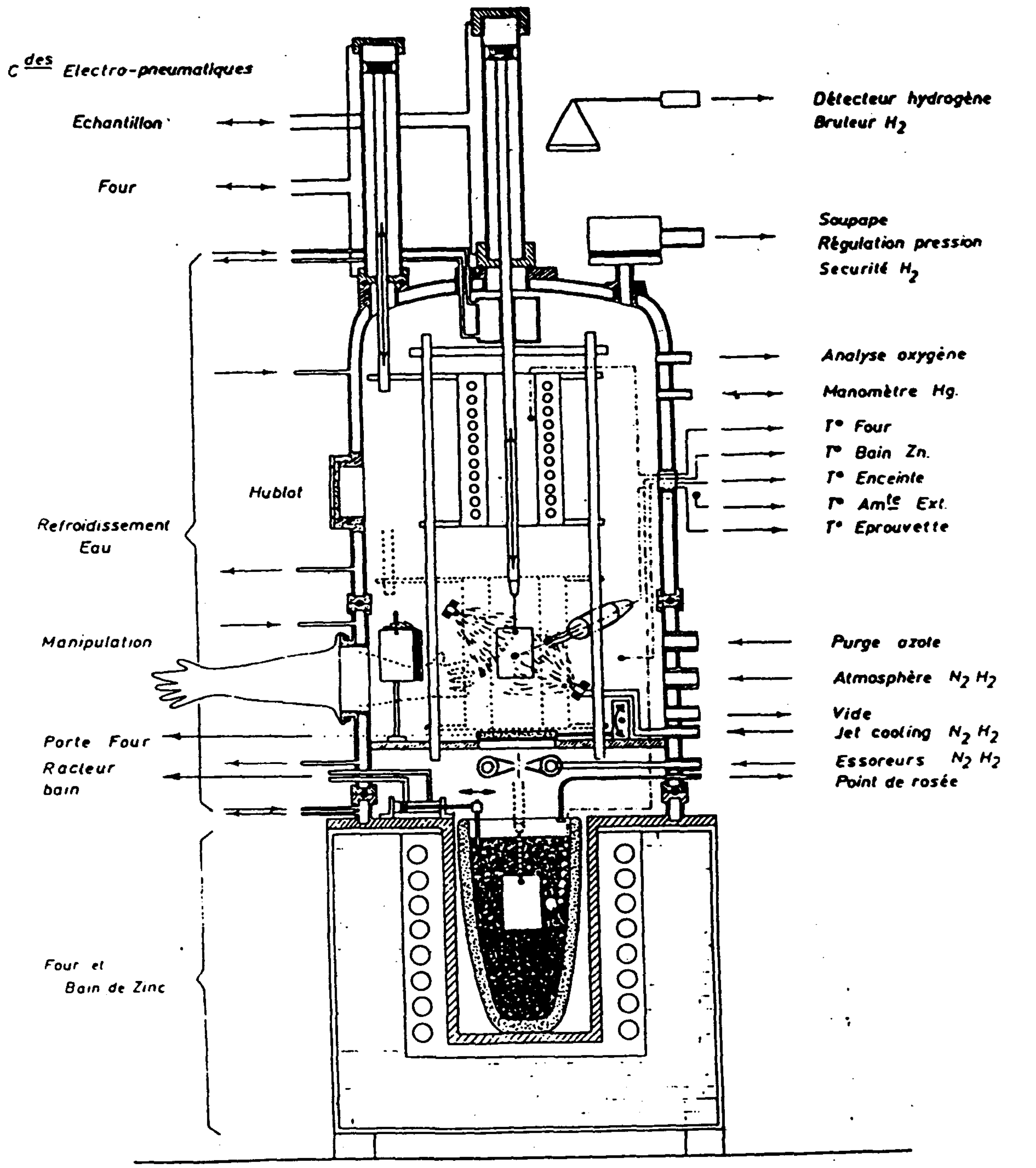
87/81/ 2000 x

1987 : TRIALS AT CRM WITH THE SIMULATION EQUIPMENT

TRIALS INTENDED TO COMPLETE INFORMATION CONCERNING THE LOWERING OF AL CONTENT (ASTM-SPECIF.)

- ZN-AL-MM ALLOY WITHOUT MAGNESIUM
- AL CONTENTS BETWEEN 4.0 AND 5.2%
- EFFECT OF MG (0.03%)
- CONTINUOUS-CAST STEEL (0.9MM IN THICKNESS)
- ATMOSPHERE N_2 - 5%H_2
- BATH TEMPERATURE = 470°C SHEET TEMPERATURE = 500°C
  IMMERSION TIME = 3 SEC
- COOLING RATES : SLOW COOLING (2-5°C/SEC)
  RAPID COOLING (20-30°C/SEC)

GALVANISATION SOUS ATMOSPHERE



CRM

D8

BATH ANALYSIS

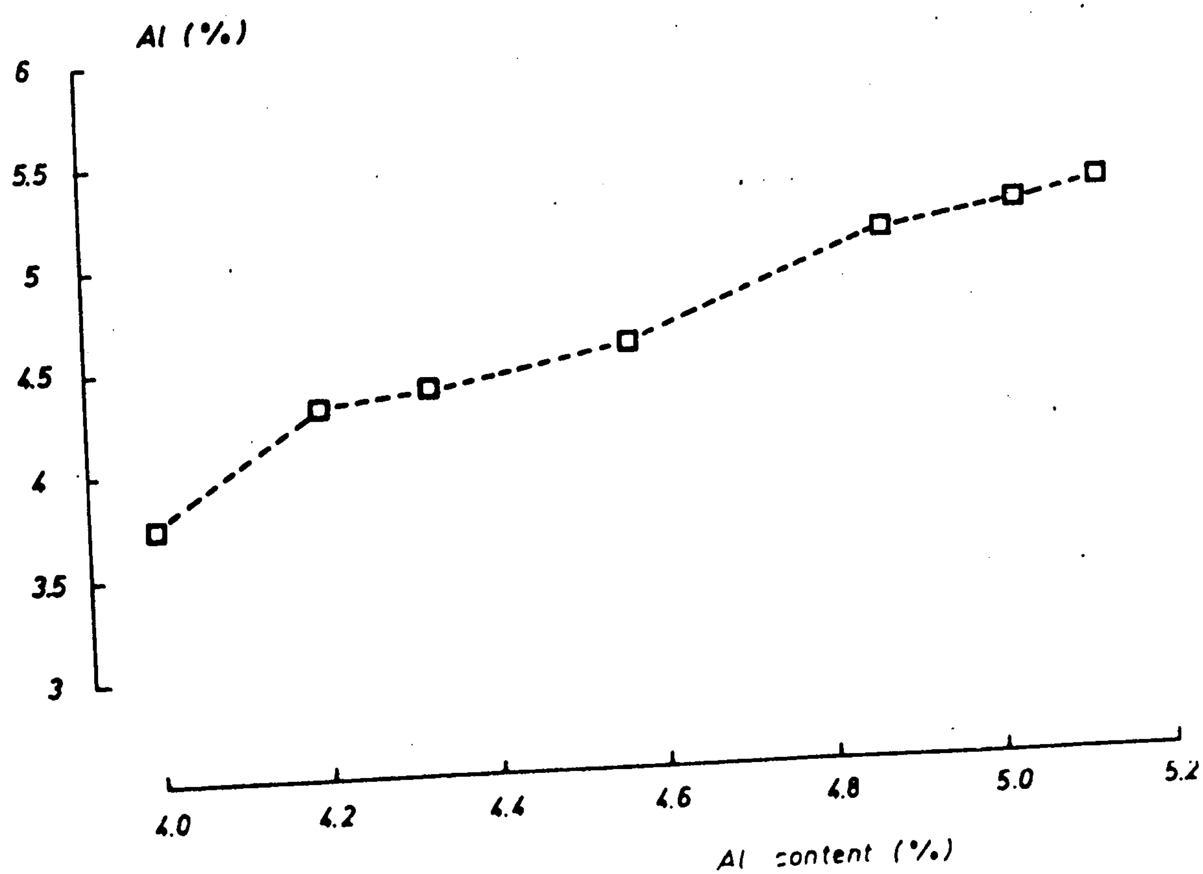
Ref.	% Al	% Mg
GF 5.1	4.02	
GF 5.2	4.02	0.029
GF 4.3	4.20	
GF 4.1	4.33	
GF 4.5	4.57	
GF 4.6	4.87	
GF 4.8	5.03	
GF 4.9	5.13	

%La = 0.003 - 0.05%
%Ce = 0.004 - 0.03%
%Pb = 0.001 - 0.003%
%Fe = 0.002 - 0.005%

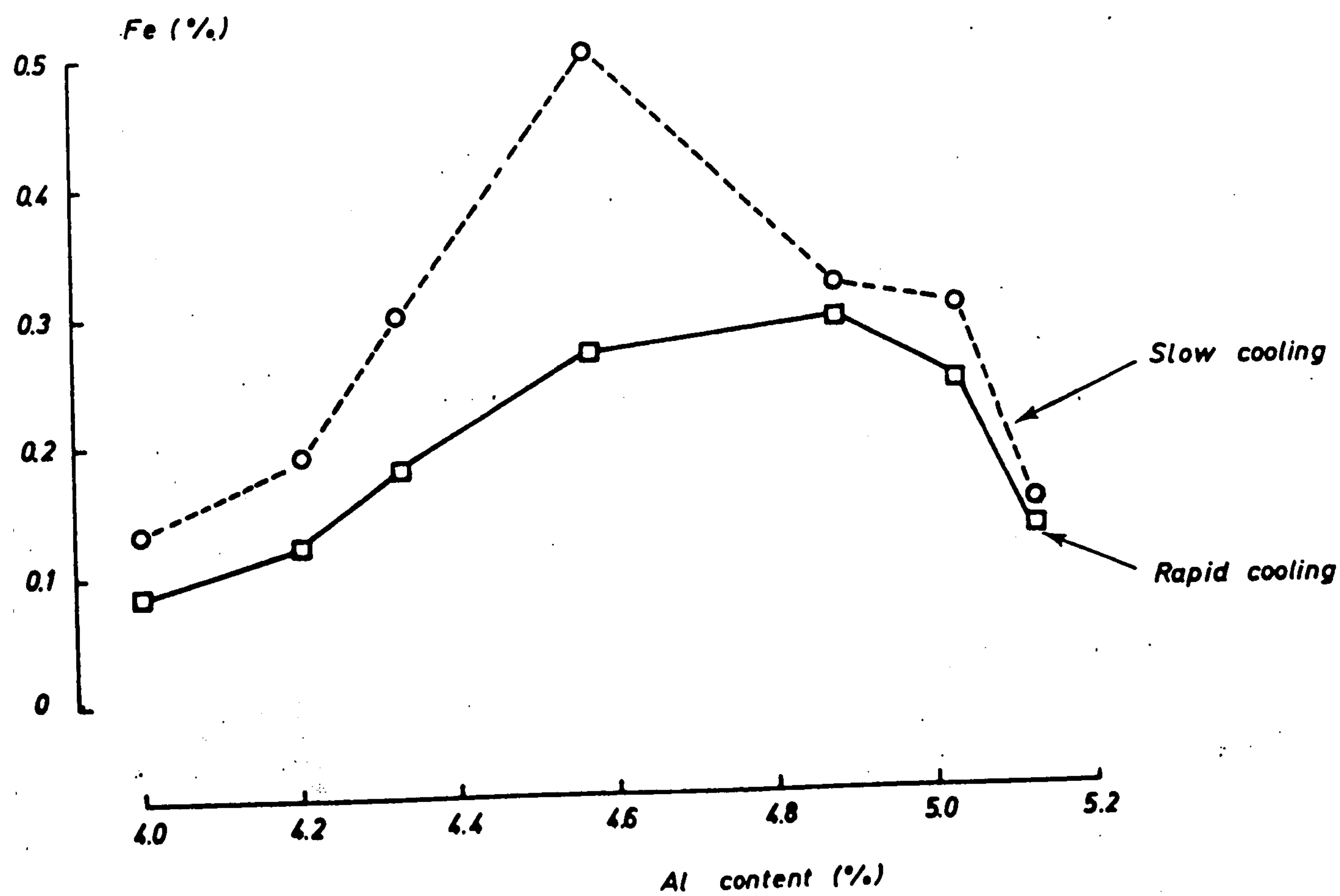
EVALUATION

- COATING ANALYSIS
- ADHERENCE TESTING (OT BEND - IMPACT TEST)
- SURFACE ASPECT
  ROUGHNESS MEASUREMENTS (THREE DIMENSIONAL SURFACE TOPOGRAPHY)
- METALLOGRAPHIC STUDY
  CROSS-SECTIONAL —> DISTRIBUTION OF PRIMARY PHASE
  SURFACE INVESTIGATION WITH SEM
- CORROSION STUDY (ACCELERATED TESTS, POLARISATION MEASUREMENTS, ATMOSPHERIC EXPOSURE)

Coating analysis - Aluminiun



Coating analysis - Iron



COATING ANALYSIS

INCREASE OF COOLING RATE

—> NO INFLUENCE ON AL CONTENT
—> CAN REDUCE THE INTERMETALLIC LAYER
WHICH MAINLY RESULTS FROM THE DIFFUSION OF AL AT THE EXIT OF THE BATH

INCREASE OF AL CONTENT OF THE BATH

—> REGULAR INCREASE OF THE AL CONTENT OF THE COATING
—> EFFECT ON THE FE-AL REACTION ESPECIALLY FOR SLOW COOLING
MAXIMUM THICKNESS (0.2µ) AT 4.6%AL

ADHERENCE TESTING

OT-BEND AND IMPACT TEST

NO PROBLEM (VERY SLIGHT CRACKING) ALONG THE WHOLE RANGE OF AL CONTENT

SURFACE ASPECT

VISUAL ASPECT

- THE GRAIN BOUNDARY DENTS BECOME DEEPER IN ACCORDANCE WITH THE INCREASE OF AL CONTENT (MAINLY ABOVE 4.6%AL)
- THEY ARE DEEPER AND WIDER WITH THE SLOW COOLING RATE

ROUGHNESS MEASUREMENTS

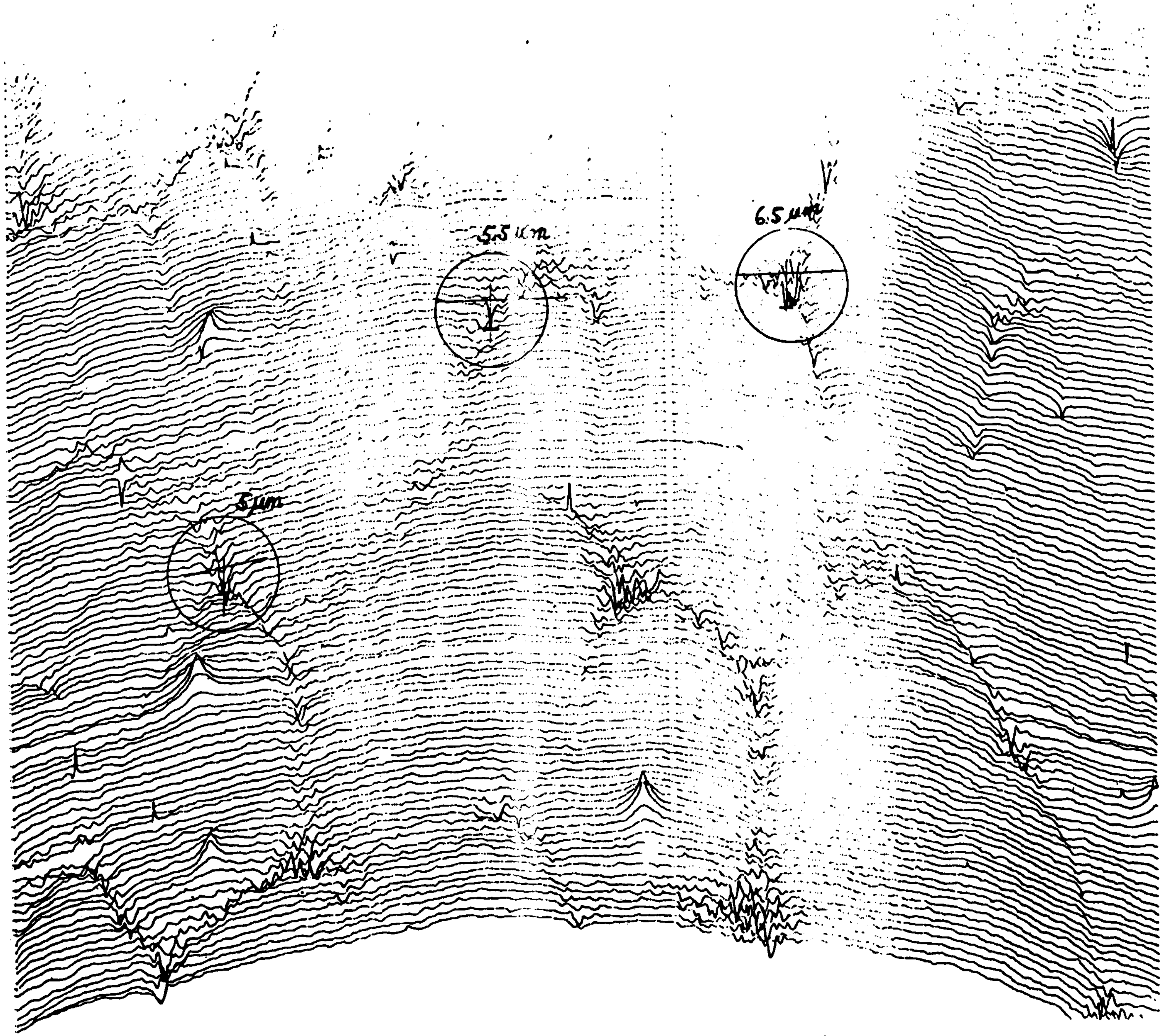
THREE DIMENSIONAL SURFACE TOPOGRAPHY
SIZE OF SAMPLES : 20 X 20 MM
SUCCESSION OF ROUGHNESS PROFILES BY STEP OF 0.15MM

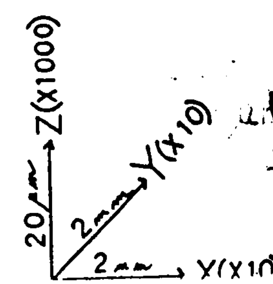
GF5.1RN

4.02 % Al

SLOW COOLIN

Depth = 5.7 μm





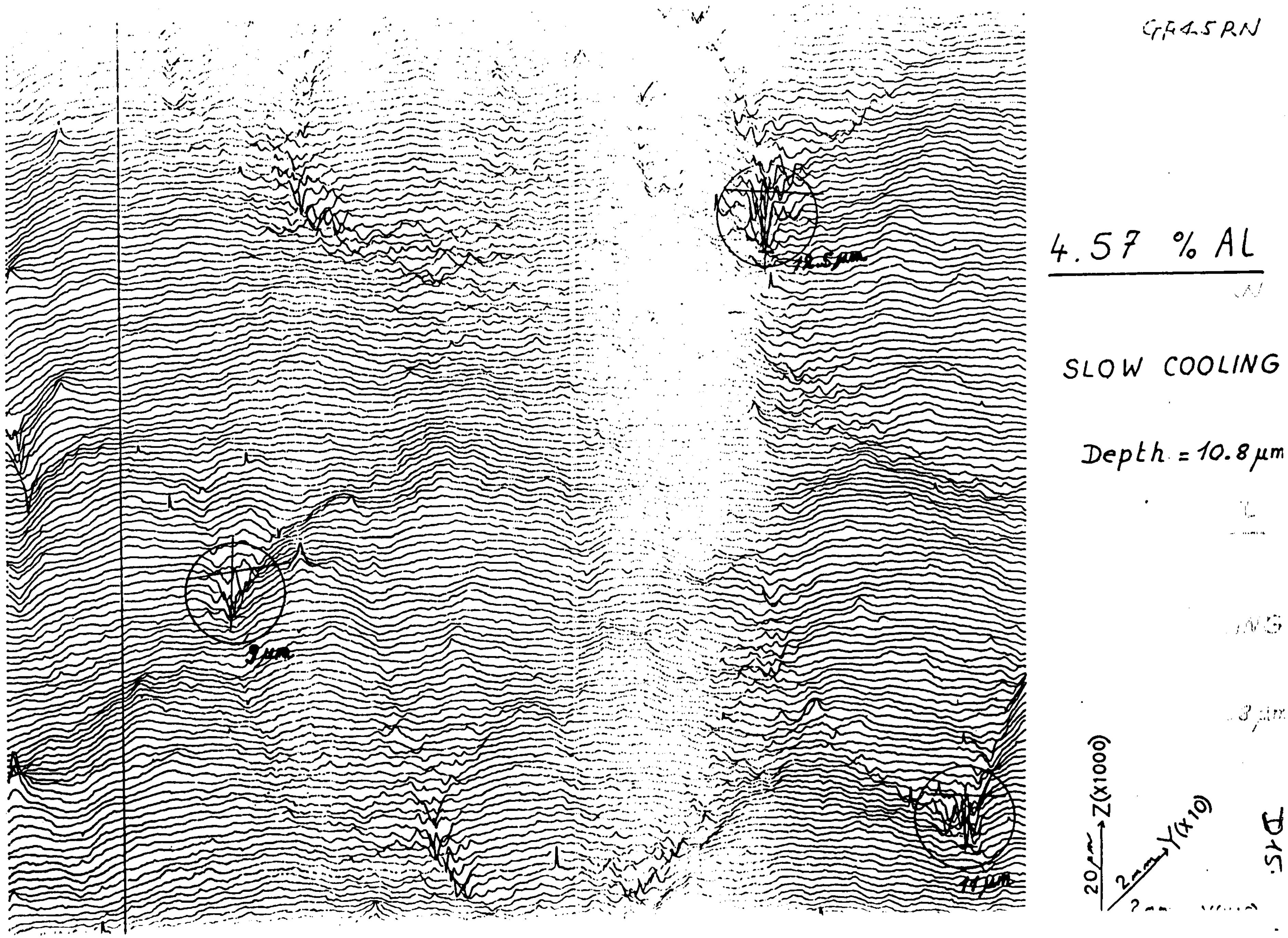
D 14

GF4.5RN

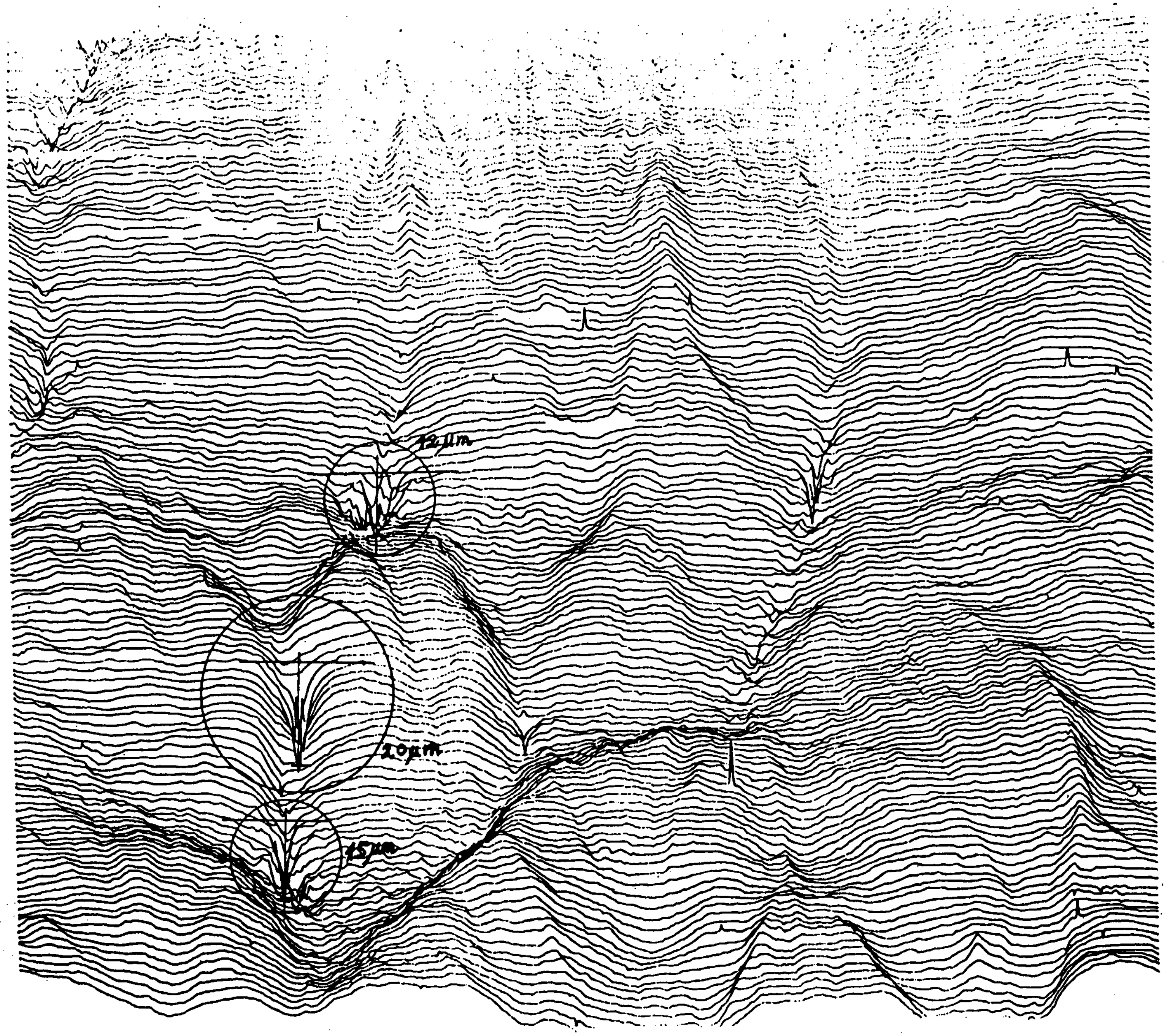
4.57 % AL

SLOW COOLING

Depth = 10.8 µm



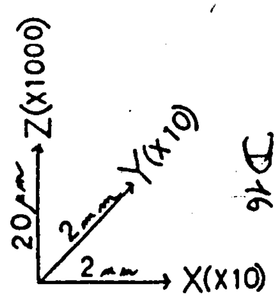
D15.



5.03 % AL

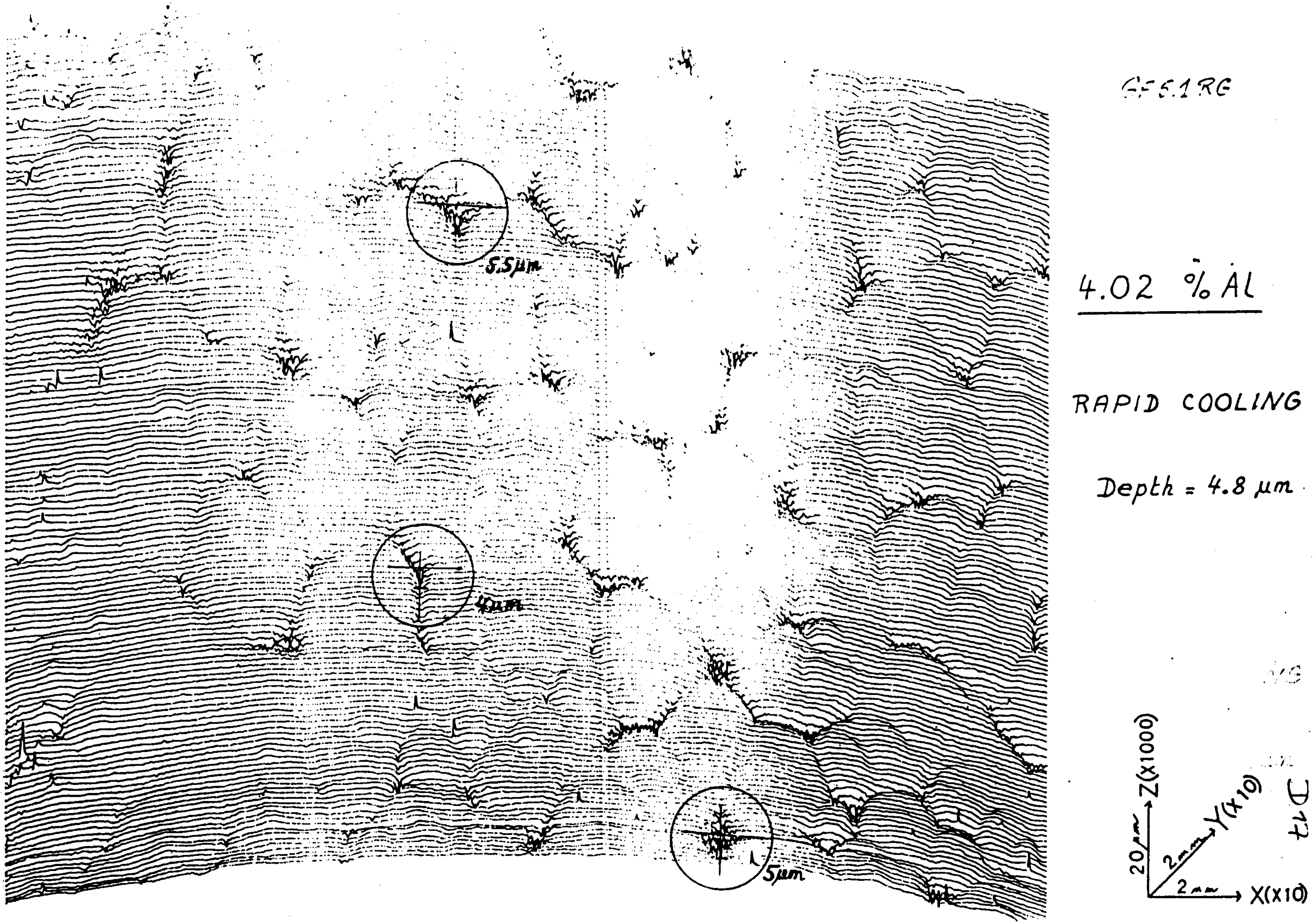
SLOW COOLING

Depth = 15.7µm



D16

GF51RG

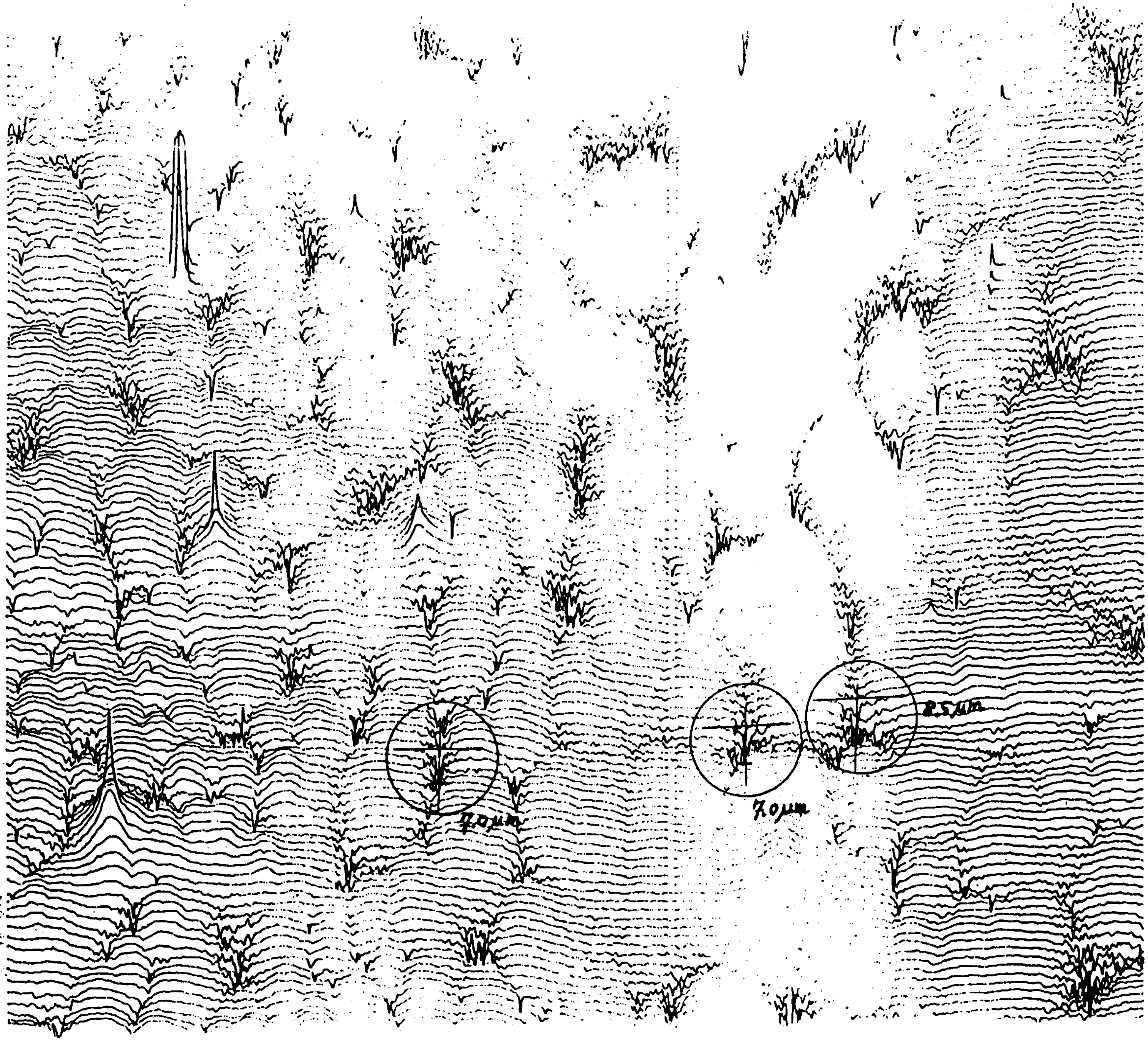


4.02 % Al

RAPID COOLING

Depth = 4.8 μm

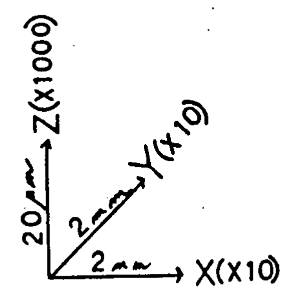
D17



4.57 % Al

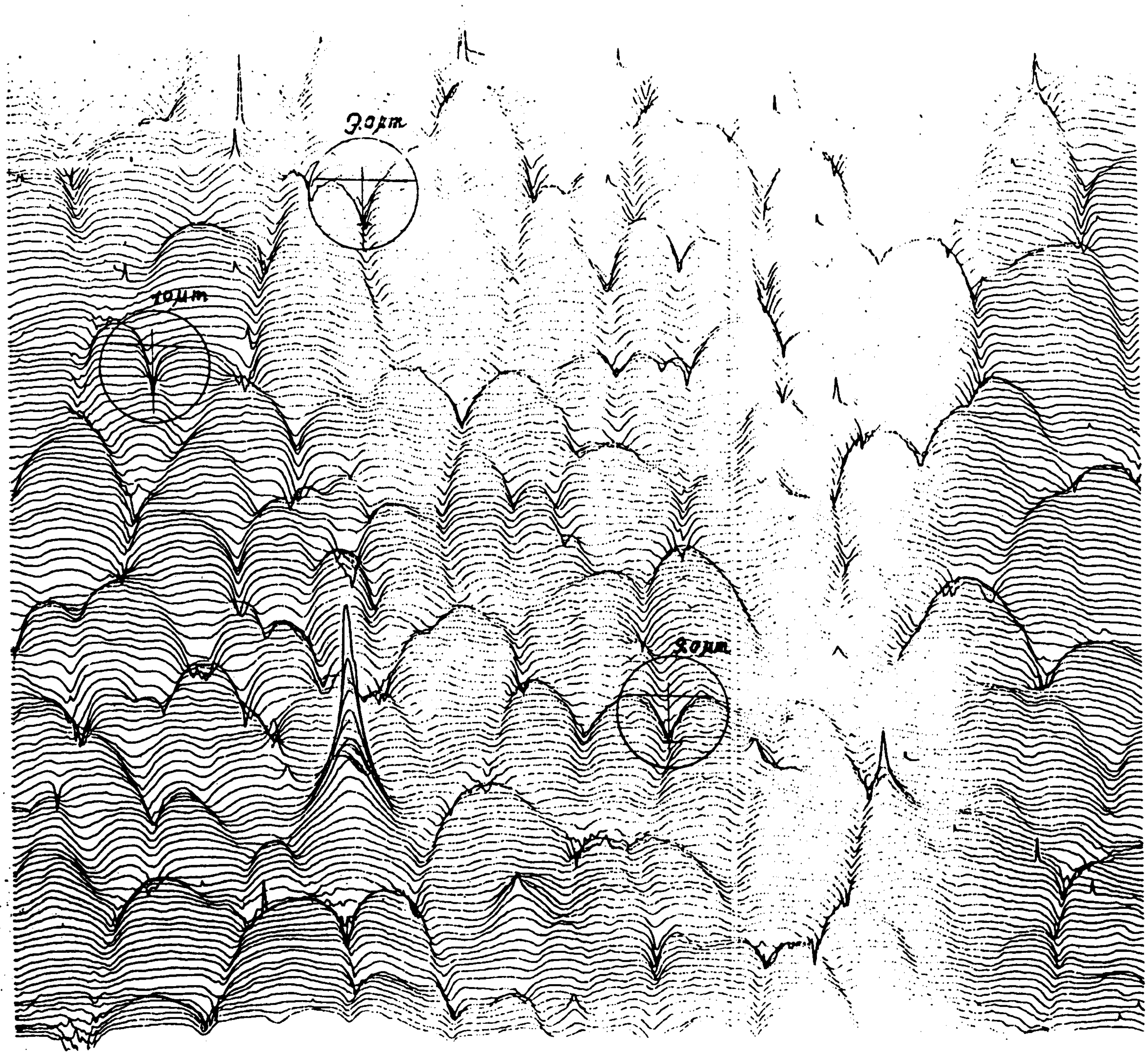
RAPID COOLING

Depth = 7.5 µm



D 18

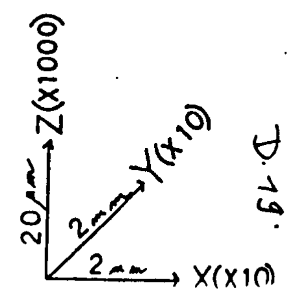
GF 9.8 RG



5.03 % AL

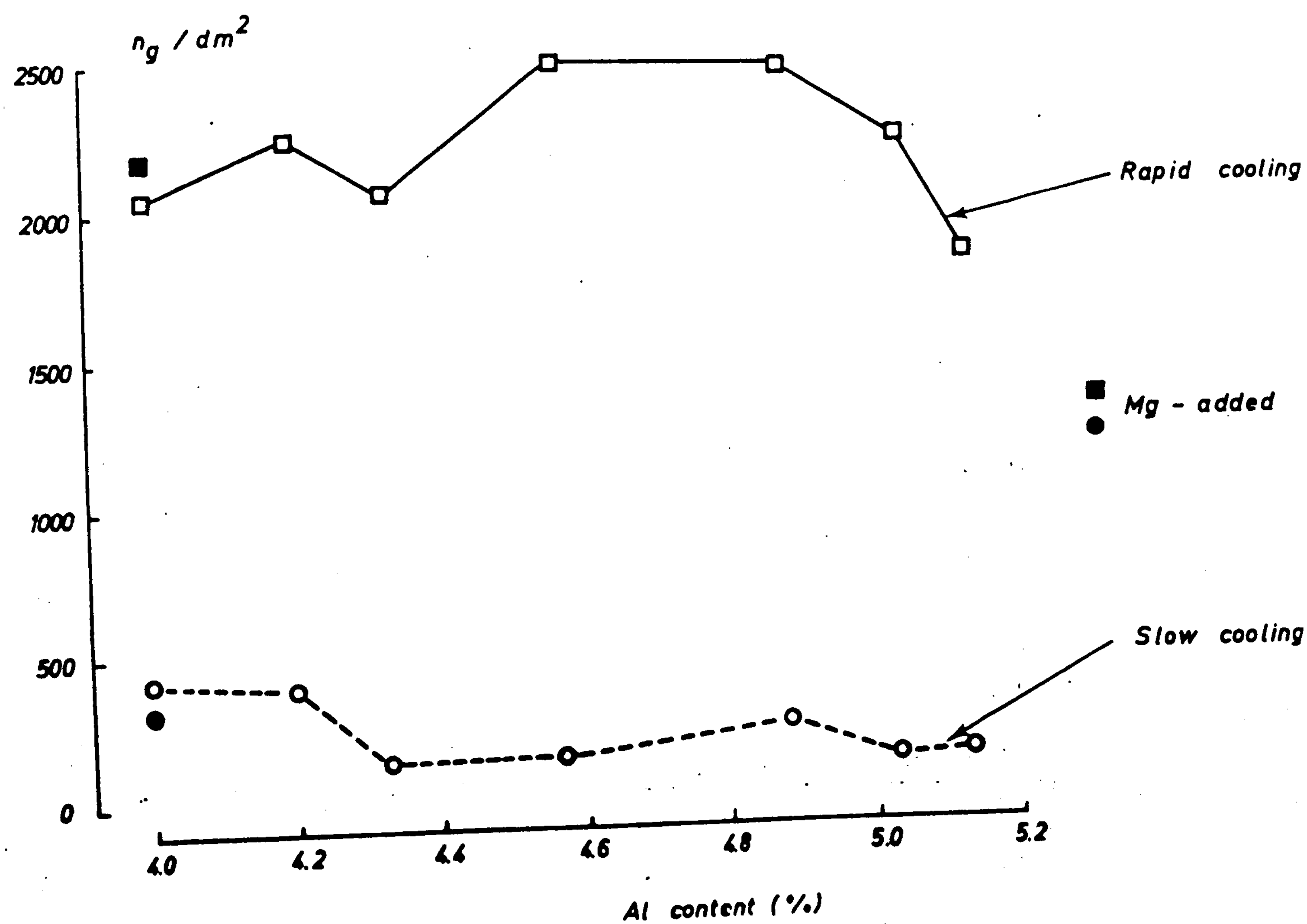
RAPID COOLING

Depth = 9.3 µm

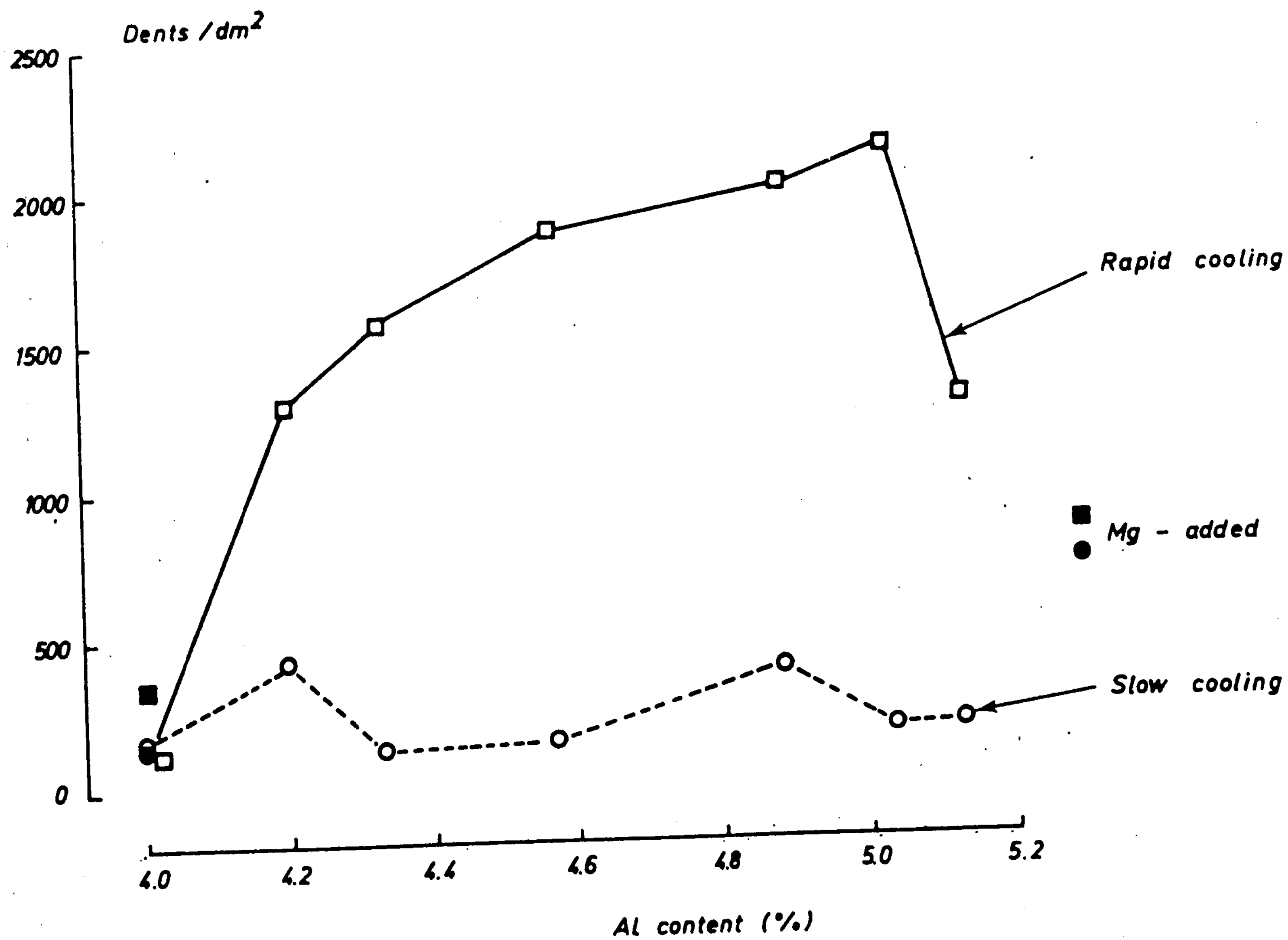


D.19.

Number of grains per unit area



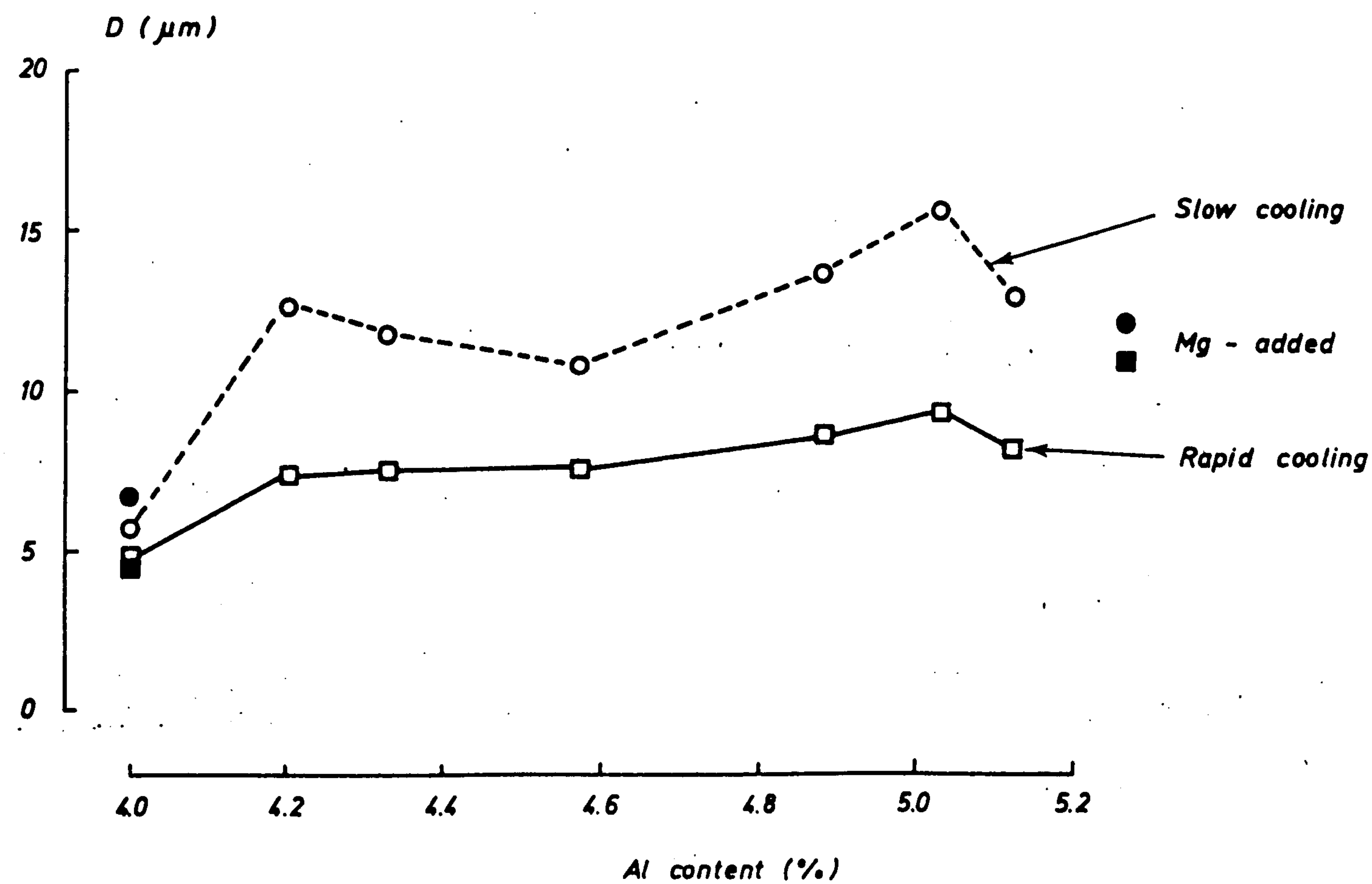
Number of dents per unit area

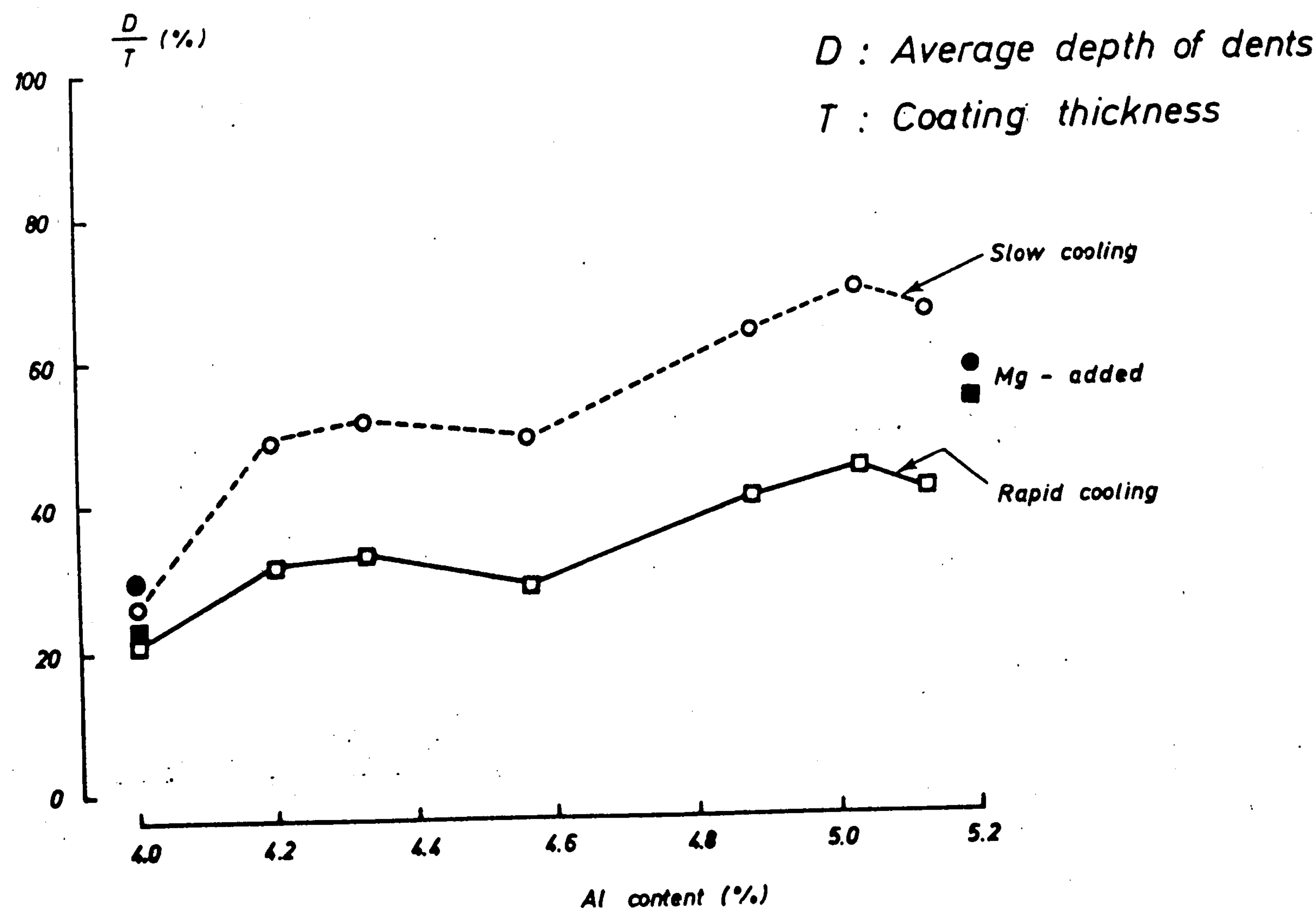


D21

D22

Average depth of grain boundary dents

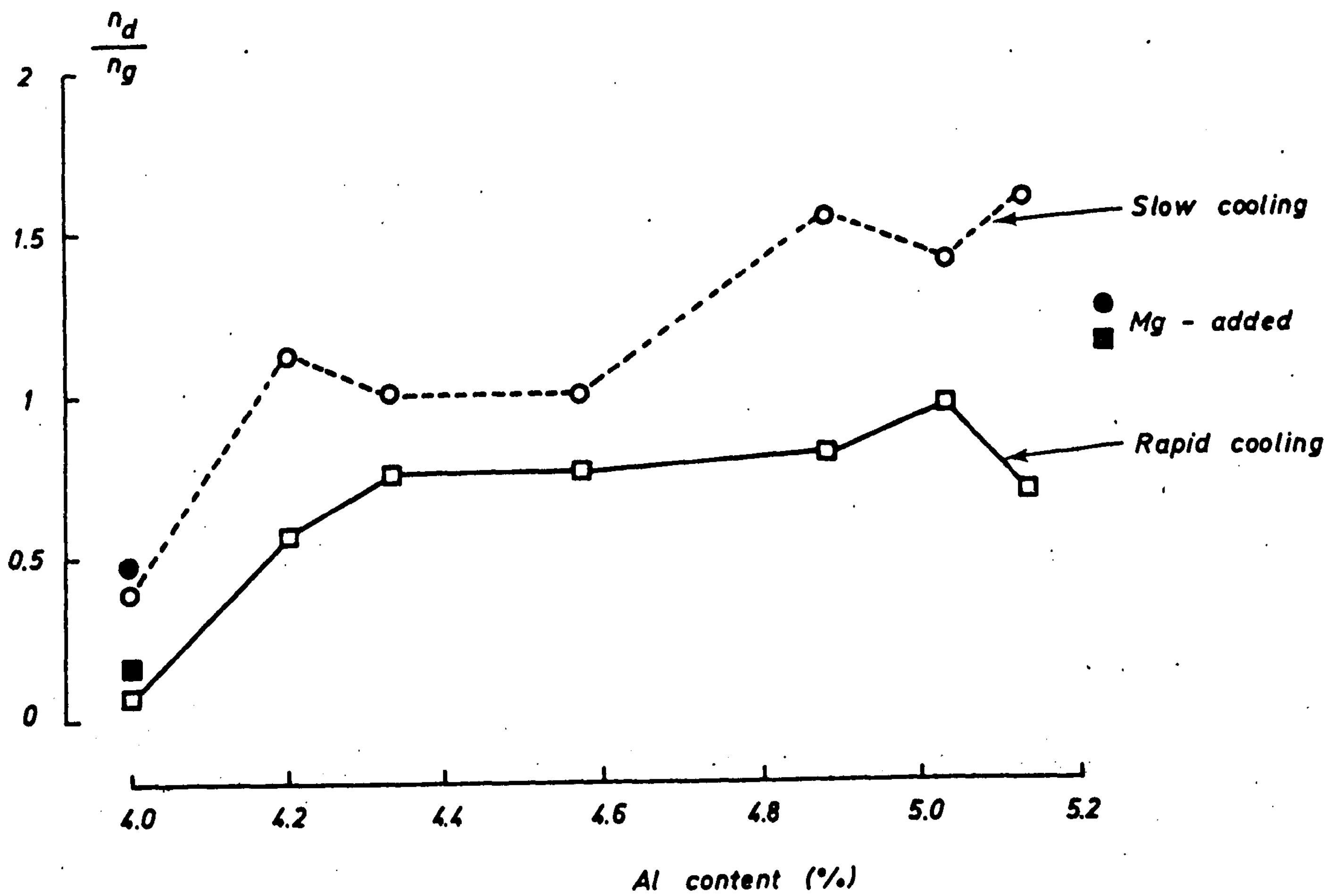




D/T (%)
100
80
60
40
20
0
4.0
4.2
4.4
4.6
4.8
5.0
5.2
Al content (%)
D : Average depth of dents
T : Coating thickness
Slow cooling
Mg - added
Rapid cooling

D23

Number of dents per grain



D24

SUSCEPTIBILITY TO DENTS FORMATION

$$SDF = \frac{N_D}{N_G} \times \frac{D}{T}$$

D = AVERAGE DEPTH OF DENTS (μ)

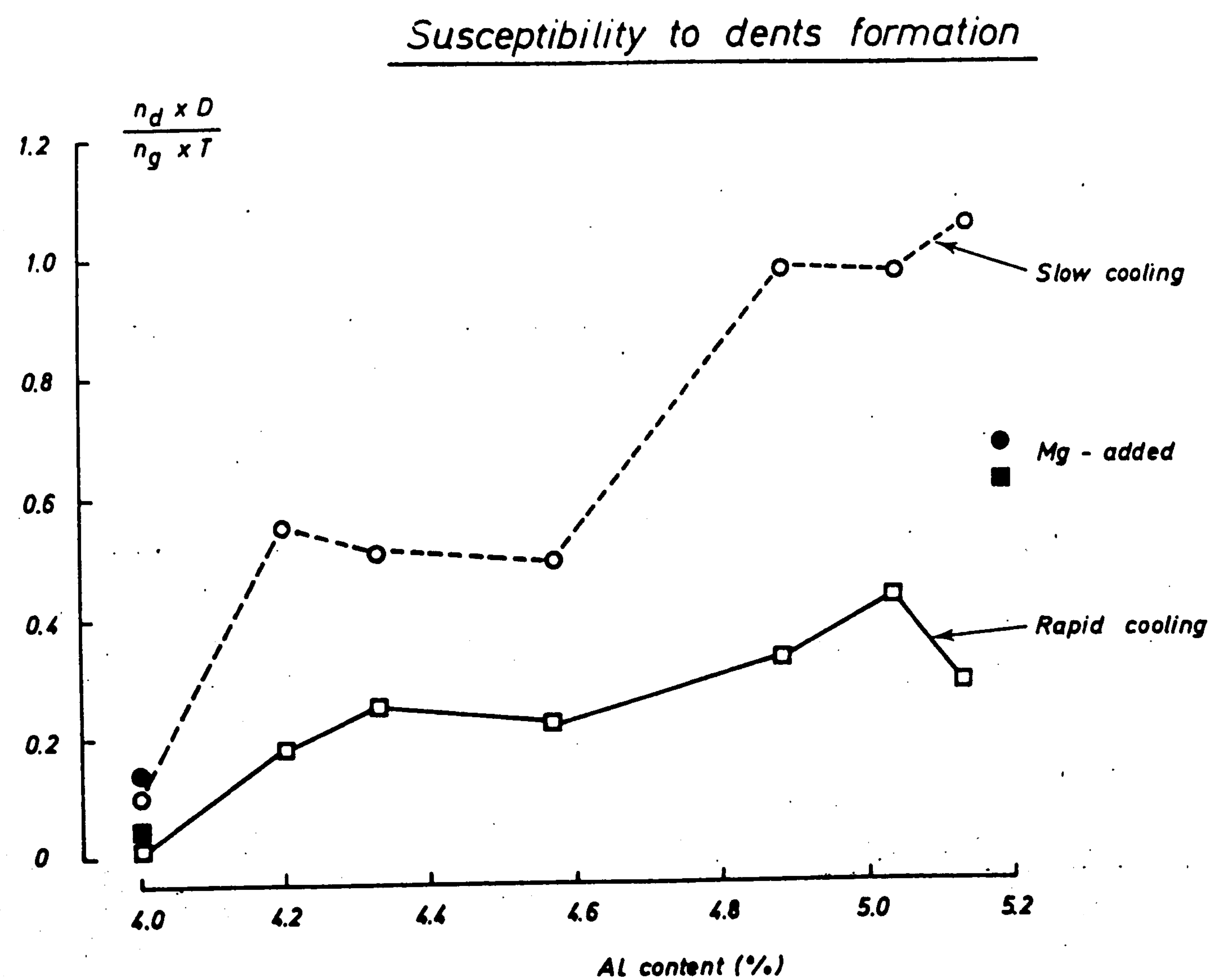
T = COATING THICKNESS (μ)

$\frac{N_D}{N_G}$ = NUMBER OF DENTS PER GRAIN

$$= \frac{N_D \times S_G}{S}$$

S_G = GRAIN SIZE (MM^2)

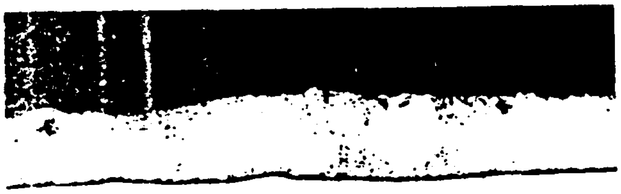
S = INVESTIGATED AREA


Susceptibility to dents formation
$\frac{n_d \times D}{n_g \times T}$
1.2
1.0
0.8
0.6
0.4
0.2
0
Slow cooling
Mg - added
Rapid cooling
4.0
4.2
4.4
4.6
4.8
5.0
5.2
AL content (%)

D.26.

SLOW COOLING | RAPID COOLING

4.02%AL + 0.03%MG



87/178/6 SC

87/178/8 RC

4.02%AL

87/178/2 SC

87/178/4 RC

4.20%AL

87/168/10 SC

87/168/12 RC

EFFECTS OF COOLING RATE AND AL CONTENT ON THE COATING MICROSTRUCTURE

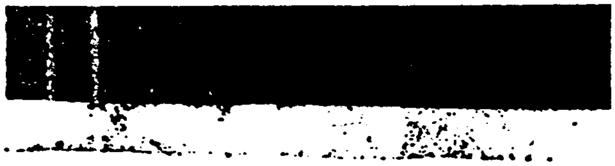
(500 x)

D28

SLOW COOLING

RAPID COOLING

4.33%AL



87/168/1 SC

87/168/4 RC

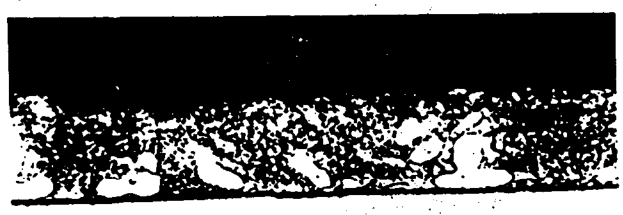
4.57%AL

87/178/15 SC

87/178/17 RC

4.87%AL

87/178/19 SC



87/178/22 RC

EFFECTS OF COOLING RATE AND AL CONTENT ON THE COATING MICROSTRUCTURE

(500 ×)

SLOW COOLING

RAPID COOLING

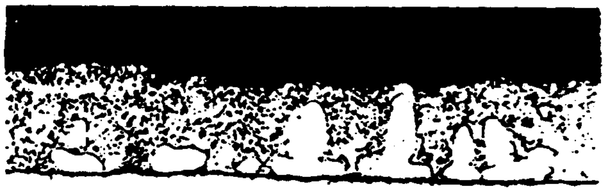
5.03%AL

87/178/23 SC

87/178/25 RC

5.13%AL

87/178/27 SC



87/178/30 RC

EFFECTS OF COOLING RATE AND AL CONTENT ON THE COATING MICROSTRUCTURE

(500 x)

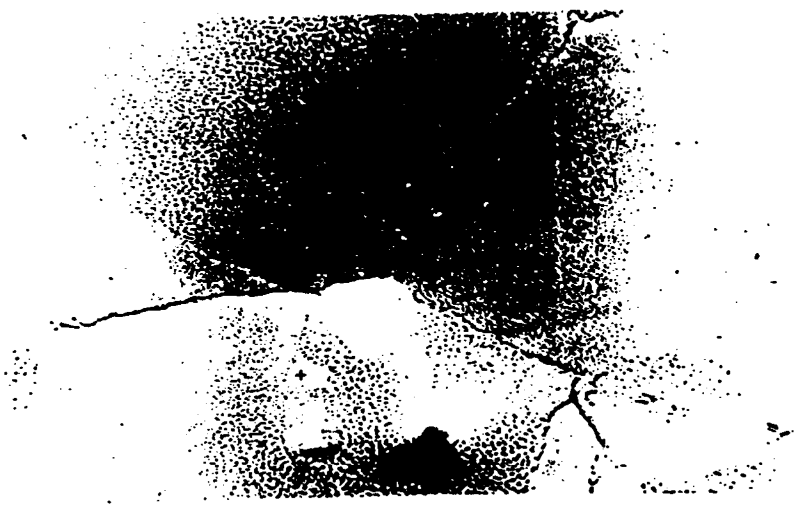
ZN - 4.33%AL - MM - SLOW COOLING

87/241/1 750x

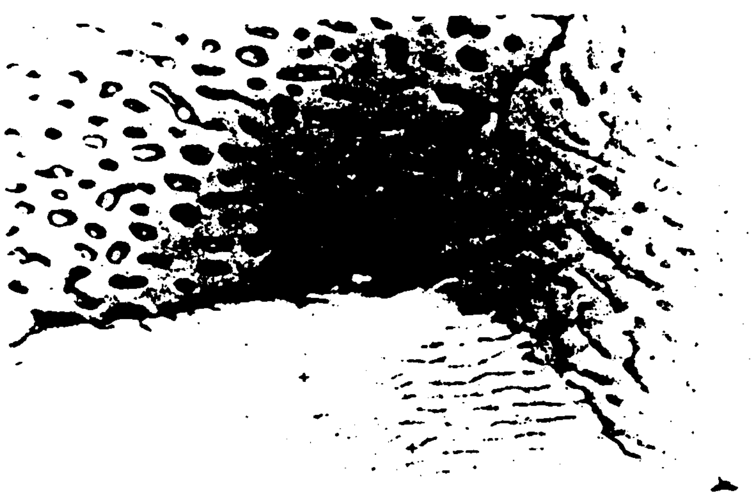
87/241/2 5000x

GALFAN SHEET FROM THE SIMULATION EQUIPMENT (SEM)

ZN - 4.57%AL - MM - SLOW COOLING



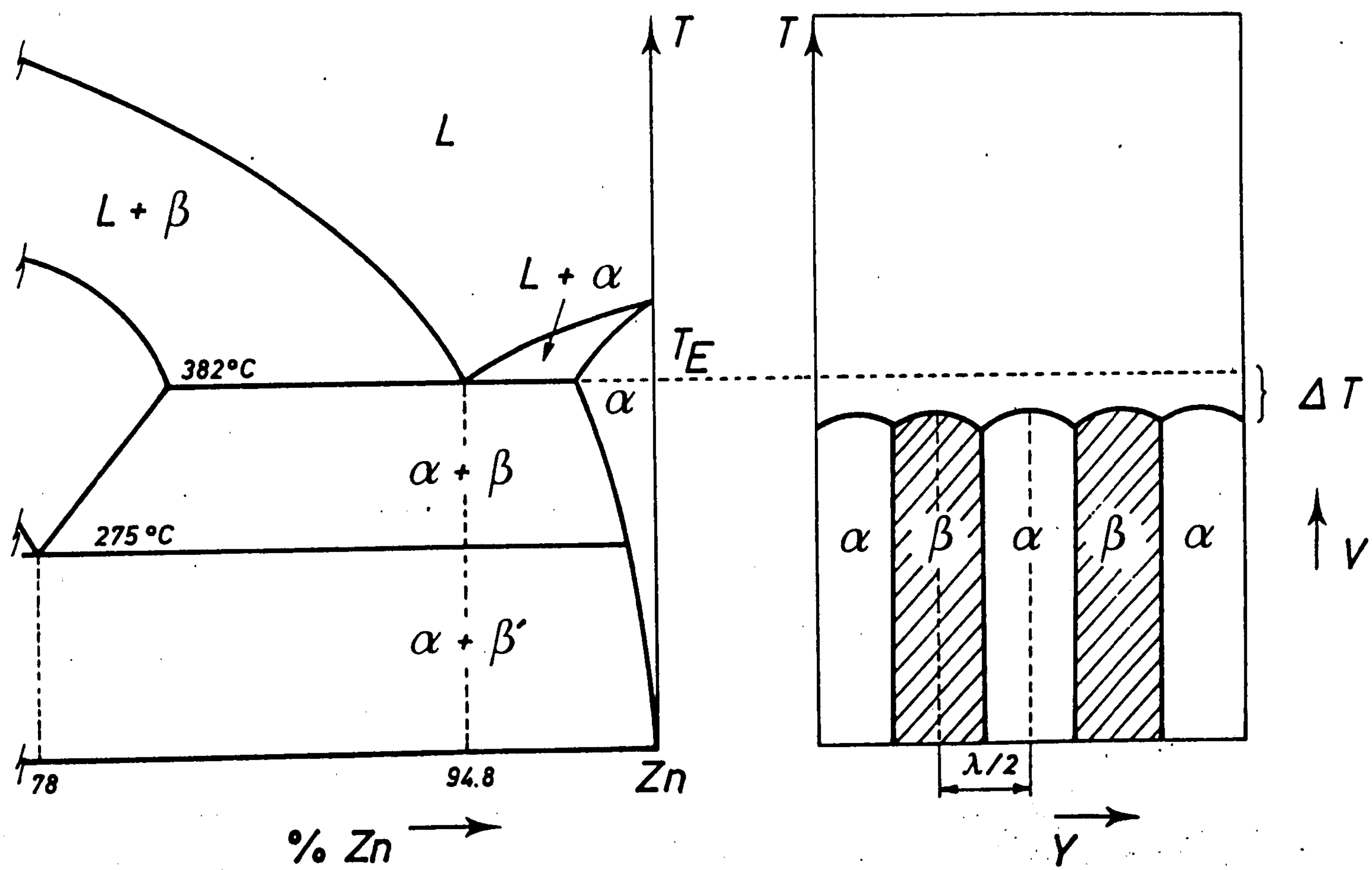
87/241/17 750x



87/241/18 5000x

GALFAN SHEET FROM THE SIMULATION EQUIPMENT (SEM)

Phase diagram and regular eutectic structure



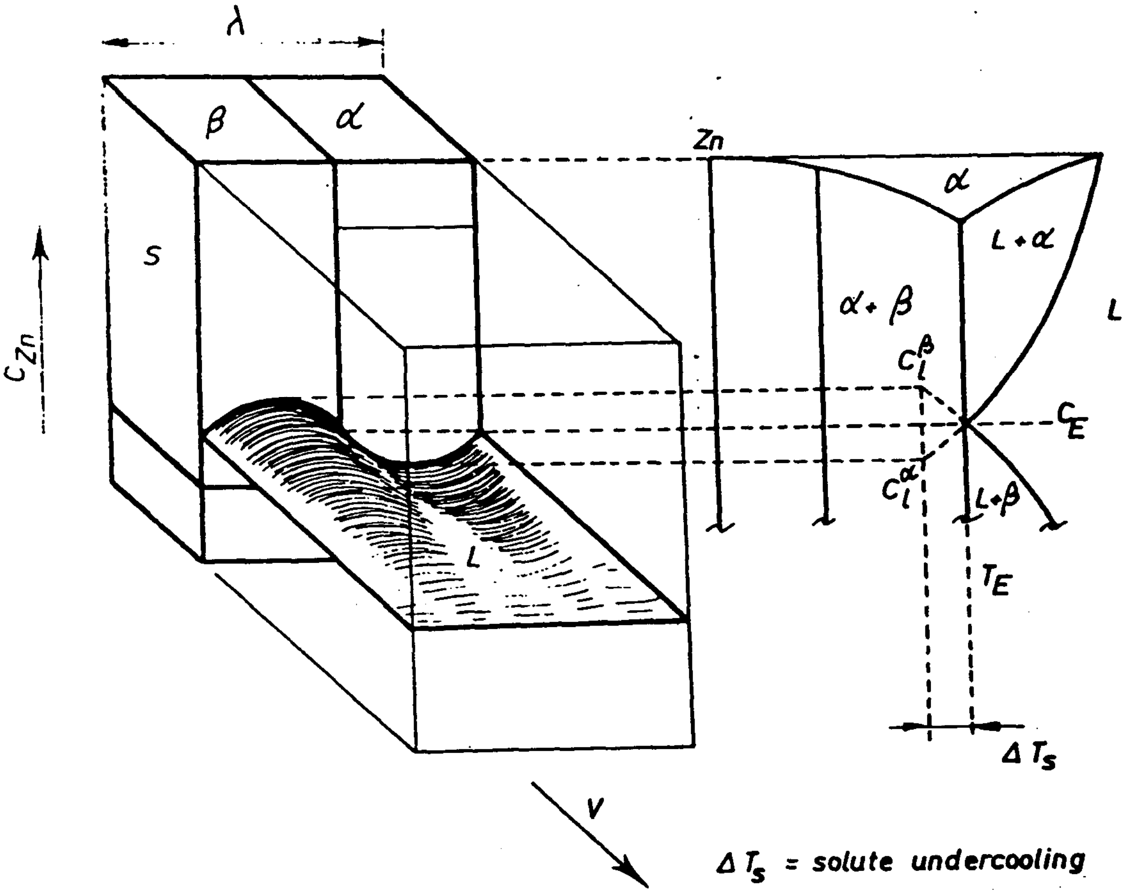
V = Growth rate of the solid-liquid interface

T_E = Equilibrium eutectic temperature

ΔT = Undercooling

λ = Interphase spacing

Eutectic diffusion field



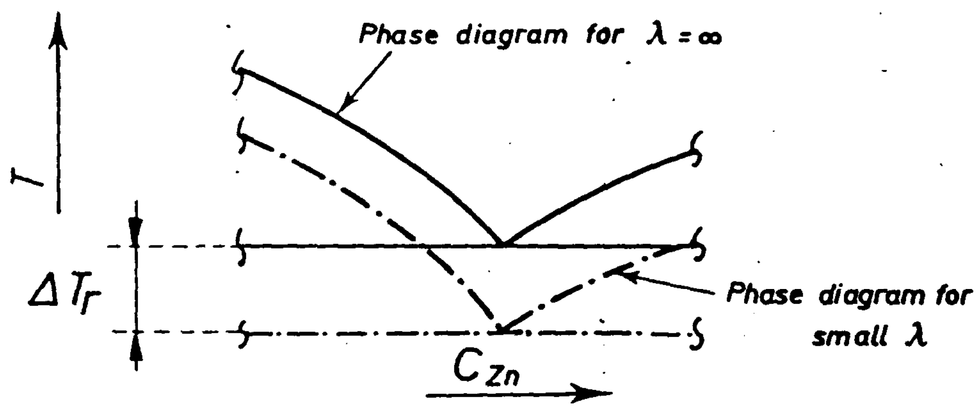
Δ T_S = solute undercooling

L = liquid phase

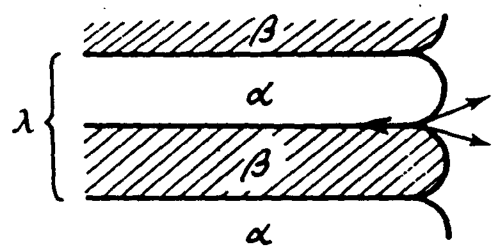
V = growth rate

$$\boxed{\Delta T_S = K_C \lambda V}$$

Curvature effects at the eutectic interface

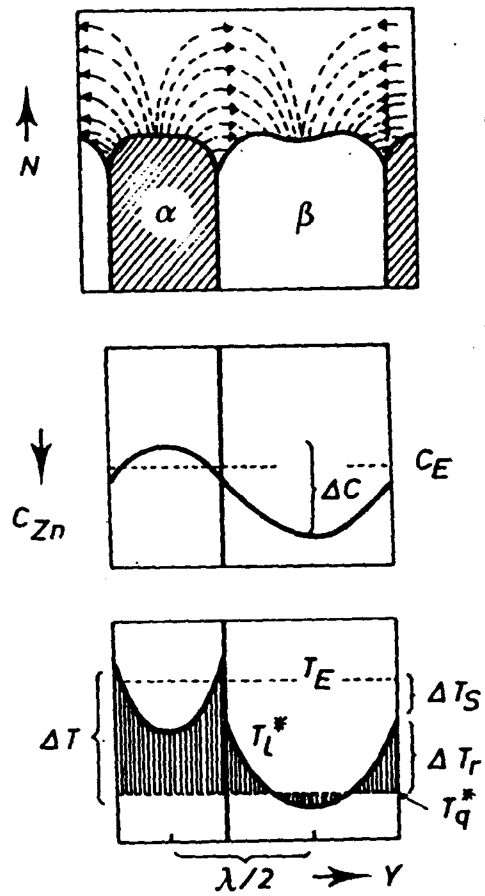


ΔT_r = curvature undercooling



$$\boxed{\Delta T_r = \frac{K_r}{\lambda}}$$

Eutectic interface concentration and temperature



T_q^* = measurable temperature of the interface

ΔT_S = solute undercooling

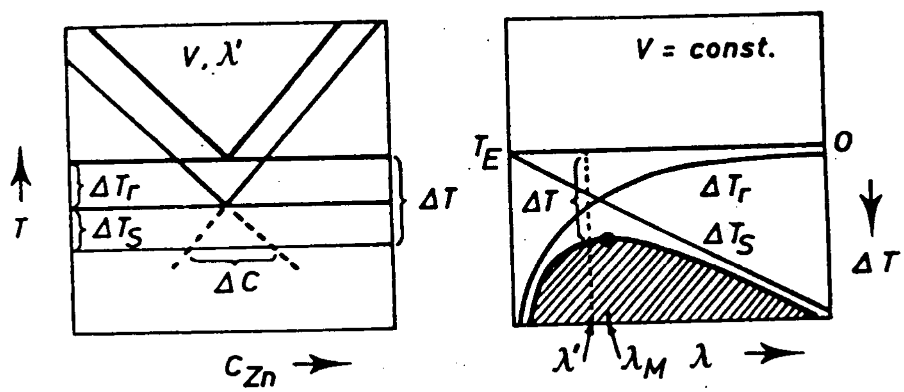
ΔT_r = curvature undercooling

ΔT = interface undercooling

$$\Delta T = \Delta T_S + \Delta T_r = T_E - T_q^* = \text{constant}$$

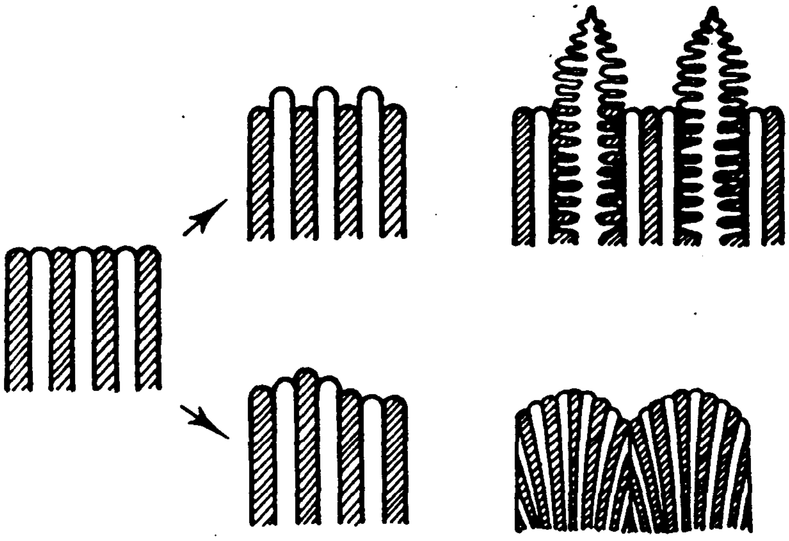
$$= K_C \lambda V + \frac{K_r}{\lambda}$$

Contributions to the total undercooling



λ_M = value of interphase spacing (λ) for which ΔT is minimum

Type of eutectic interface instability

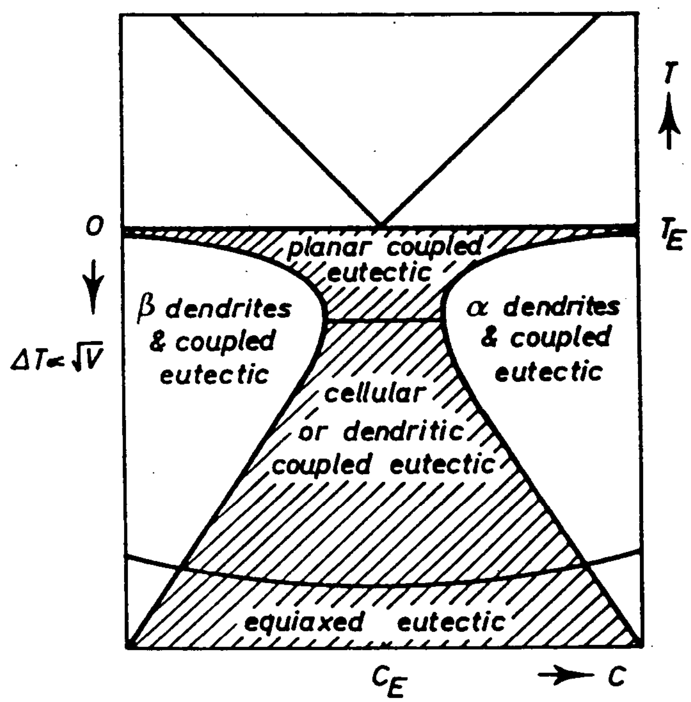


a. single phase instability

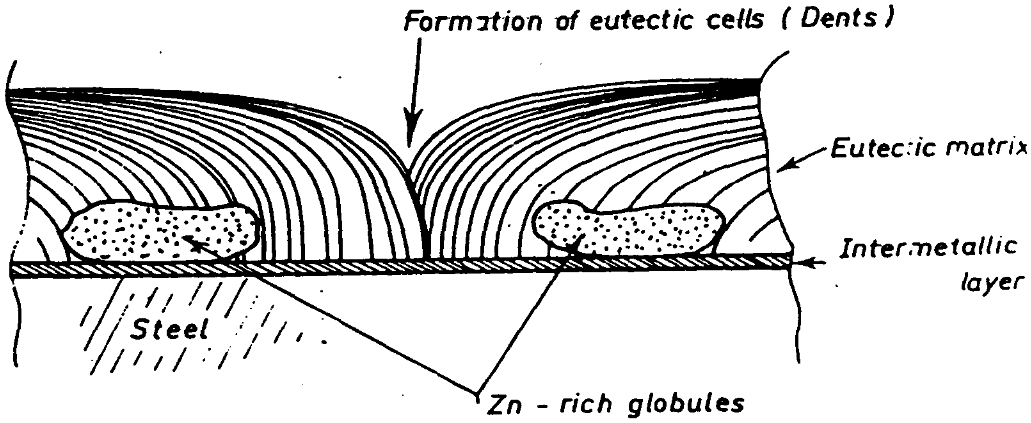
b. appearance of two-phase eutectic cells

⟶ grain boundary dents

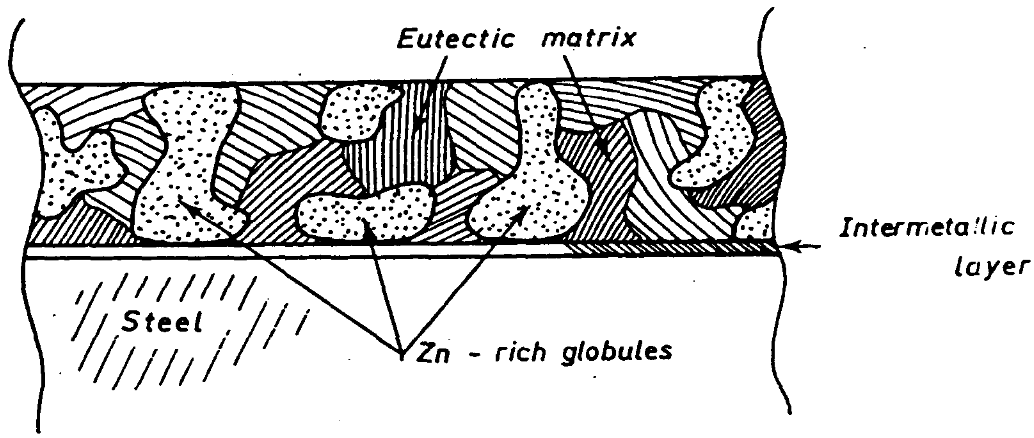
Coupled zone of eutectics



Slow cooling - High Al content



Rapid cooling - Low Al content



CONCLUSIONS

GRAIN BOUNDARY DENTS = PROBLEM OF EUTECTIC SOLIDIFICATION

THIRD ALLOYING ELEMENT SIMILARLY PARTITIONED BETWEEN BOTH SOLID PHASES (LAMELLAE)

—> APPEARANCE OF EUTECTIC CELLS

THE DENTS FORMATION IS REDUCED BY :

- DECREASING AL CONTENT —> GREATER PERCENTAGE OF ZN-RICH GLOBULES
- INCREASING COOLING RATE —> OTHER DISTRIBUTION OF GLOBULES WHICH OFTEN REACH THE COATING SURFACE

—> DECREASE OF EUTECTIC PHASE AT THE SURFACE.

EVEN AT 4.0%AL, THE PROBLEM IS NOT COMPLETELY SOLVED.

MOREOVER THE CORROSION RESISTANCE WAS OBSERVED TO DECREASE IN PRESENCE OF PRIMARY PHASE AT THE SURFACE (4.7%AL COATING).

GALFAN MEETING

REIMS (FRANCE)

18 - 22 JANUARY 1988

RESULTS PRESENTED BY CRM

I. ATMOSPHERIC CORROSION OF GALFAN, GALVANIZED AND 55AL-ZN COATED SHEETS AFTER 5 YEARS

1. THICKNESS LOSS DATA
2. CATHODIC PROTECTION
3. SURFACE ASPECT OF EXPOSED PANELS
4. CROSS-SECTIONAL MICROSTRUCTURES
5. MECHANISMS OF ATMOSPHERIC CORROSION OF GALFAN, GALVANIZED AND 55AL-ZN COATED SHEETS : A SEM APPROACH.

TABLE 1 - WEIGHT LOSS DATA FOR GALFAN AND GALVANIZED COATINGS AFTER 1 YEAR OF OUTDOOR EXPOSURE IN DIFFERENT SITES.

COATINGS	SPANGLE	CR (+/-)	MAR. (μM)	IND. (μM)	RUR. (μM)
GALFAN	R	-	4.5	1.2	0.7
GALFAN	R	+	3.8	0.8	0.5
GALVANIZED	R	+	6.0	1.7	1.0

TABLE 2 - WEIGHT LOSS DATA FOR GALFAN AND GALVANIZED COATINGS AFTER 5 YEAR OF OUTDOOR EXPOSURE IN DIFFERENT SITES.

	COATINGS	GALFAN 4	GALFAN 10	GALVA
THICKNESS	(μM)	15	30	20
CR	(+/-)	-	+	+
SPANGLE	(R/M)	M	R	R
MARINE	(μM)	11.2	9.5	100%RR
INDUSTRIAL	(μM)	5.5	5.2	15.0
RURAL	(μM)	3.8	3.0	10.4

TABLE 3 - CORRODING FACTOR (CF) OF GALFAN AND GALVANIZED COATINGS IN DIFFERENT SITES.

$$CF = \frac{\text{THICK.LOSS 5 YEARS}}{\text{THICK LOSS 1 YEAR}}$$

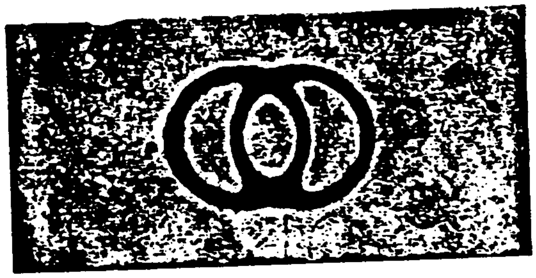
	MARINE	INDUSTRIAL	RURAL
GALFAN	2.5	5.0	6.0
GALVA	>5.0	9.0	10.0

TABLE 4 - CATHODIC PROTECTION OF BARE EDGES. PROGRESS OF CORROSION FROM BARE EDGES, IN µM AFTER 5 YEARS OF OUTDOOR EXPOSURE.

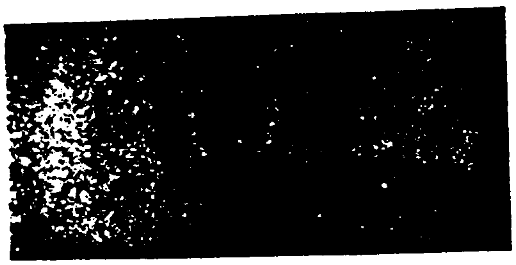
		G4	G10	GALVA	55AL-ZN
STEEL GAGE	(MM)	1.0	0.6	0.8	0.75
COATING THICK	(µM)	15	30	20	25
CR	(+/-)	-	+	+	+
MARINE	(µM)	600	110	100%RR	300
INDUSTRIAL	(µM)	250	20	900	375
RURAL	(µM)	125	5	85	75

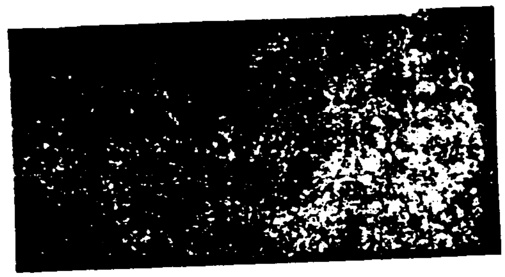
INDUSTRIAL SITE – 5 YEARS

GAGE (mm) COATING THICK (μm)

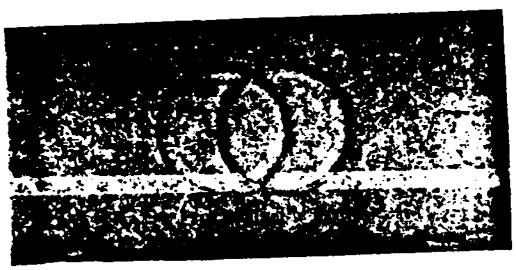


0,8 GALVANIZED 30

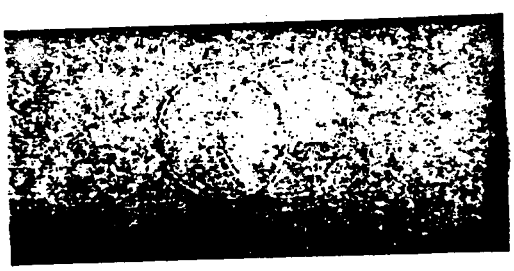


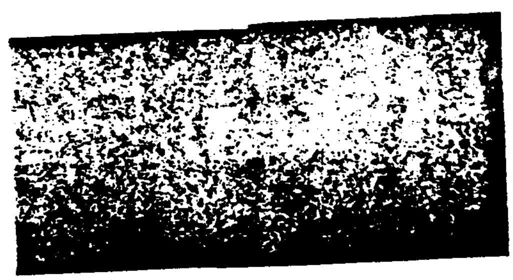


0,74 GALVALUME 25



1 GALFAN 4 15



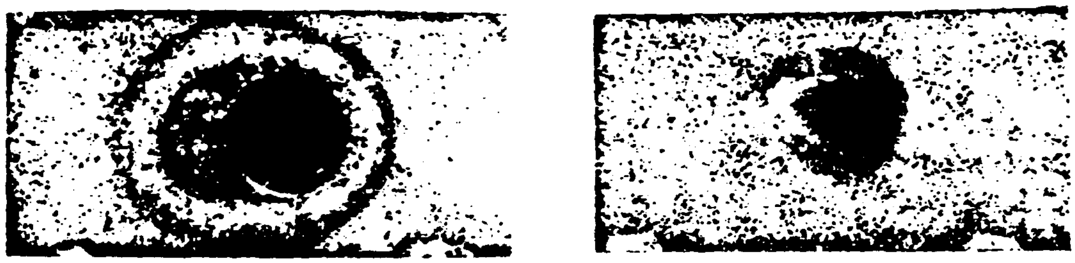


0,6 GALFAN 10 30

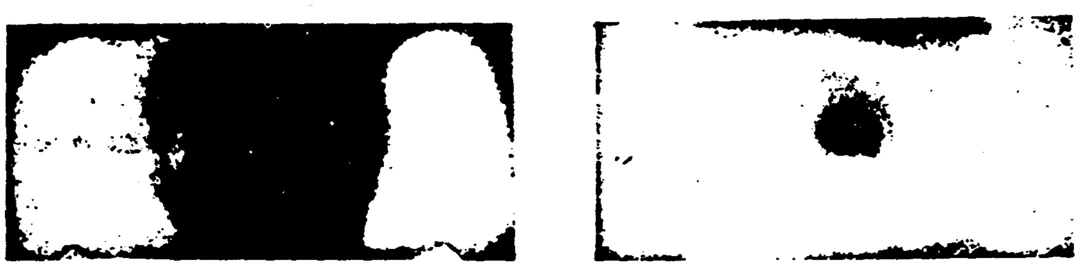
SEVERE MARINE SITE - 5 YEARS

GAGE (mm) COATING THICK (µm)

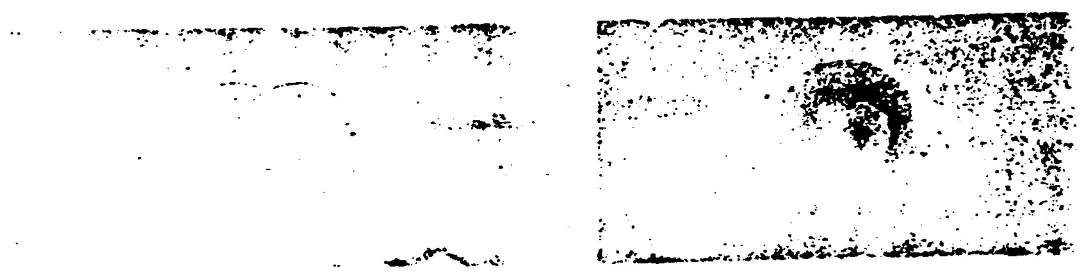
0,8 GALVANIZED 30



0,74 GALVALUME 25



1 GALFAN 4 15 unchromate

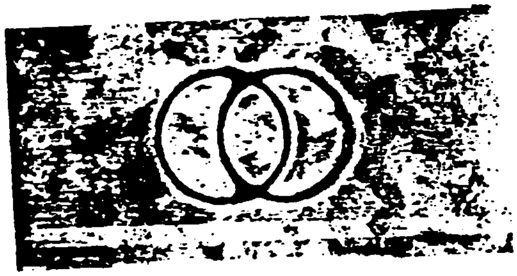


0,6 GALFAN 10 30.

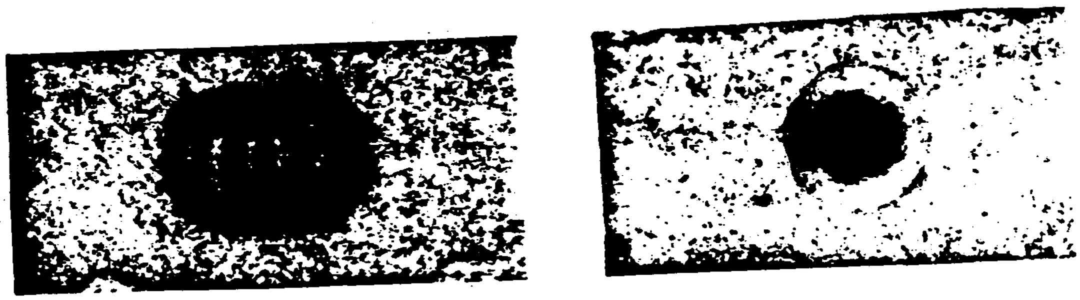
Figure 16

RURAL SITE – 5 YEARS

GAGE (mm) COATING THICK (μm)

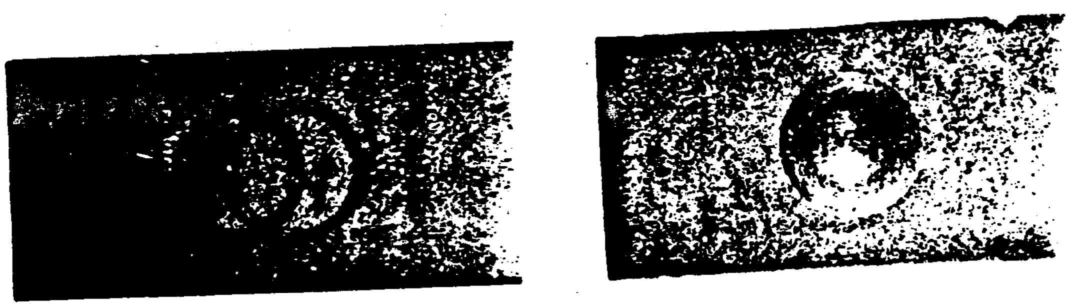


0,8 GALVANIZED 30



0,74 GALVALUME 25

1 GALFAN 4 15 unchromat



0,6 GALFAN 10 30

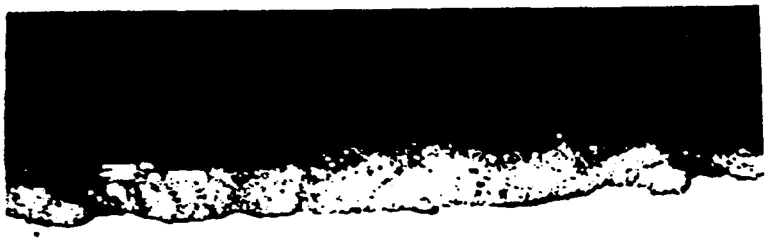
Figure 15

Figure 5 : Cross-sectional microstructures (500x) of Galfan (n°4) coated sheets after 5 years of outdoor exposure in 4 different sites.

Exposure sites

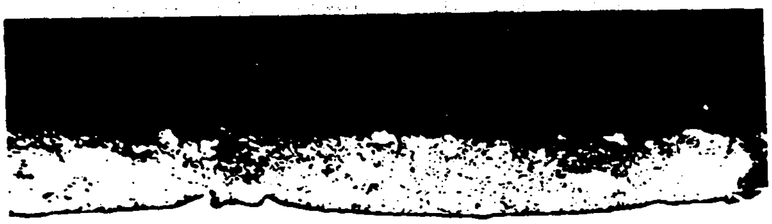
a. severe marine

087/197/2



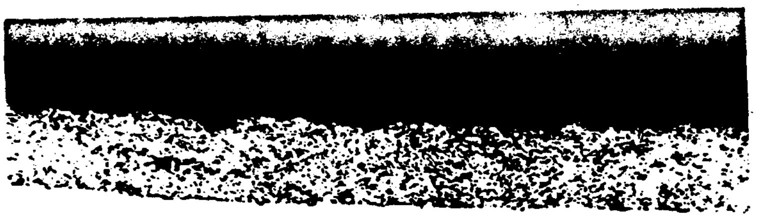
b. marine

087/197/13



c. industrial

087/198/12



d. rural

087/198/22

<u>Figure 6</u> : Cross-sectional microstructures (500x) of Galfan (N 10) coated sheets after 5 years of outdoor exposure in 4 different sites.

<u>Exposure sites</u>

a. severe marine

087/197/10

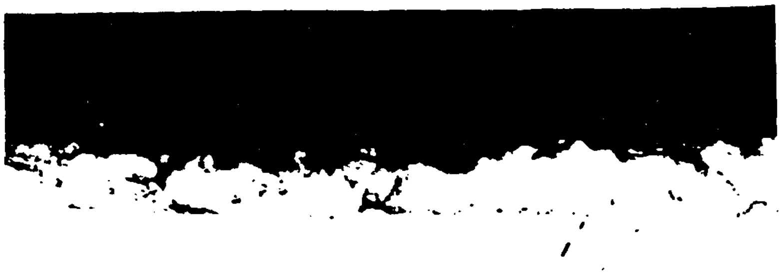
087/197/23

b. marine

087/197/19

Figure 7 : (continued)

Exposure sites

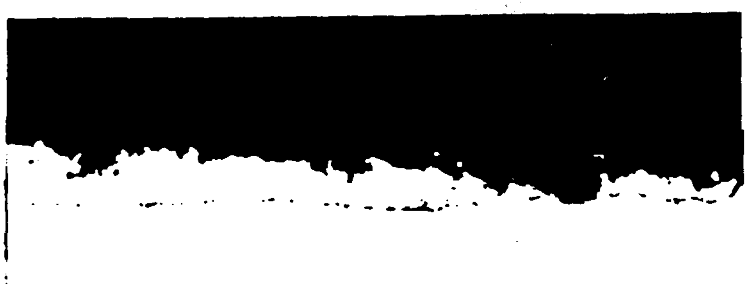


a. marine

087/197/27

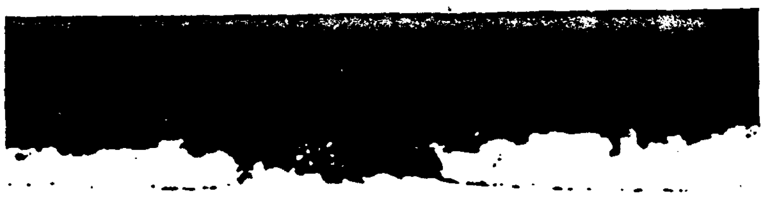
b. industrial

087/203/9



c. rural

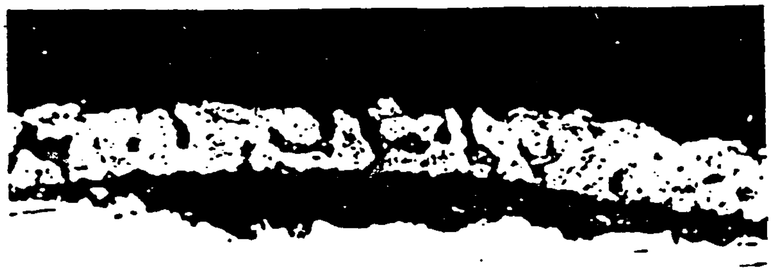
087/203/6



087/203/7

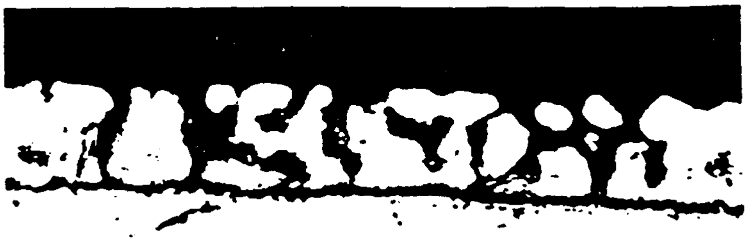
Figure 8 : Cross-sectional microstructures (500x) of ~~Galfan~~ GALVALUME coated sheets after 5 years of outdoor exposure in different sites.

Exposure sites



a. severe marine

087/197/25



087/203/13

b. marine

087/203/10

087/197/26

Figure 8 : (continued)

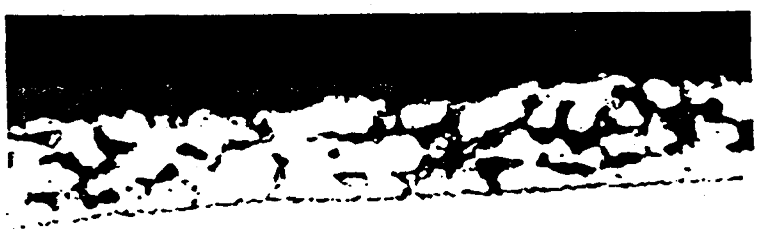
Exposure sites

c. industrial

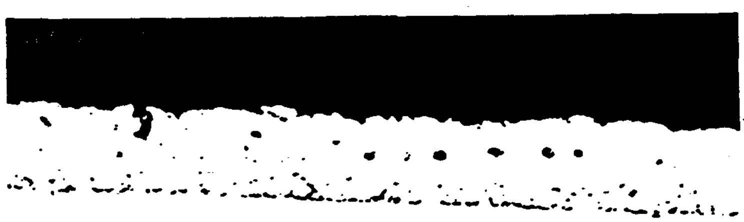
087/198/2

087/198/27

d. rural



087/203/2



087/203/12

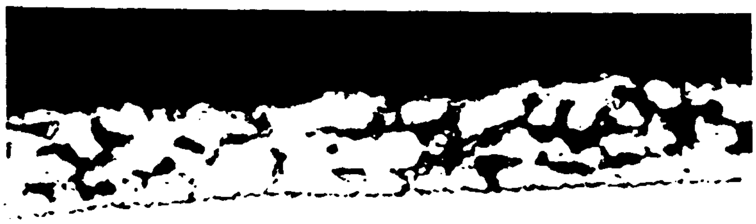
Figure 8 : (continued)

Exposure sites

c. industrial

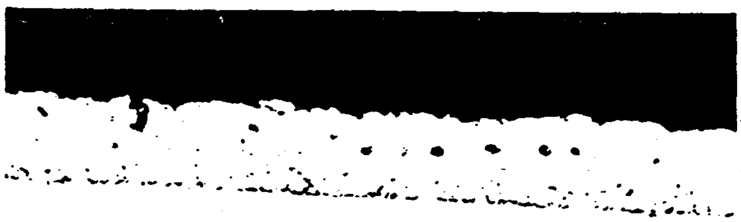
087/198/2

087/198/27



d. rural

087/203/2

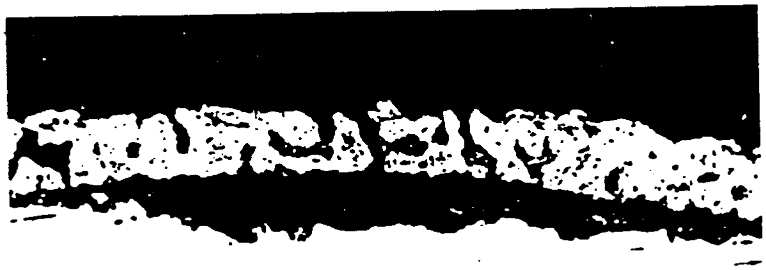


087/203/12

GALVALUME GALVALUME

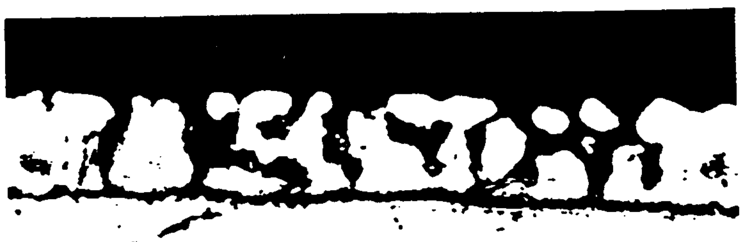
Figure 8 : Cross-sectional microstructures (500x) of ~~Galfan~~ GALVALUME coated sheets after 5 years of outdoor exposure in different sites.

Exposure sites

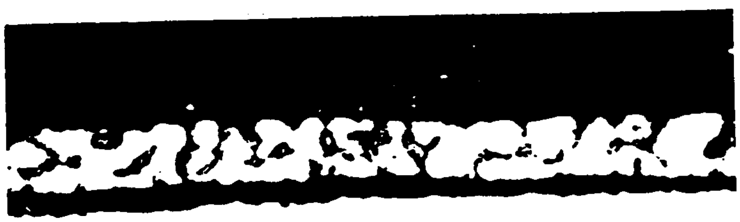


a. severe marine

087/197/25



087/203/13



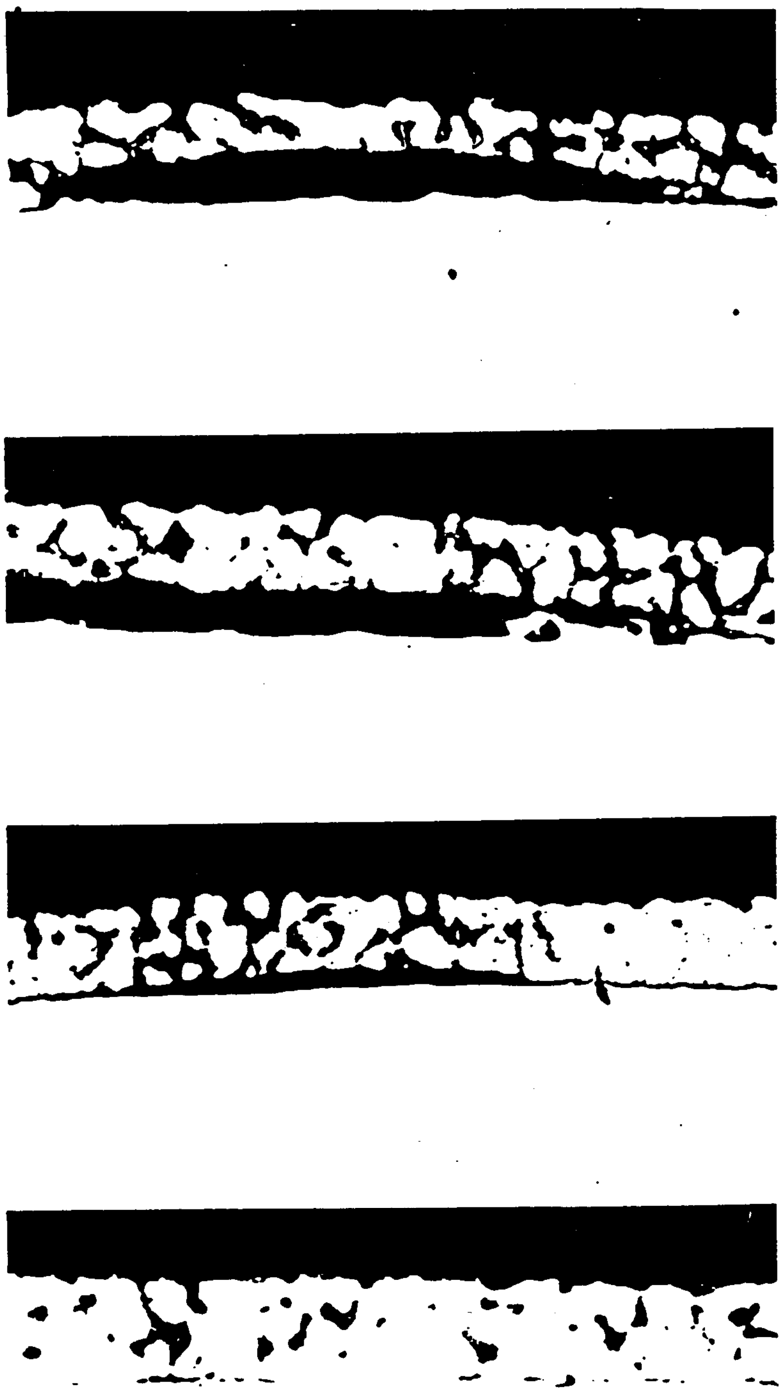
b. marine

087/203/10

087/197/26

Figure 9 : Cross-sectional microstructures (500x) of corroded Galvalume coated sheets (5 years of outdoor exposure) after dipping in the chromate solution as specified in the Anderson-Reinhard method.

Exposure sites



a. severe marine

087/189/3

b. marine

087/189/1

c. industrial

087/189/7

d. rural

087/189/2

ATMOSPHERIC CORROSION OF GALVANIZED COATINGS

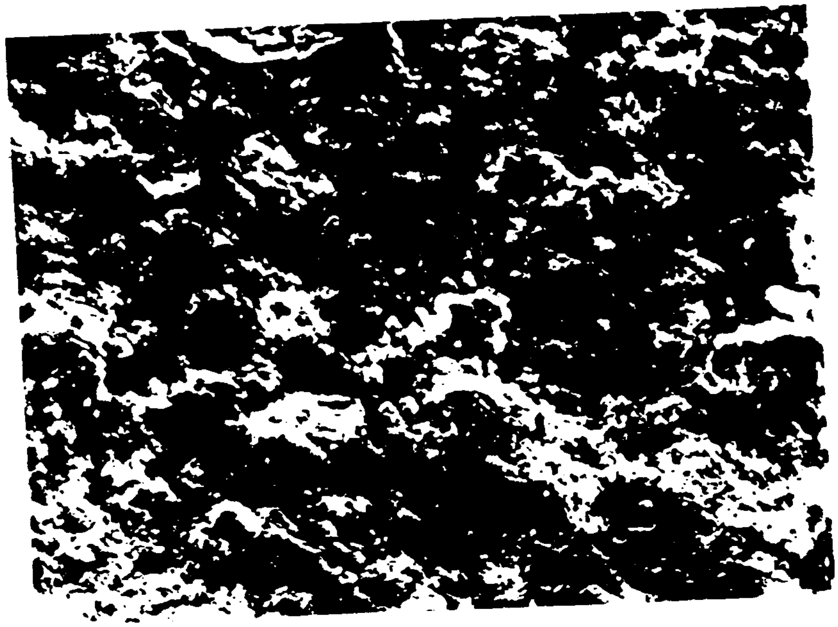
—> IN MARINE ENVIRONMENTS : EQUILIBRIUM OF ZINC DISSOLUTION - REPRECIPITATION IN A ZINC OXIDE FORM (ZnO).

—> ZnO : HIGHLY POROUS AGGREGATES.

—> CORROSION THROUGH PREFERENTIAL PATHWAYS (OF HIGHER POROSITY)

—> LEADS TO INTERGRANULAR AND PITTING CORROSION

Figure 12 : Surface SEM examination (800x) of a Galvanized coating after 1 year of outdoor exposure in a severe marine site.



86/250/3

Figure 13 : Surface SEM examination (2000x) of a Galfan coating after 3 years of outdoor exposure in an industrial site.

87/332/7

ATMOSPHERIC CORROSION OF GALFAN COATINGS : A FIRST CHARACTERISTIC (MARINE AND INDUSTRIAL SITES)

—> FORMATION OF 2 CORRODED LAYERS :

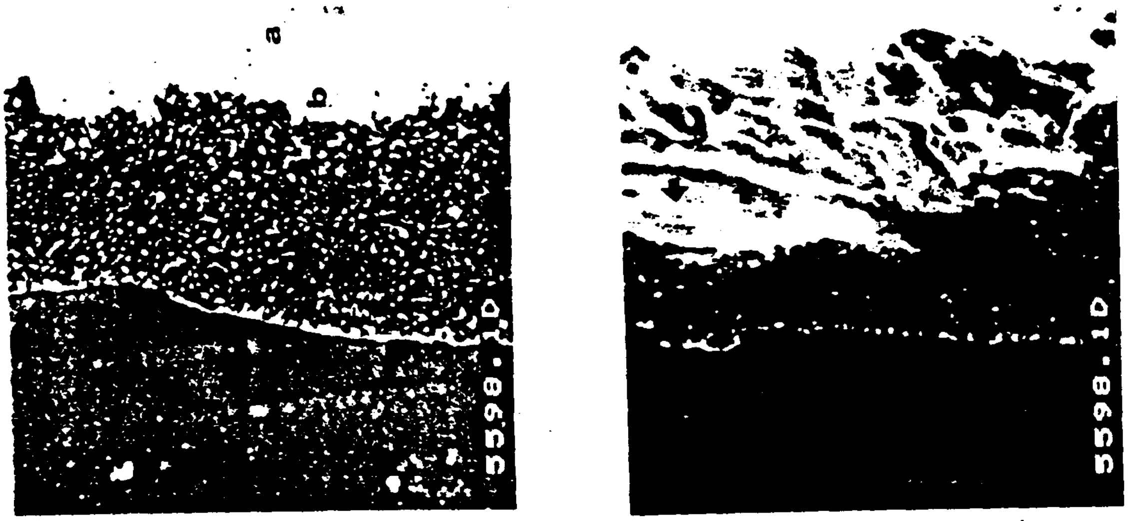
- SUPERFICIAL LAYER : $ZnSO_4$
- SUBSUPERFICIAL LAYER : MIXED CORROSION PRODUCTS.

—> POSSIBLE MECHANISM :

- FIRST STAGE : BECAUSE OF ITS HIGHER MOBILITY AND OXIDIZABILITY, ALUMINUM DIFFUSES TOWARDS THE SURFACE, IS OXIDIZED AND FORMS A TEMPORARY PASSIVATION LAYER
- SECOND STAGE : ZINC DIFFUSION ACROSS THIS LAYER TO FORM A SUPERFICIAL $ZnSO_4$ LAYER
- CORRODED AREAS IN THE BULK OF THE COATING : RATIO ZN/AL DECREASES BECAUSE ZN DIFFUSES TOWARDS ZONES OF HIGHER ZINC CORROSION. THESE ZONES CAN EVEN BE SITUATED IN THE CORE OF THE COATING.

  AL-RICH LAMELLAE TEND TO CONCENTRATE IN CONTIGUOUS ZONES AND ARE RAPIDLY ENTRAPED BY OXYGEN.

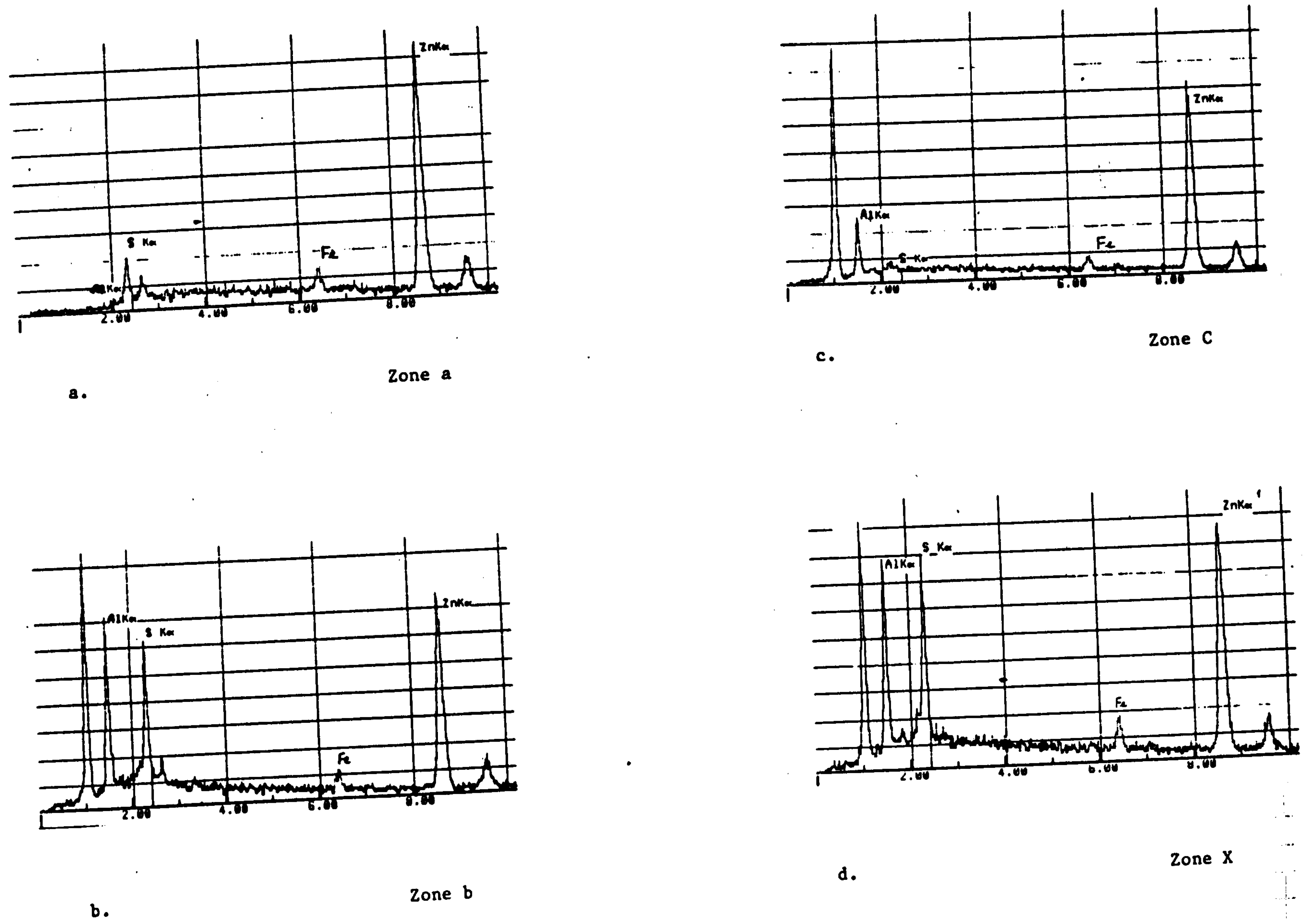
Figure 16 : Cross-sectional SEM(*) examination (BSE-1500x) of a minimized unchromated Galfan after 1 year of outdoor exposure in a severe marine site. a) Normal corrosion evolution. b) Severe corrosion.



a. 87/174/6 b. 87/174/7

(*) Normal SEM. No sensibility to Oxygen and Carbon.

<u>Figure 17</u> : SEM spectra. a, b, c) corresponding to figure 16.a. d) corresponding to figure 16.b.



Figur 18 : Cross-sectional SEM+ examination (BSE-2000x) of a Cal n coating (normal spangle, chromated) after 1 year of outdoor exposure in a severe marine site.

ATMOSPHERIC CORROSION OF GALFAN COATINGS : A FOURTH CHARACTERISTIC : CORROSION INDUCED BY THE PRESENCE OF ZINC-RICH GLOBULES

To avoid dents and boundaries shrinkage, manufacturers lowered the Al content leading to the increase of the concentration of Zn-rich globules.

Consequences :

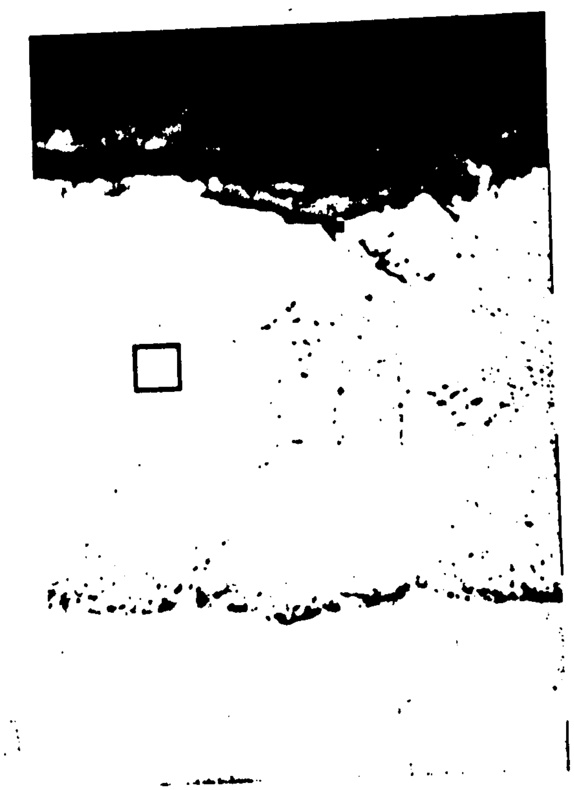
—> Zn-rich globules can concentrate at the top of the coating (specially at high ~~corrosion~~ rates) which behaves, in this area, as a galvanized coating.
Corrosion rate is locally increased when compared to those of adjacent eutectic areas

cor: NG

—> Zone of Al-rich nodules can form close to a Zn-rich globule. These zones corrode faster than eutectic structures.

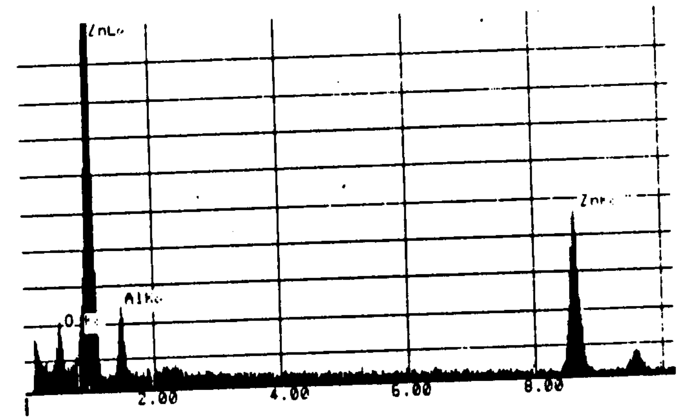
—> Al precipitation at Zn-rich globules/eutectic boundaries can lead to an increased intergranular corrosion.

Figure 18 : Cross-sectional SEM+ examination (BSE-2000x) of a Galfan coating (normal spangle, chromated) after 1 year of outdoor exposure in a severe marine site.

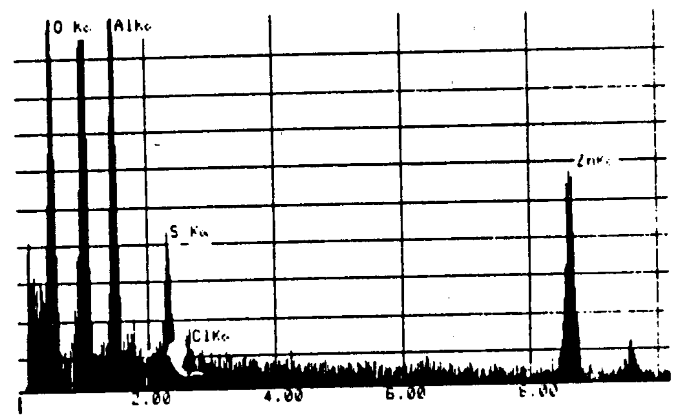


87/263/28

Figure 20 : SEM+ spectra corresponding to figure 18

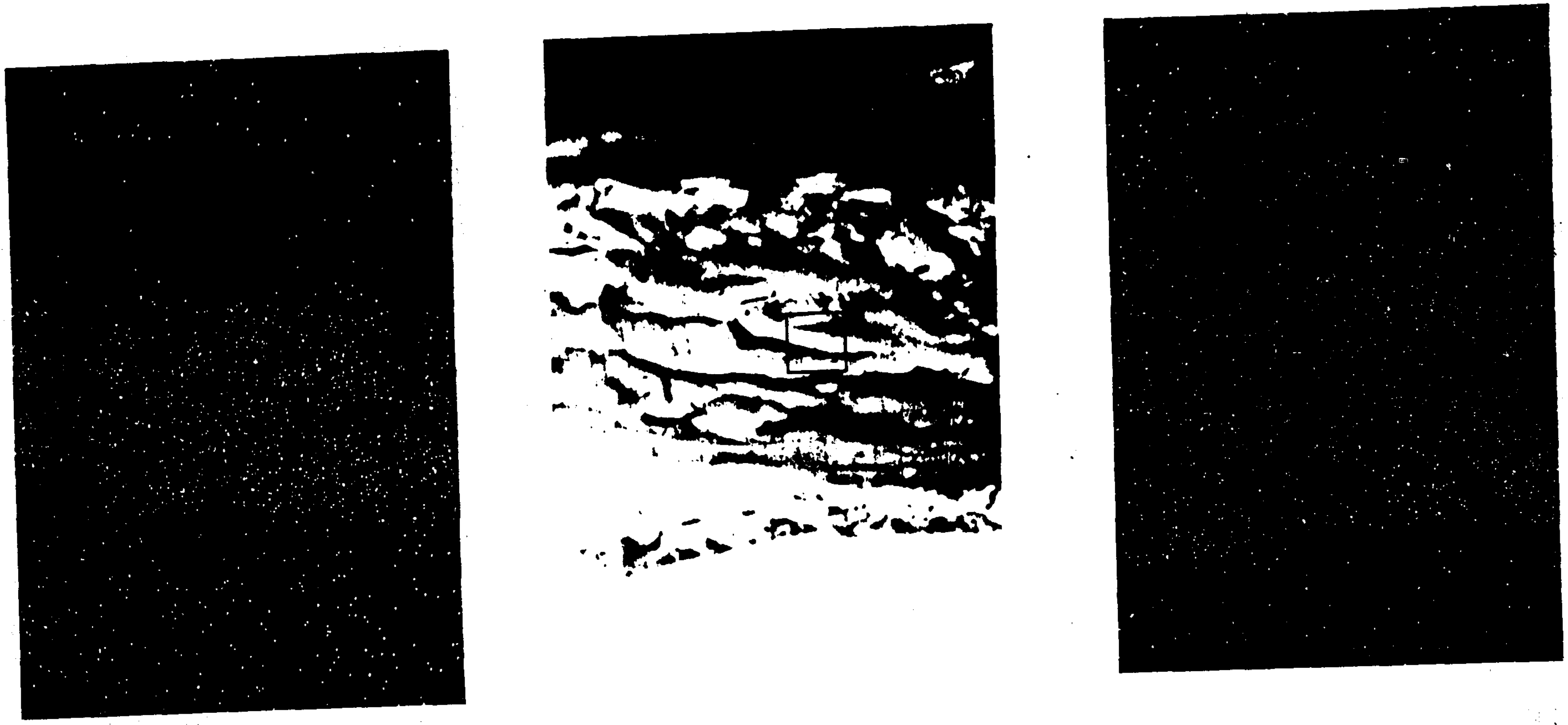


a. Arrow : interface coating/corrosion layer



b. Zone a

Figure 14 : a) Cross-sectional SEM +(*) examination (BSE.2500x) of a corroded area of a minimized unchromated Galfan coating afte: 1 year of outdoor exposure in a severe marine site. b) and c) are respectively the corresponding Oxygen and Aluminum X-ray images



b. 87/263/15

a. 87/263/14

c. 87/263/17

(*) Oxygen and Carbon sensible

ATMOSPHERIC CORROSION OF GALFAN COATINGS : A SECOND CHARACTERISTIC : INFLUENCE OF THE ORIENTATION OF THE AL-RICH LAMELLAE

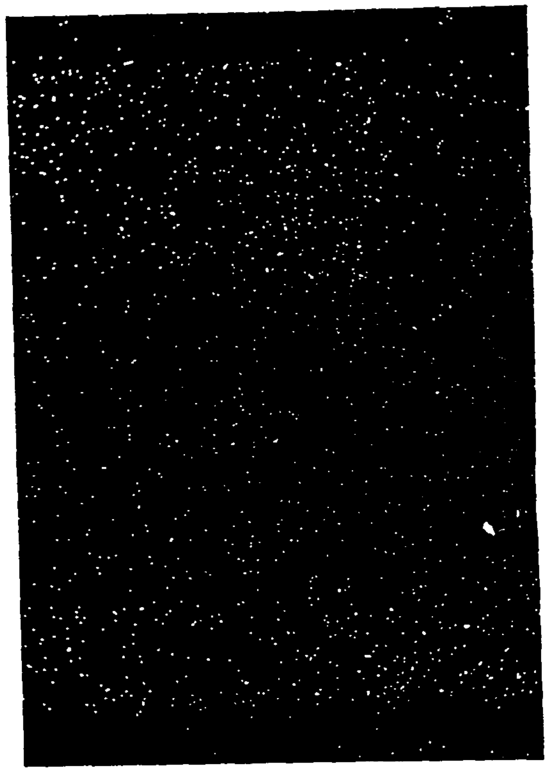
- CORROSION EVOLVES ALONG THE AL-RICH LAMELLAE BY FOLLOWING THEIR DIRECTIONS.
  AL-RICH LAMELLAE ARE ANODIC SITES EMBEDDED IN A ZN CATHODIC MATRIX.

- OPTICAL MICROSCOPY AND SEM EXAMINATIONS REVEALED 3 MAIN ORIENTATIONS OF AL-RICH LAMELLAE.

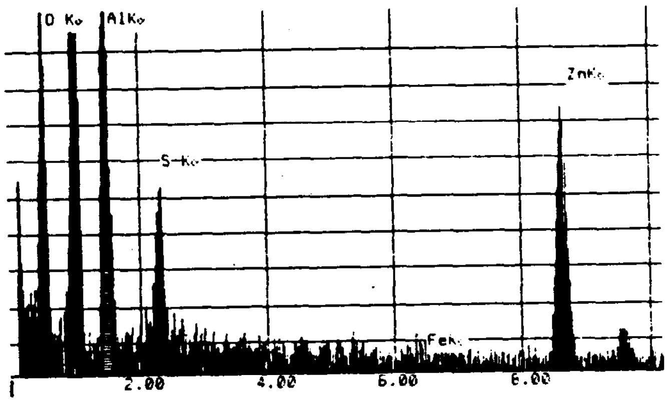
  —> HORIZONTAL LAMELLAE (PARALLEL TO THE STEEL) LEADING TO A LOW CORROSION RATE AND A UNIFORM CORROSION EVOLUTION.
  —> VERTICAL LAMELLAE (NORMAL TO THE STEEL) LEADING TO HIGHER CORROSION RATES AND TO PREFERENTIAL CORROSION PATHWAYS.
  —> INTERMEDIATE ORIENTATIONS.

Figure 22 : a, d) Cross-sectional SEM+ examination (BSE) of a Galfan coating (minimized, unchromated), after 1 year of outdoor exposure in a severe marine site. b, e) corresponding Aluminum X-ray image. c) corresponding spectrum performed in the window.

a. (3540x) 87/263/20



b. 87/263/21



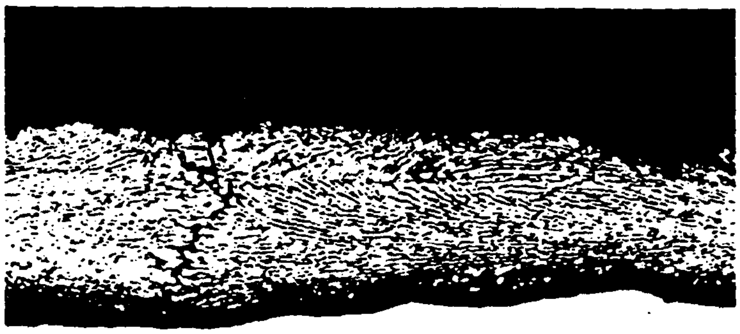
c. SEM+ spectrum in the window

Figure 23 : Cross-sectional microstructures (800x) of a chromated [illegible] Zirconium coating, after 3 years of outdoor exposure in an industrial site. Effect of vertically oriented lamellae on preferential corrosion paths.

a. 087/206/8

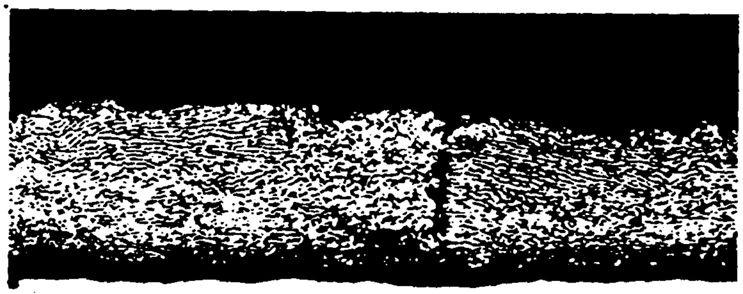
b. 087/206/11

Figure 29 : Cross-sectional microstructures (800x) of a chromated Galfan-Zirconium coating, after 3 years of outdoor exposure in an industrial site. Joints between cells.



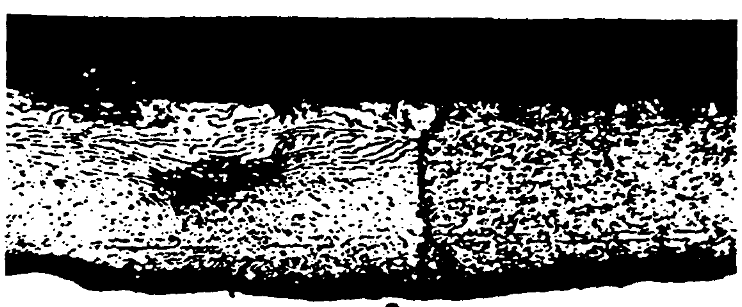
a.

087/206/2



b.

087/206/1



c.

087/206/6

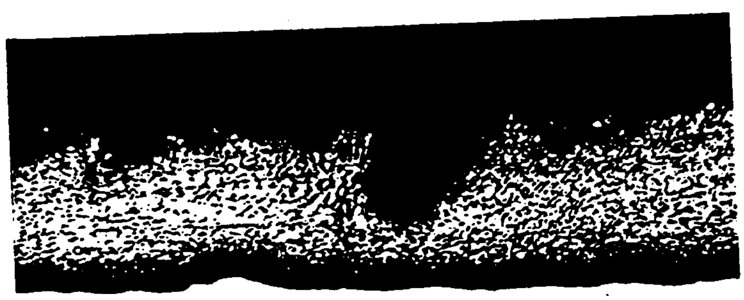
Figure 24 : Cross-sectional SEM examination (BSE-3000x) of a Galfan coating (normal spangle, chromated) after 1 year of outdoor exposure in a severe marine site.

87/263/25

Figure 23 (continued)

b. 087/206/4

c. 087/206/5



d. 087/206/3

ATMOSPHERIC CORROSION OF GALFAN COATINGS : A THIRD CHARACTERISTIC : CORROSION THROUGH DENTS AND GRAIN BOUNDARIES

DENT : AREA OF LOW COATING THICKNESS WHERE LAMELLAE ARE MORE LIKELY TO BE VERTICALLY ORIENTED

BOUNDARIES : SEPARATE 2 CELLS OF DIFFERENTLY ORIENTED LAMELLAE.

—› DURING CORROSION, MICROCRACKS NETWORK CAN DEVELOP AROUND THESE AREAS

—› EVEN AFTER 5 YEARS, NO RED RUST OCCURRED IN THESE AREAS BECAUSE OF THE SURROUNDING CATHODIC PROTECTION.

Figure 25 : Surface SEM examination of Galfan coatings at the grain boundaries. a) Minimum spangle. b,c) Regular spangle.

a.

(BSE-3500x)

87/251/5

c. (BSE - 1000x) 087/251/1

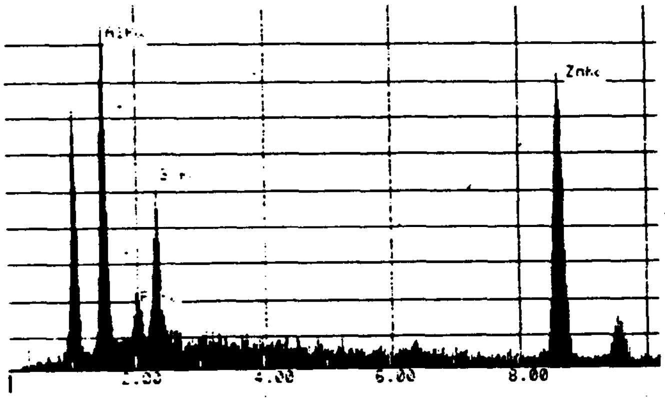
Note : b) and c) are the same pictures, taken respectively in SE and BSE.

Figure 27 : Surface SEM examination of an unchromated Galfan-Zirconium coating. Cracks localized at grain boundaries.

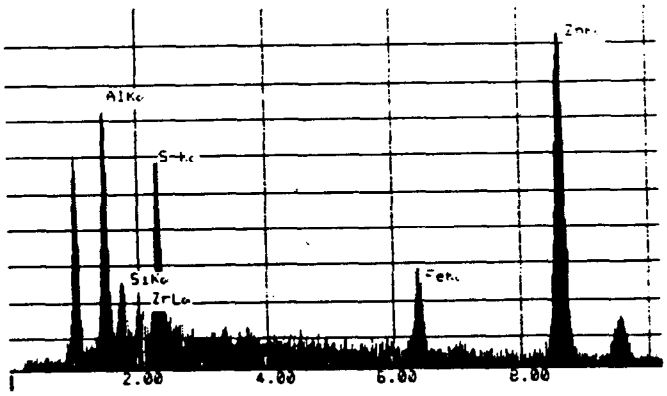
a. (SE - 750x) 87/332/1

b. (SE - 1500x) 87/332/5

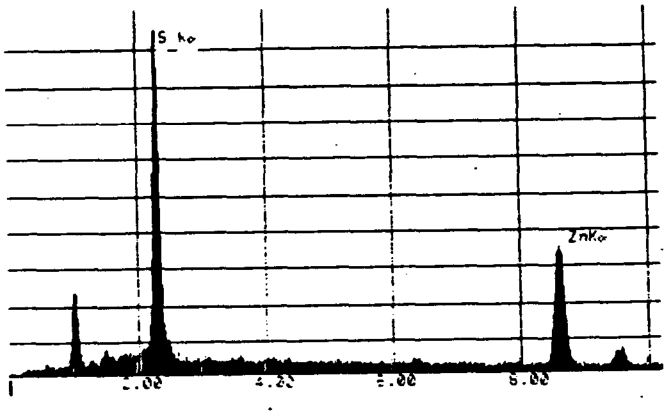
Figure 28 : SEM spectra. a) corresponding to figure 27.a.
b, c) corresponding to figure 27.b..



a. Arrow in figure 27.a

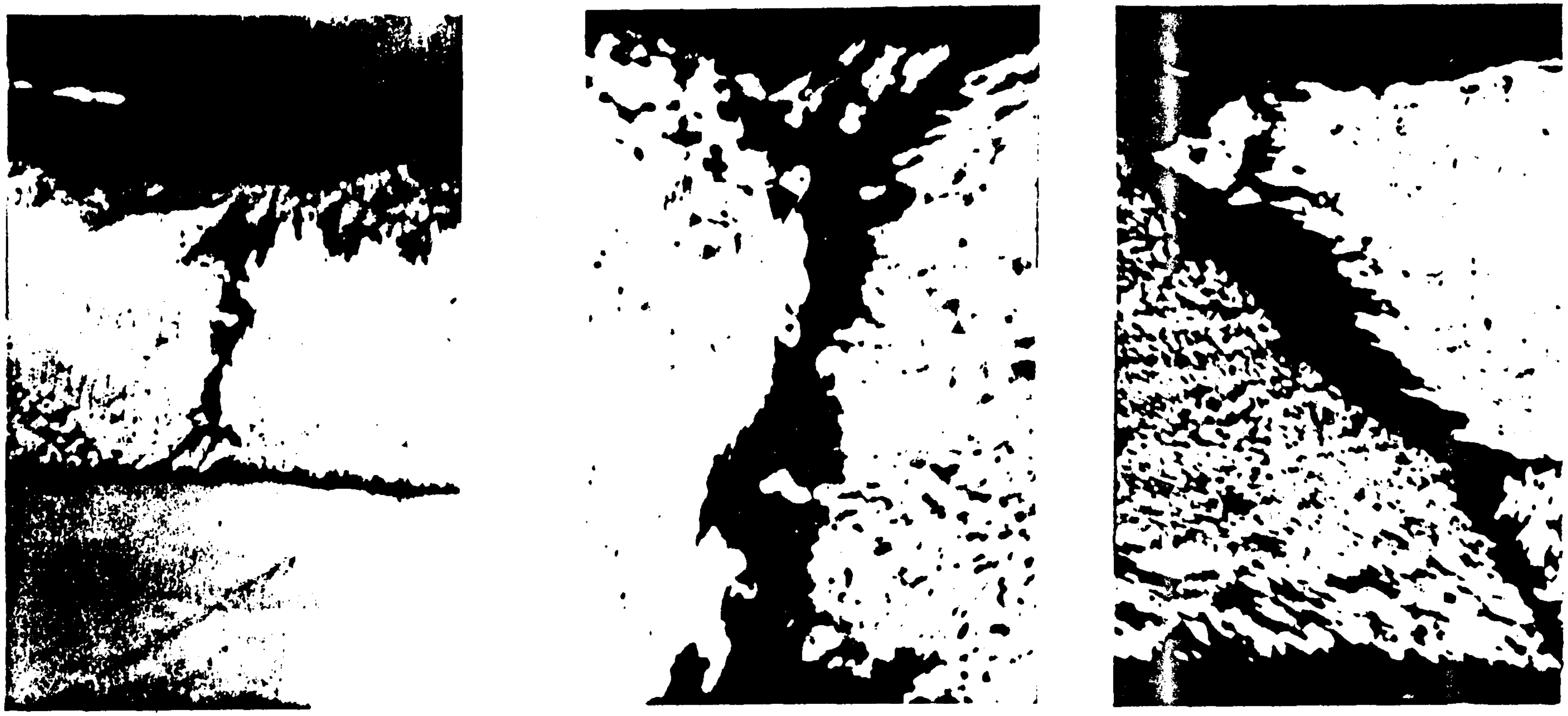


b. Arrow 1 in figure 27.b



c. Arrow 2 in figure 27.b

Figure 31 : Cross-sectional SEM+ examination (BSE) of a minimized Galfan coating, after 1 year of outdoor exposure in a severe marine site. a, b, c) Cracks between 2 cells of different lamellae orientations



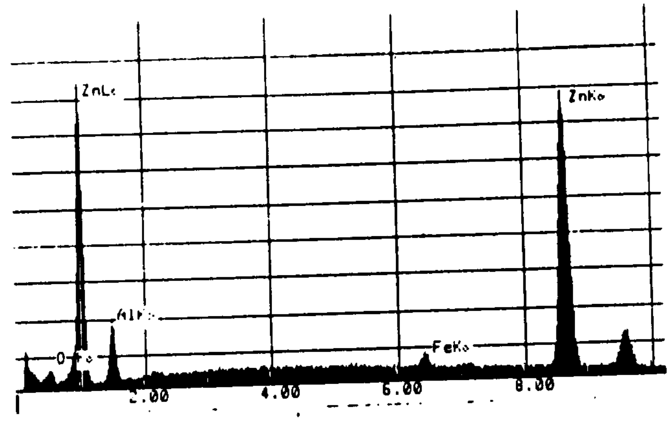
a. (2000x) 87/349/1

b. (6000x) 87/349/2
Detail of (a)

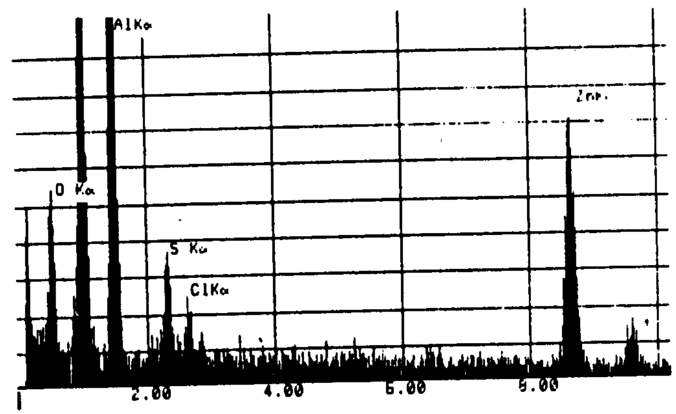
c. (4000x) 87/349/8

Figure 31 (continued) :
d) severe corrosion at a boundary between adjacent cells.
e) spectrum of 31.b (arrow)
f) spectrum of 31.d at Zone A
g) spectrum of 31.d at Zone B

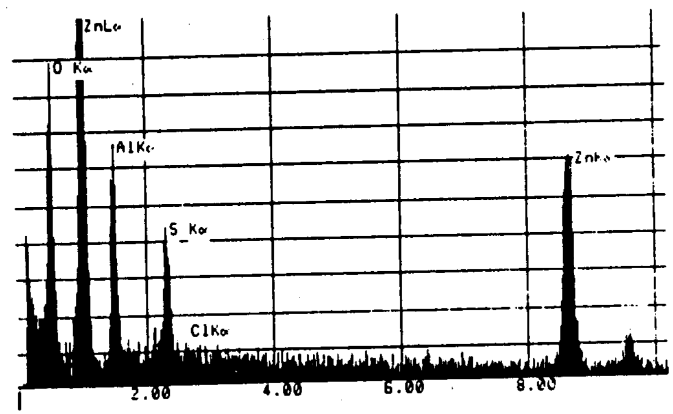
d. (2000x) 87/263/23



e.



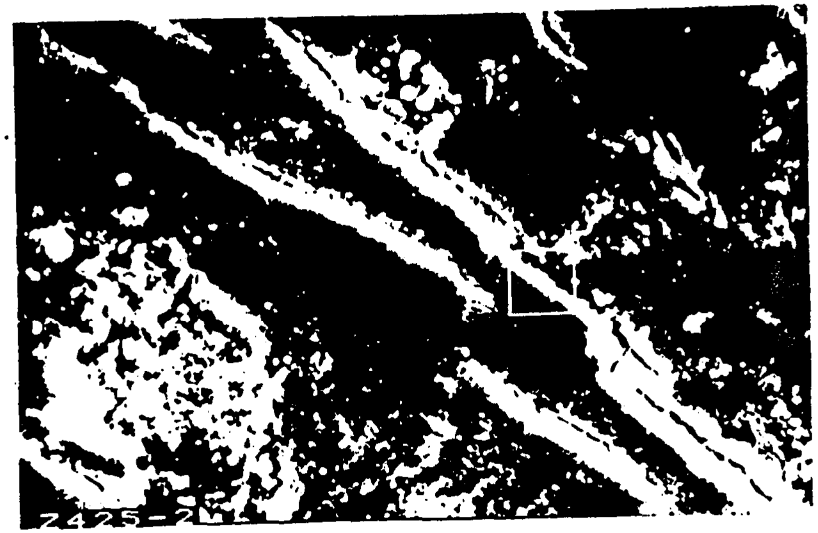
f.



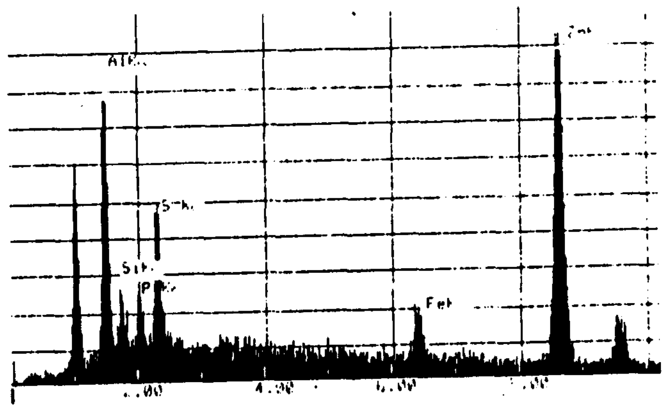
g.

Figure 33 :
a) surface SEM examination (SE) of a chromated Galfan-Zr coating, after 3 years of outdoor exposure in an industrial site. Cracks network surrounding a dent.
b) detail of a crack in figure 33.a
c) SEM spectrum in the crack (window).

a. (200x) 87/332/9



b. (1500x) 87/332/10

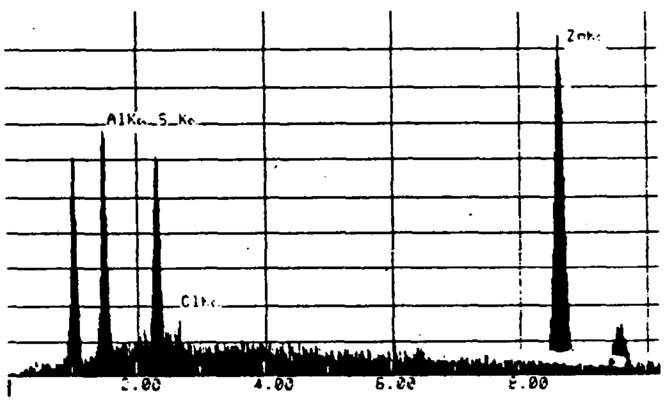


c. spetrum in a crack (window)

Figure 32 : a) Surface SEM examination of a Galfan-Zr coating, after 3 years of outdoor exposure in an industrial site. Corrosion in a dent.

b) SEM spectrum in the dent (Zone X)

a. (BSE-1000x) 87/332/3

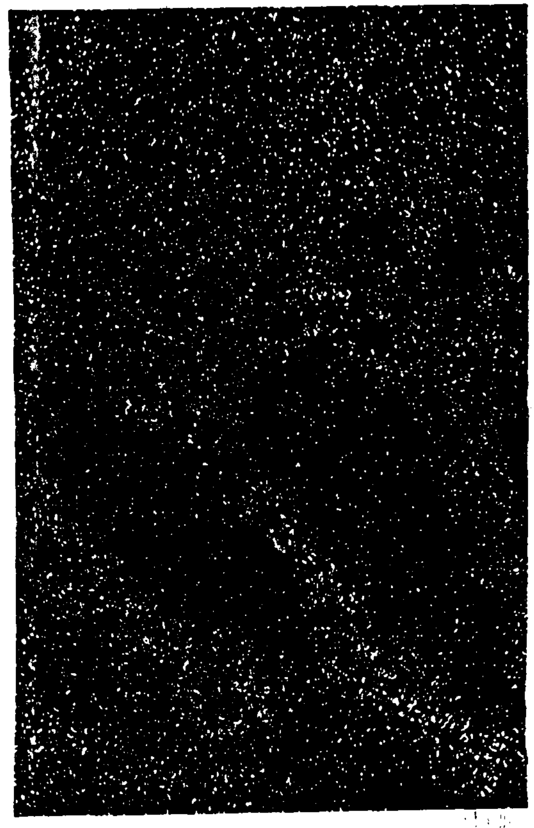


b. spectrum of Zone X

Figure 36 : Cross-sectional SEM+ examination (BSE) of a chrom ted, minimized Galfan coating. a) Coarse Aluminum precipitation at the interface Zn-rich globules/eutectic matrix. b) detail of a). c) corresponding Aluminum X-ray image of (b)

a. (3000x) 87/349/4

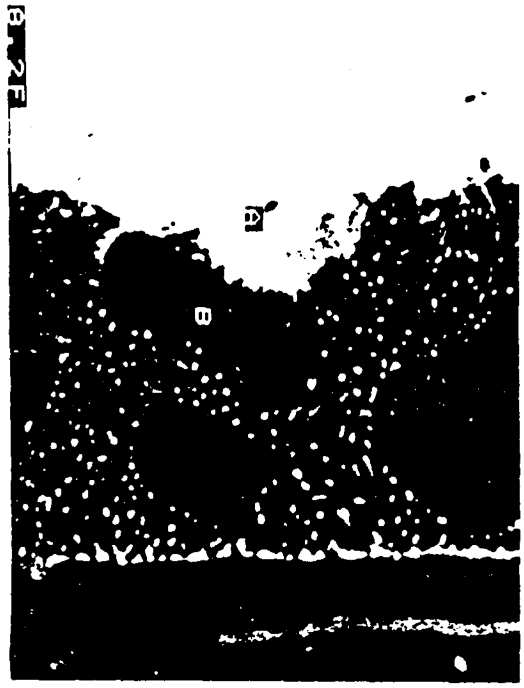
b. (6000x) 87/349/10



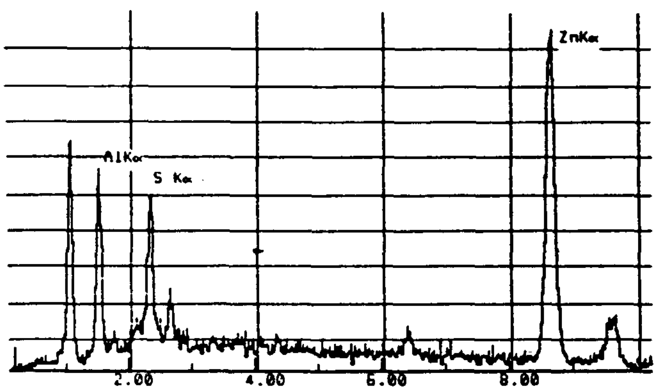
c. 87/349/12

Figure 35 :
a, b) Cross-sectional SEM examination (BSE-2000x) of a chromated, normal spangle Galfan coating, after 1 year of outdoor exposure in a severe marine site.
c) SEM spectrum of Zone C
d) spectrum of Zone B.

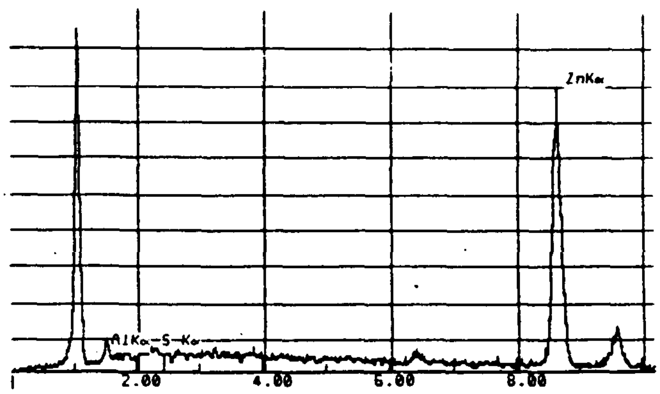
a. 87/174/17



b. 87/174/18

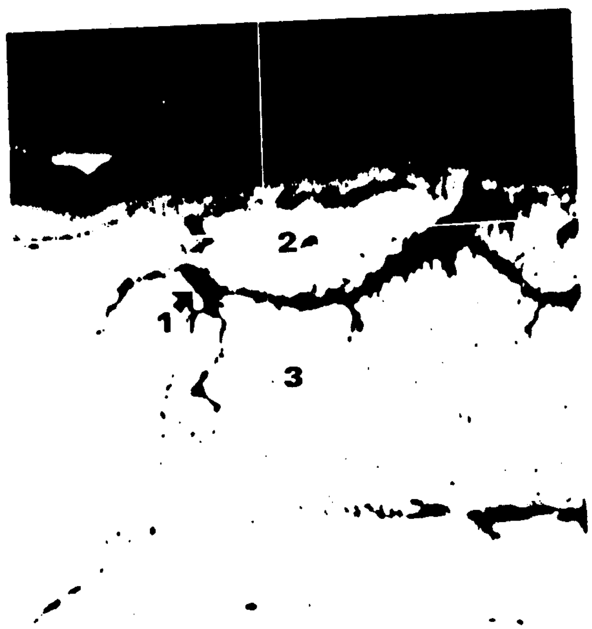


c. spectrum of Zone C

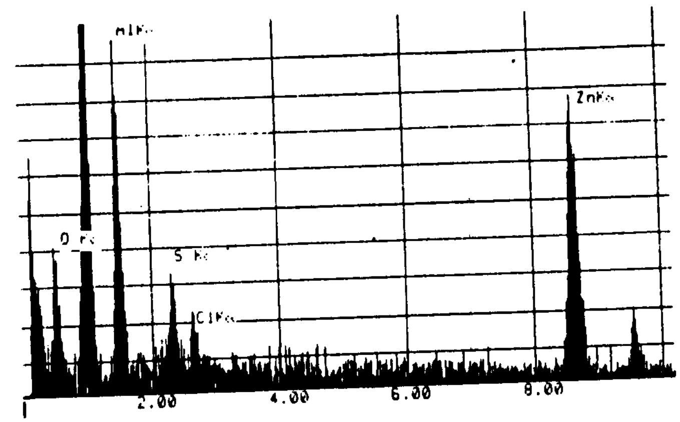


d. spectrum of Zone B

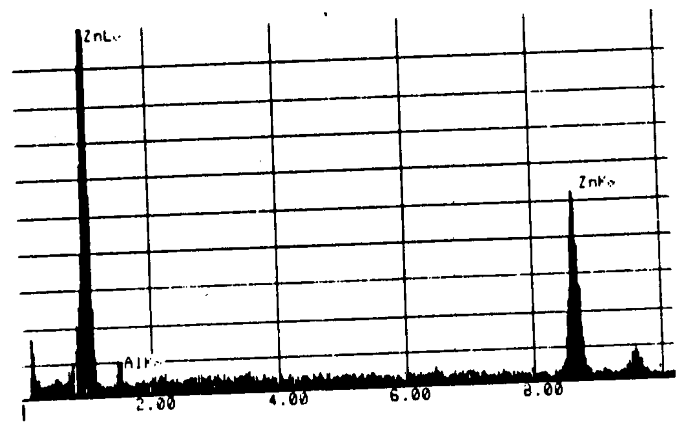
Figure 36 (continued) f) preferential corrosion at a boundary between a Zinc-rich globule (Zone 3) and an eutectic phase (Zone 2). g) spectrum of Zone 1. h) spectrum of Zone 2.



f. 87/263/22



g. spectrum of Zone 1



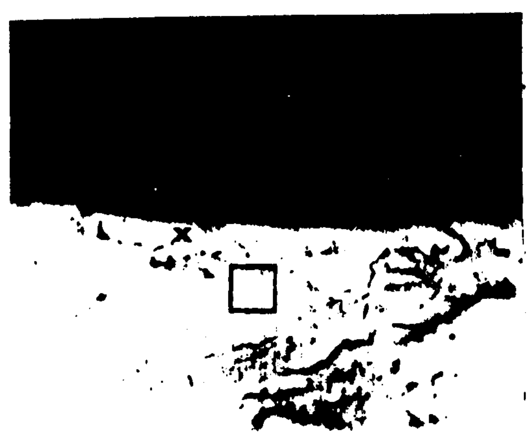
h. spectrum of Zone 2

Figure 36 (continued) : d) same as (a). e) preferential corrosion of areas containing coarse Aluminum phases in the Zinc matrix 1 year of outdoor exposure in a severe marine site.

d. (2000x) 87/349/9

e. (3000x) 87/349/3

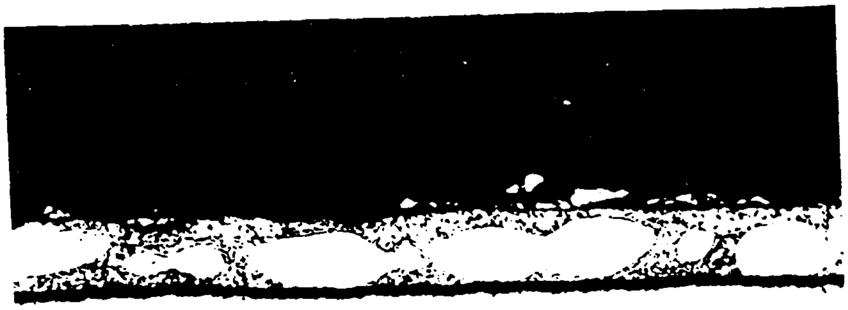
Figure 38 Cross-sectional SEM+ examination of a 150ppm Pb containing Galfan coating, after 1 year of outdoor exposure in a rural site. a) a severely corroded area. b) intercristalline corrosion.



a. (BSE-2000x) 87/263/41

b. (BSE-2000x) 87/263/46

Figure 37 Cross-sectional microstructure (500x) of a Galfan coating containing 4.0% Aluminum.
a) normal cooling rate
b) rapid cooling rate



a)

087/178/2

b)

087/178/3

ATMOSPHERIC CORROSION OF GALFAN COATINGS : CONCLUSIONS AND RECOMMENDATIONS

FROM FIRST OBSERVATIONS, CORROSION SEEMS TO BE CONDITIONED BY :

—> THE ORIENTATION OF AL-RICH LAMELLAE, THE HORIZONTAL DIRECTION PROVIDING THE LOWEST CORROSION RATE.
—> THE CONCENTRATION OF ZN-RICH GLOBULES, THUS THE AL CONTENT
—> THE DENTS AND BOUNDARIES SHRINKAGE DENSITIES (TO A LOWER EXTENT)
—> THE PB CONTENT

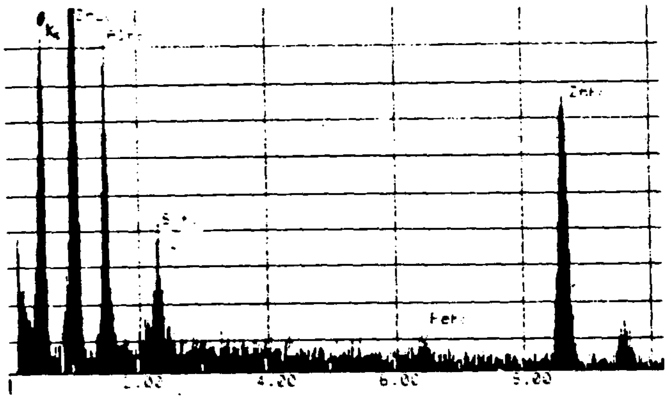
THE ORIENTATIONS OF THESE LAMELLAE COULD BE INFLUENCED BY :

—> THE HEAT FLOW DURING THE SOLIDIFICATION OF THE COATING, THUS THE COOLING RATE.
—> THE PRESENCE OF ZN-RICH GLOBULES, THUS THE AL CONTENT

BESIDES, DENTS AND BOUNDARIES SHRINKAGE SEEM TO OCCUR WHEN :

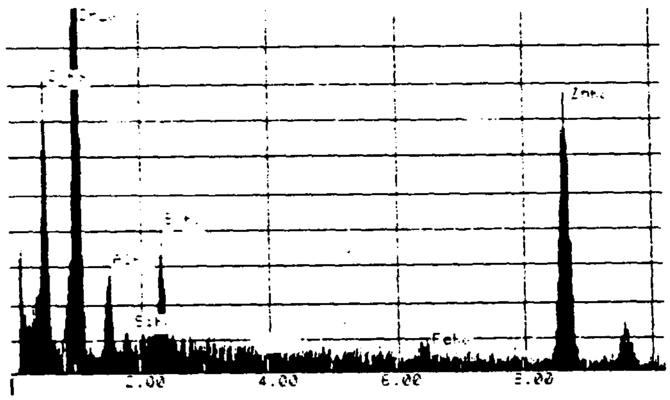
—> THE AL-RICH LAMELLAE BETWEEN 2 ADJACENT CELLS ARE DIFFERENTLY ORIENTED
—> THESE LAMELLAE TENDS TO BE VERTICAL AT CELLS BOUNDARIES.

Figure 39 : SEM+ spectra of areas in figure 38.a and b.



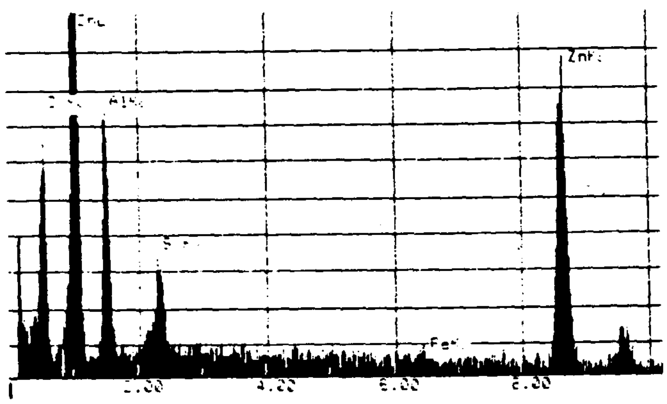
a. Fig.38.a

window



b. Fig.38.a

Zone X



c. Fig.38.b

arrows

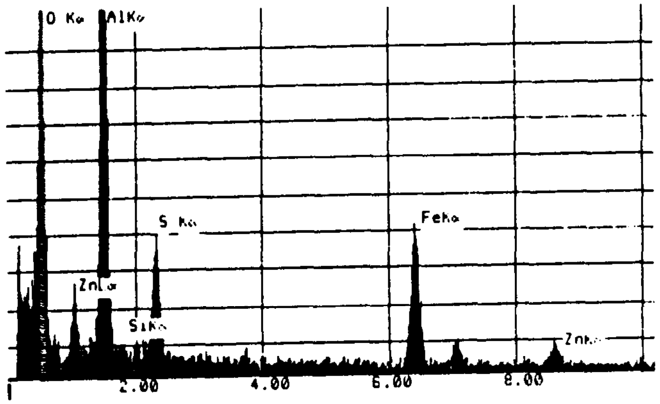
Figure 41 : Cross-sectional SEM+ examination of chromated Galvalume coating after 5 years of outdoor exposure in a marine site.
a) Local corrosion : coating failure
b) Detail of 41.a
c) Oxygen X-ray image of 41.b

a. (BSE-750x) 87/263/13

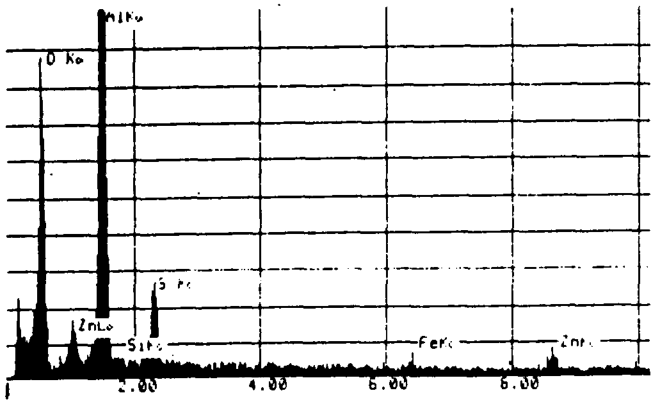
b. (BSE-2000x) 87/263/11

c. 87/263/12

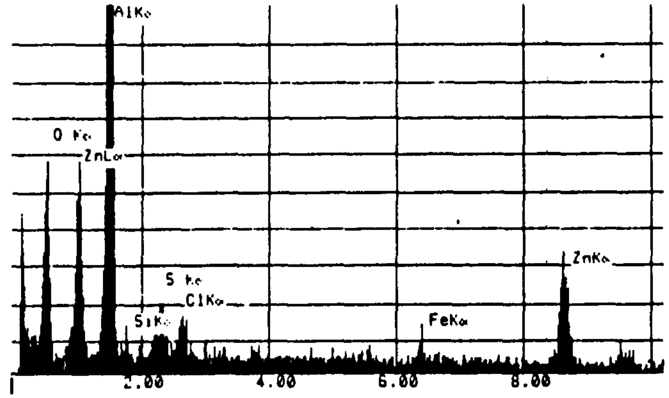
Figure 42 : SEM+ spectra of Zones A, B, C and D in figure 41.b.



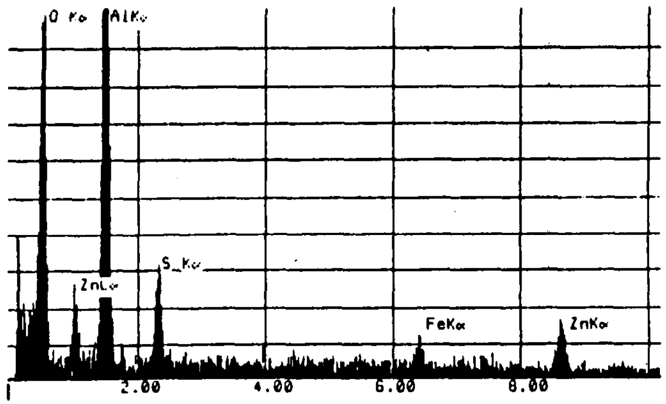
a. Zone A in figure 41.b



b. Zone B in figure 41.b



c. Zone C in figure 41.b.

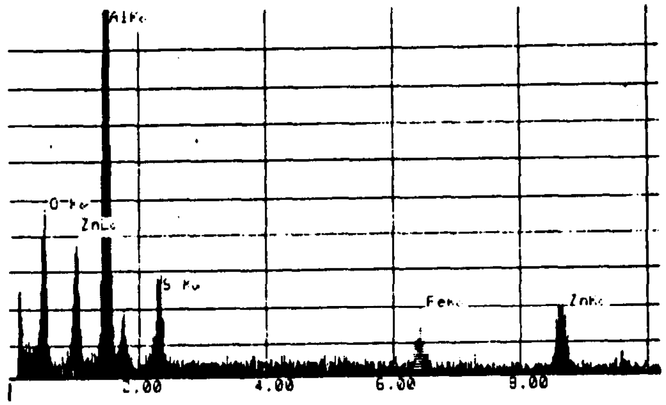


d. Zone D in figure 41.b.

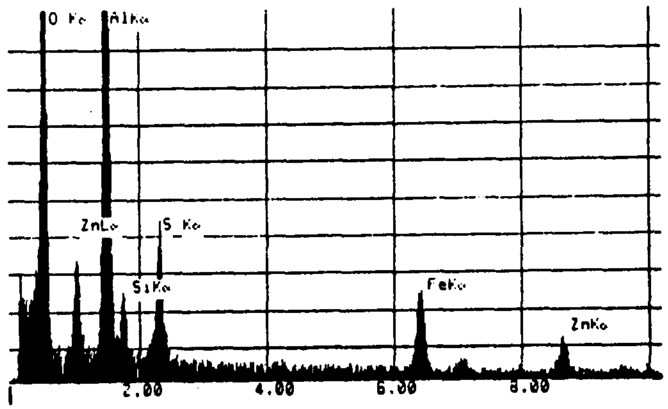
Figure 43 : Cross-sectional SEM+ examination of a chromated Galvalume coating, after 5 years of outdoor exposure in a marine site Local failure.
a) cracks network
b) corroded areas
c, d) SEM+ spectra of Zones A (between the steel and the coating) and B (intermetallics, close to the substrate)

a. ((SE-2000x) 87/263/9

b. (BSE-2000x) 87/263/10

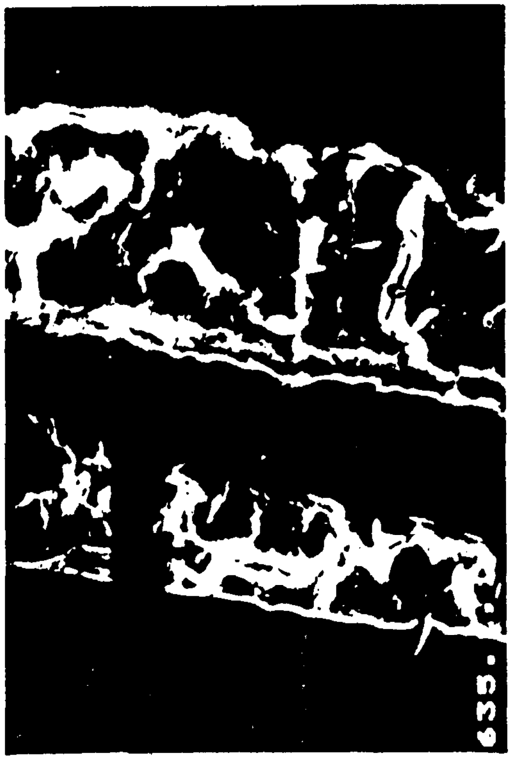


c. Spectrum of Zone A

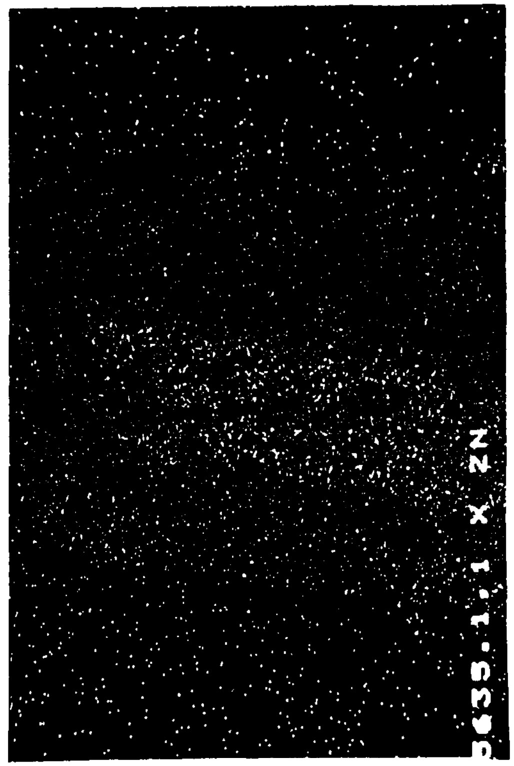


d. Spectrum of Zone B

Figure 44 : a) Cross-sectional SEM examination of a chromated Aluzinc coating, after 1 year of outdoor exposure in a marine site. Local failure (*)
b) Zinc X-ray image.



a. (BSE-750x) 87/174/16

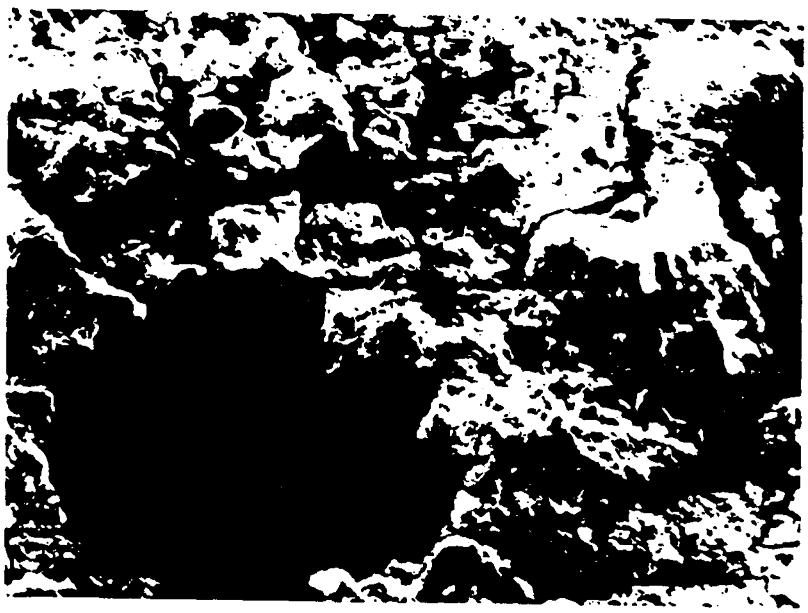


c. Zn X-ray image 87/174/15

Note : Zone B is situated behind the local corrosion zone (a, b, c)

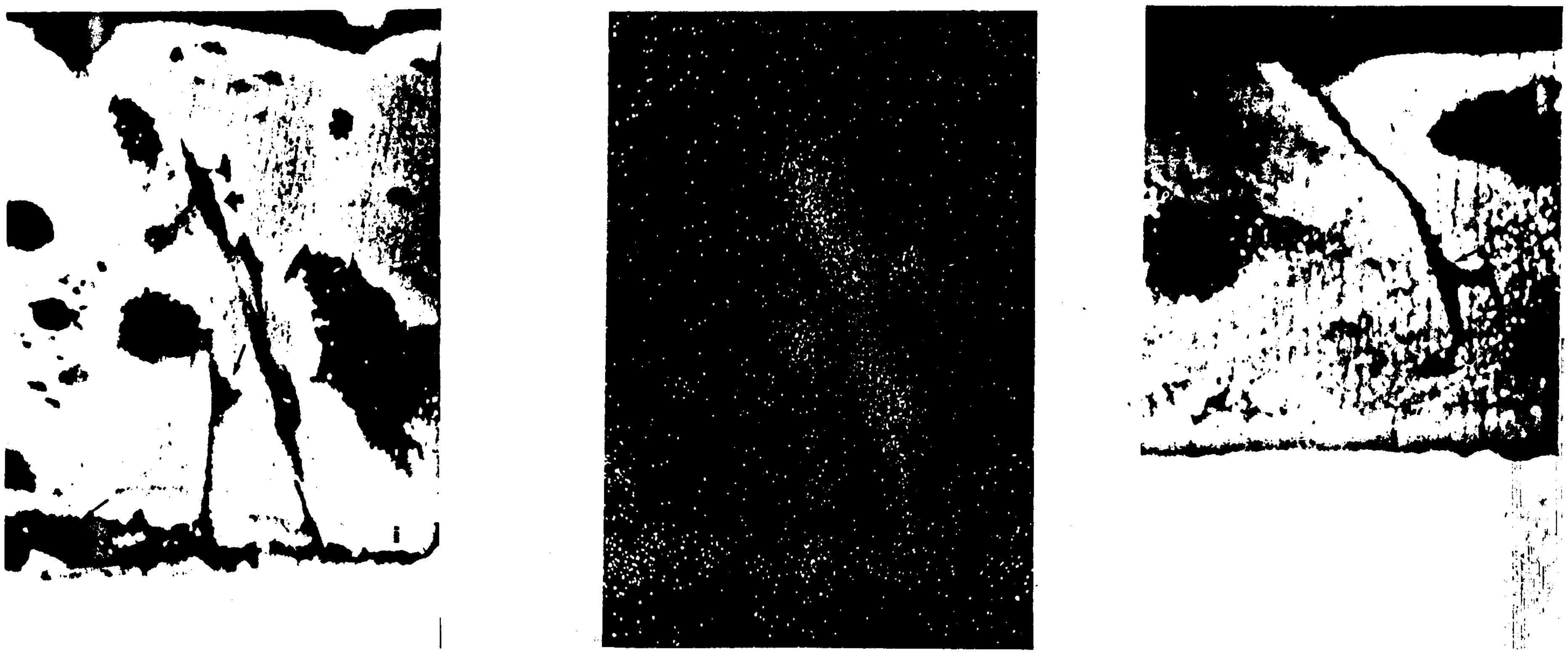
Figure 45 : a) Surface SEM examination of a chromated Aluzinc, after 1 year of outdoor exposure in a marine site. Surface microstructure of a locally failed area. Arrows are showing holes in the coating.
b) Detail of a hole

a. (SE-200x) 86/250/5



b. (SE-400x) 86/250/4

Figure 46 : a) Cross-sectional SEM+ examination of a chromated Galvalume coating. Detail of phase A in figure 40.a b) Silicon X-ray image of 46.a. c) Cross-sectional SEM examination of a chromated Aluzinc. Silicon-rich phase going through all the coating.



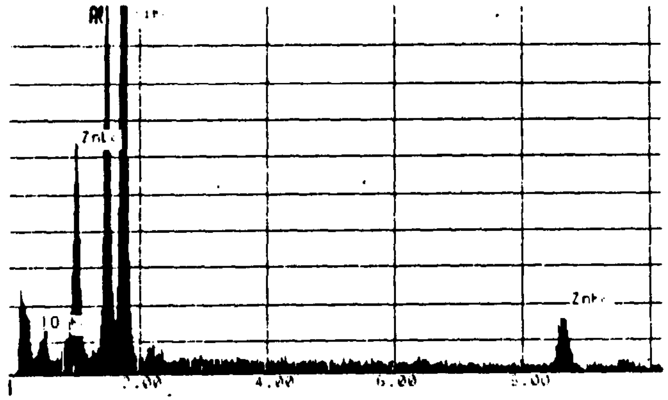
a. (BSE-3100x) 87/263/2

b. Si X-ray image 87/263/3

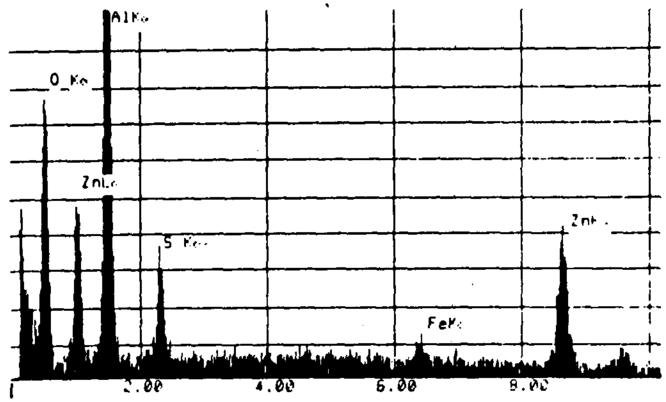
c. (BSE-4020x) 87/263/52

Figure 47 : a) Cross-sectional SEM+ examination of a chromated Aluzinc coating, after 1 year of outdoor exposure in a marine si[illegible]
b, c) Spectra of, respectively, zone a and in a crack (arrow)

a. (BSE-4000x) 87/263/30



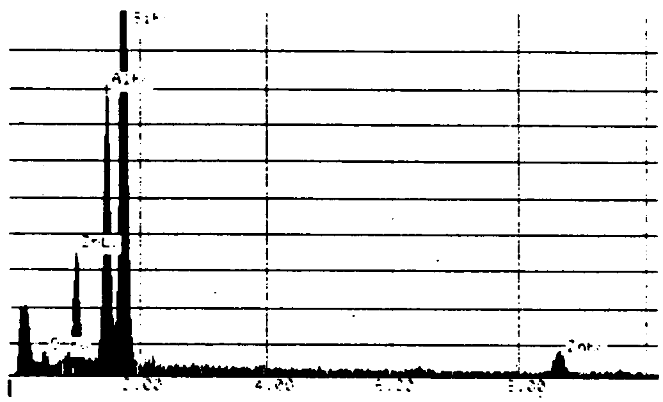
b. Spectrum of Zone a



c. Spectrum in the crack (arrow)

Figure 48 : a) Cross-sectional SEM+ examination of a chromated Aluzinc coating, after 1 year of outdoor exposure in a marine site. Differently shaped Silicon-rich phase.
b) Spectrum of this phase (arrow)

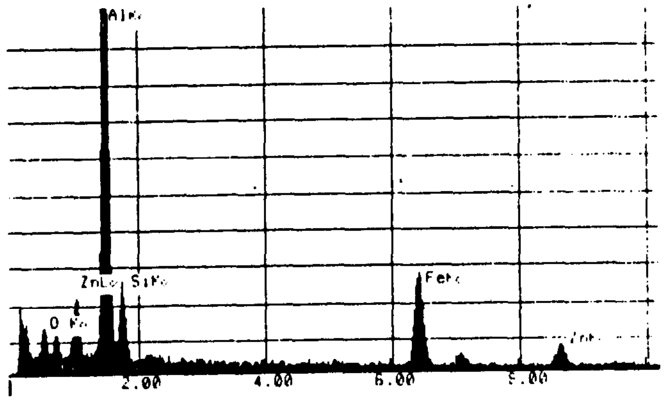
a. (BSE-4000x) 87/263/29



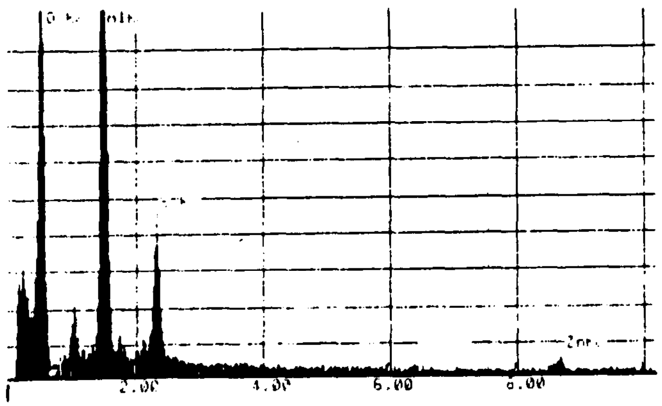
b. Spectrum of phase pointed by the arrow

Figure 49 : a) Cross-sectional SEM+ examination of a chromated Aluzinc coating, after 1 year of outdoor exposure in a marine sit
b) Spectrum of nolules (arrows).
c) Spectrum of zone X .

a. (BSE-2000x) 87/263/33



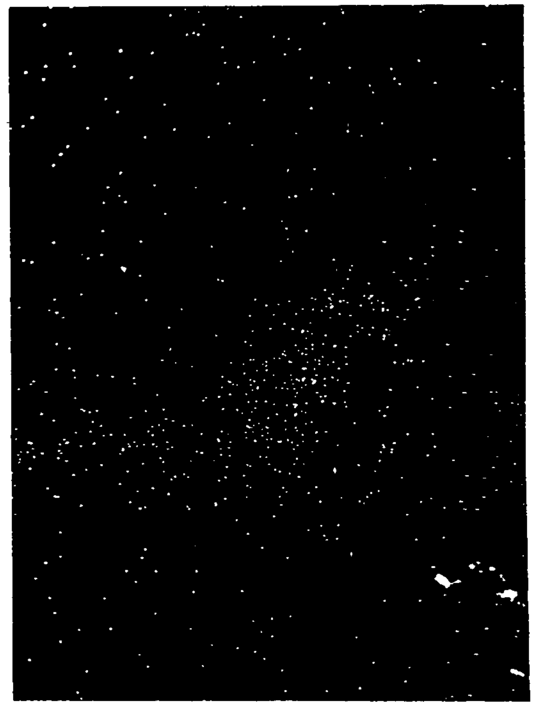
b. Spectrum of nodules (arrows)



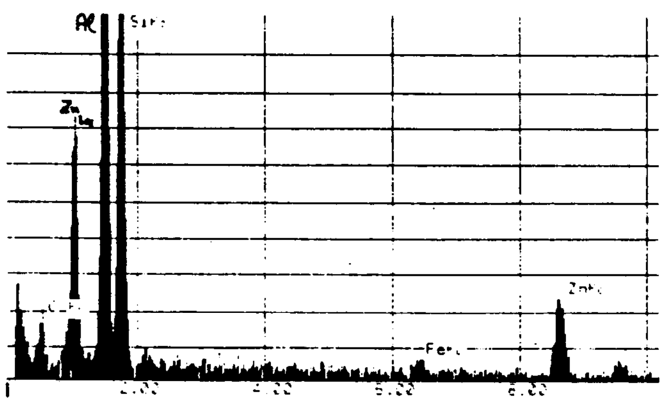
c. Spectrum of Zone X

Figure 50 : a) Cross-sectional SEM examination of a chromated Aluzinc coating, after 1 year of outdoor exposure in a marine site. Primary and secondary intermetallic layers.
b) Corresponding silicon X-ray image .
c) Spectrum in the window .

a. (BSE-5000x) 87/263/34



b. Si X-ray image 87/263/35

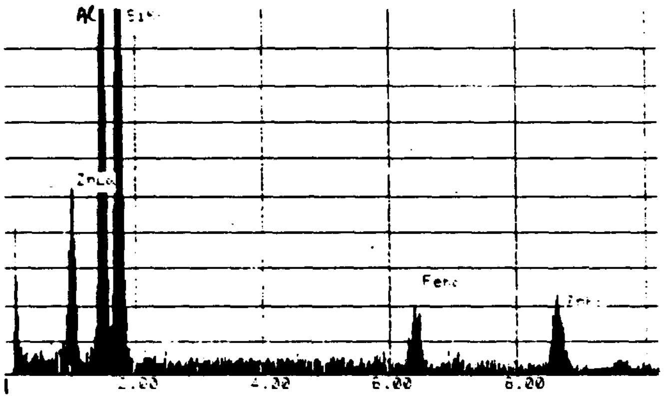


c. Spectrum in the window

Figure 51 : Cross-sectional SEM+ examination of a chromated Aluzinc coating, after 1 year of outdoor exposure in a rural site. a) Heterogeneity of the secondary intermetallics (Zone A) and cracks in the primary intermetallic layer (thin arrows).
b) Excessive primary intermetallics growth
c) SEM+ spetrum of Zone A (between the arrows)

a. (BSE-4000x) 87/263/48

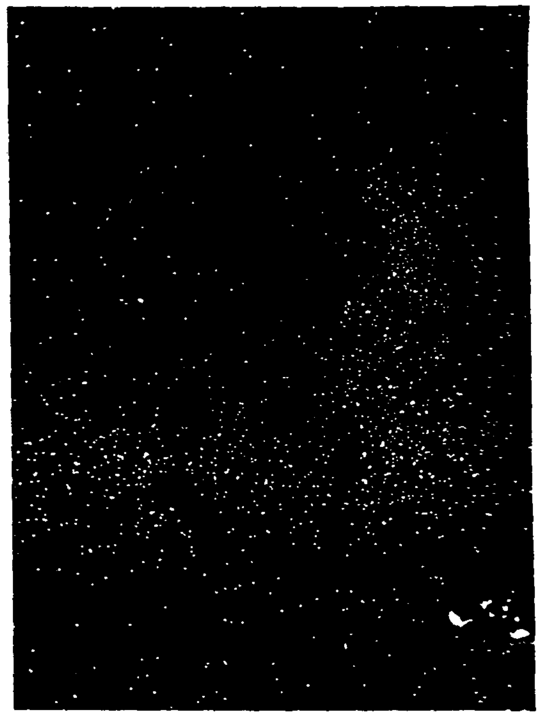
b. (BSE-2500x) 87/263/36



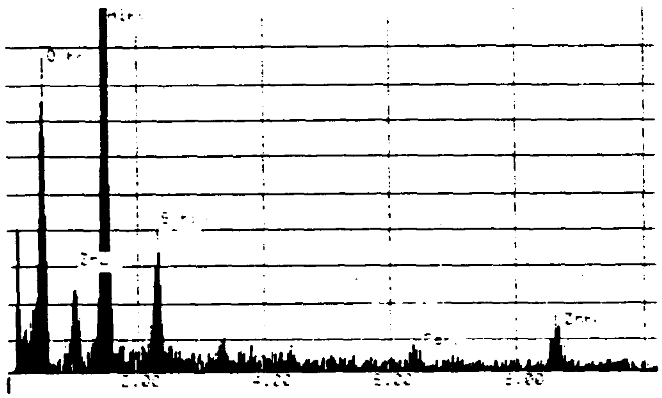
c. Spectrum of Zone A (between the arrows)

Figure 52 : a) Cross-sectional SEM+ examination of a chromated Aluzinc coating after 1 year of outdoor exposure in a rural site. Corrosion within a secondary intermetallics phase.
b) Silicon X-ray image .
c) SEM+ spetrum of Zone Z.

a. (BSE-8000x) 87/263/50



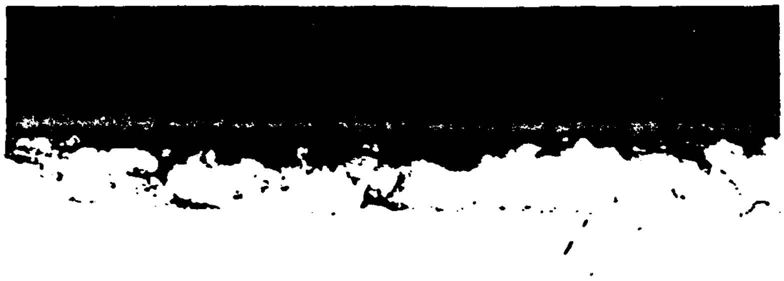
b. Si X-ray image 87/263/51



c. Spectrum of Zone Z

Figure 7 : (continued)

Exposure sites

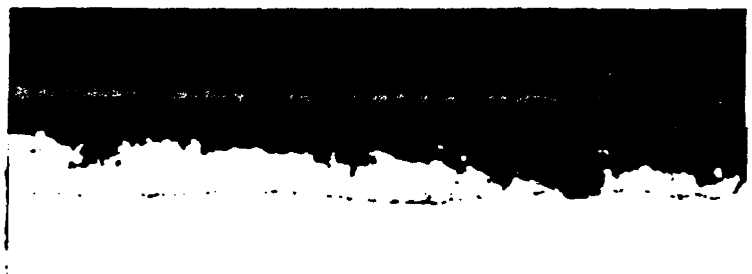


a. marine

087/197/27

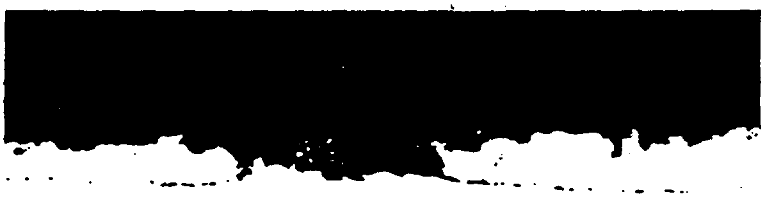
b. industrial

087/203/9



c. rural

087/203/6



087/203/7

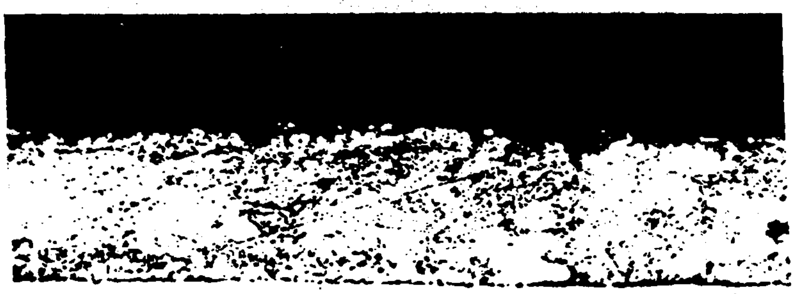
Figure 6 : Cross-sectional microstructures (500x) of Galfan (N 10) coated sheets after 5 years of outdoor exposure in 4 different sites.

Exposure sites

a. severe marine

087/197/10

087/197/23

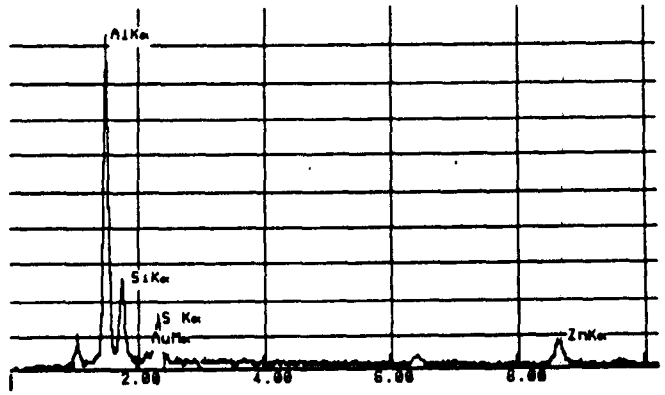


b. marine

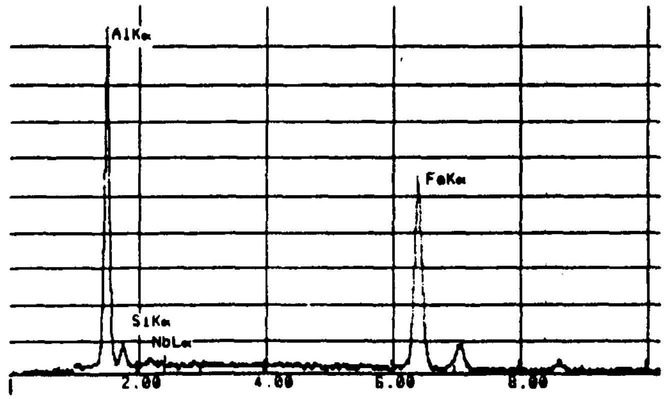
087/197/19

Figure 54 : a) Cross-sectional SEM+ examination of a chromated Aluzinc coating, after 1 year of outdoor exposure in an industria site
b, c) SEM spectra of respectively Zones X and Y

a. (BSE-3500x) 87/174/2



b. Spectrum of Zone X



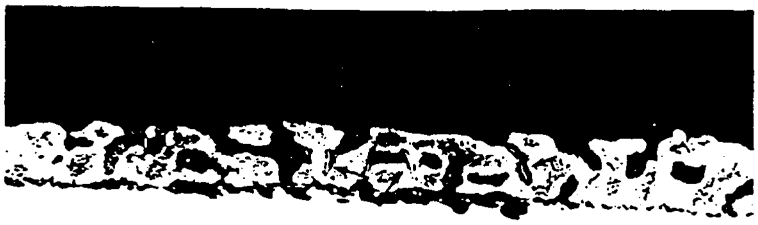
c. Spectrum of Zone Y

Figure 55 : Cross-sectional microstructures (500x) of a chromated Galvalume coating, after 5 years of outdoor exposure in different sites. Corrosion evolution all around secondary intermetallics phases (some of it being shown by arrows).

Exposure sites

a. severe marine

087/203/11



b. industrial

087/197/33

c. rural

087/203/1

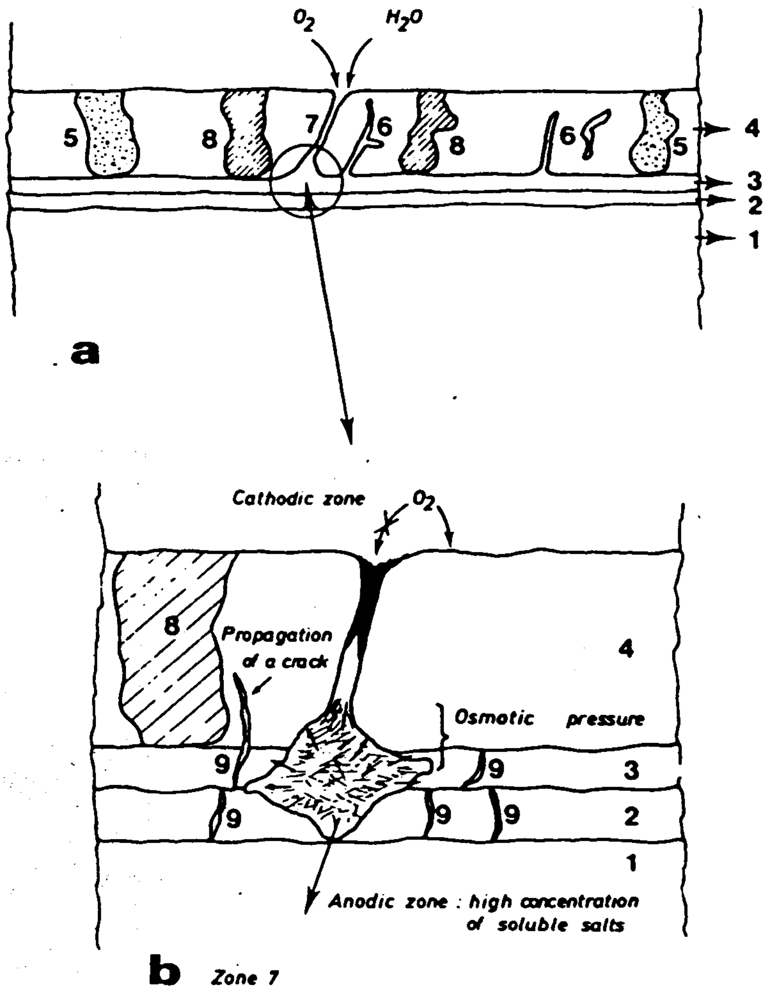
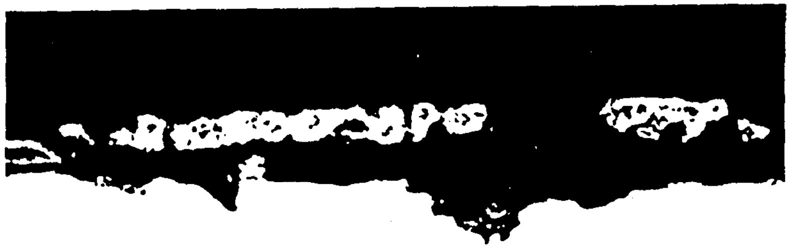


Figure 56 Mechanisms of corrosion of a Galvalume coating. a) Formation of cracks in the coating. b) Osmotic pressure generation.

Notes :

1. Steel substrate
2. Intermetallic : Fe, Al, Si, Zn
3. Intermetallic : Al, Si, Zn (Si highly concentrated)
4. Galvalume coating
5. Zinc rich phase
6. Intermetallic (Al,Si, Zn) phase
7. Pore
8. Corroded zinc rich phase
9. Crackings generated by osmotic pressure and propagating into the coating

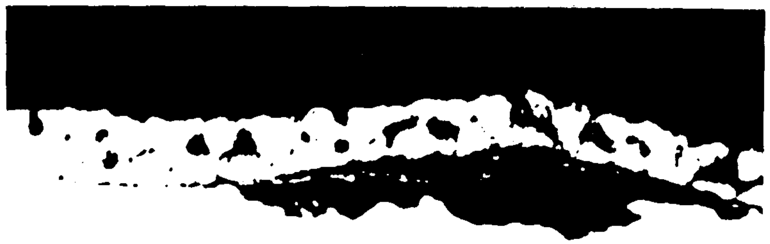
Figure 57 : Cross-sectional microstructures of a chromated Galvalume coating, after 5 years of outdoor exposure in different sites. Different types of local failures.



a. Marine site 087/245/10

b. Industrial site 087/197/34

Marine site 087/189/5



c. Rural site 087/189/9

ATMOSPHERIC CORROSION OF 55 AL-ZN COATINGS : CONCLUSIONS

1. NORMAL CORROSION OCCURS IN 2 STEPS

   —> FIRST : CORROSION OF INTERDENDRITIC ZN-RICH PHASES
   —> SECOND : CORROSION EXTENDS TO THE AL-RICH DENDRITES.
   THE SECOND STEP IS SLOWER THAN THE FIRST ONE.

2. LOCAL FAILURE PHENOMENON, DUE TO :

   —> THE INSOLUBILITY AND THE INCREASED VOLUME OF THE INTERDENDRITIC CORROSION PRODUCTS.
   STRESSES IN THE COATING
   —> PRESENCE OF A BRITTLE SECONDARY INTERMETALLIC PHASE AS A :
   - DISCONTINUOUS LAYER BETWEEN THE PRIMARY INTERMETALLICS AND THE COATING
   - SHARP SHAPED PHASES WITHIN THE COATING.
   —> LOW FORMABILITY OF 55AL-ZN COATINGS, WHICH CANNOT ACCOMODATE INTERNAL STRESSES.

Galfan-related Research at the University of Wales, Cardiff

For some years workers in the Division of Materials Engineering have been working on various aspects of coatings on steel, initially concentrating on aluminised coatings but subsequently studying galvanized and zinc-aluminium coatings. This presentation describes some of the work carried out on coatings containing about 5% aluminium in zinc.

FIGURE 1 lists the three areas of work that will be discussed. All have been funded to a considerable extent by the U.K. Science and Engineering Research Council (SERC).
The deformation studies on Galfan have been part of a larger programme of work aimed at rationalising the forming behaviour of a number of types of coated steel sheet. The structural studies arose from a realisation that the properties of eutectic or near-eutectic zinc-aluminium coatings were likely to be very dependent on structure. An earlier study on cast Zn-Al structures by one of the Cardiff group (Dr. J. A. Spittle) had revealed the considerable dependence of structure on factors such as composition and freezing rate. The fluxing study developed from a special SERC programme aimed at promoting the more effective use of waste materials. Our overall aim was to establish whether scrap zinc containing appreciable amounts of aluminium (e.g. remelted scrap die-castings) could be used as a feedstock for general galvanizing.

FIGURE 2 lists the main findings of our deformation work on Galfan. Unlike much hot-dipped galvanized strip, the Galfan samples we examined did not have a strong basal texture FIGURE 3. This permitted plastic deformation of the coating during deformation, a process further aided by the presence of some face-centred cubic aluminium-rich phase and the fine-scale eutectic structure. The result was minimal cracking in the Galfan coatings and a less severe degradation of corrosion-resisting performance in the deformed condition by comparison with conventional hot-dip galvanized coatings FIGURE 4. Low-lead hot-dip coatings had performances similar to Galfan in this respect, a result that can be linked to a much reduced basal texture. FIGURE 5 summarises the reasons for the better formability of Galfan coatings.

FIGURE 6 outlines the structural variations we have established in binary near-eutectic zinc-aluminium alloys. The cooling rate effects can be rationalised in terms of an assymmetric eutectic coupled zone as shown in FIGURE 7. In hypereutectic compositions this predicts initially increasing proportions of the eutectic component of the microstructure with increasing cooling rate. With very fast cooling rates it is possible to produce primary zinc-rich phase in hyper-eutectic alloys. Titanium additions appear to mave a marked influence on nucleation of the eutectic mixture and the alpha prime phase but little effect on the nucleation of the zinc-rich phase. Further details of this work can be found in: **Structural Variation in Near-Eutectic Zinc-Aluminium Alloys, P.A. Porot et al., Metallography, 1987, 20, 181-197.**

Intermetallic formation in zinc-aluminium alloys has also been studied by us and FIGURE 8 lists the main findings reported in a recent publication: **Mechanisms of formation and growth ..... etc., P.G. Caceres et al., Mat. Sci. Tech., 1986, 2, 871-877.**
It is clear that the rapid solid-liquid reactions occurring in this system are very complex and, of course, will have implications for industrial practice. In general "Galfanising" there will be problems with rough coatings arising from entrappment of intermetallic in the liquid coating withdrawn form the bath. Conventional bath hardware in both general and continuous operation may be subject to rapid dissolution attack unless specially resistant alloys are used or the aggressiveness of the bath is reduced. We have confirmed that silicon in solution in zinc-aluminium melts has a pronounced effect in limiting attack on the steel (FIGURE 9). This phenomenon was reported by Neemuchwalla and Hershman of the British Non-Ferrous Research Association (BNF) in the Proceedings of the 7th International Galvanizing Conference. They attributed the finding to Mann and Hunt, also of BNF, who reported their work in an unpublished report. Of course, silicon is also well-known as an intermetallic growth inhibitor in the production of Galvalume and aluminised steel.

Our data on the influence of silicon is shown in FIGURE 10. Generally silicon is effective in virtually eliminating attack on steel but in some regions the attack will be as severe as in silicon-free baths, presumably as the result of silicon-depletion. Neemuchwalla and Hershman attributed the beneficial influence of silicon to its ability to remove iron from solution in the bath and therefore to speed up dissolution of the intermetallic layer. Our data on total thickness shows that the accelerated dissolution explanation is untenable. Further we have detected a thin intermetallic layer adjacent to the steel which is rich in aluminum and silicon. It may be that this acts as a means of inhibiting rapid intermetallic growth. However the addition of silicon to the zinc-aluminium baths may not be without drawbacks. It has recently been reported that silicon additions promote embrittlement in zinc-12%aluminium casting alloys.

FIGURE 11 gives some details of a preflux technique termed "UNIGALVA" we have developed for hot dipping in zinc or zinc-aluminium alloys. The electrolytic process eventually produces an array of lead chloride crystals on the surface of the steel component which acts as a low-fuming flux. We have used the process successfully on a pilot line for the production of wire and for batch processing using a barrelling pretreatment method. Lead pick-up will clearly take place in the coating which might be seen as a major objection to the adoption of the method for "Galfanising" although accelerated corrosion tests carried out by us still showed an improvement in time to first red rust compared with conventional galvanized coatings of the same thickness. Patent protection is being sought for the UNIGALVA process.

Dr. R. D. Jones

UNIVERSITY OF WALES, CARDIFF

"GALFAN-RELATED" RESEARCH

1. DEFORMATION STUDIES.

2. STRUCTURAL STUDIES OF STEEL/MELT REACTIONS.

3. FLUXING STUDIES.

FIGURE 1

DEFORMATION STUDIES

Galfan studied as one of a large group of coated steel products which includes:

Galvalume, hot dip galvanized, electro-zinc (inc. some EZ 'alloys'), hot dip aluminised.

MAIN FINDINGS

1. GALFAN TEXTURE NON-BASAL.

2. MINIMAL CRACKING.

3. 10% REDUCTION IN CORROSION LIFE AFTER DEFORMATION. (30%+ REDUCTION FOR GALV.)

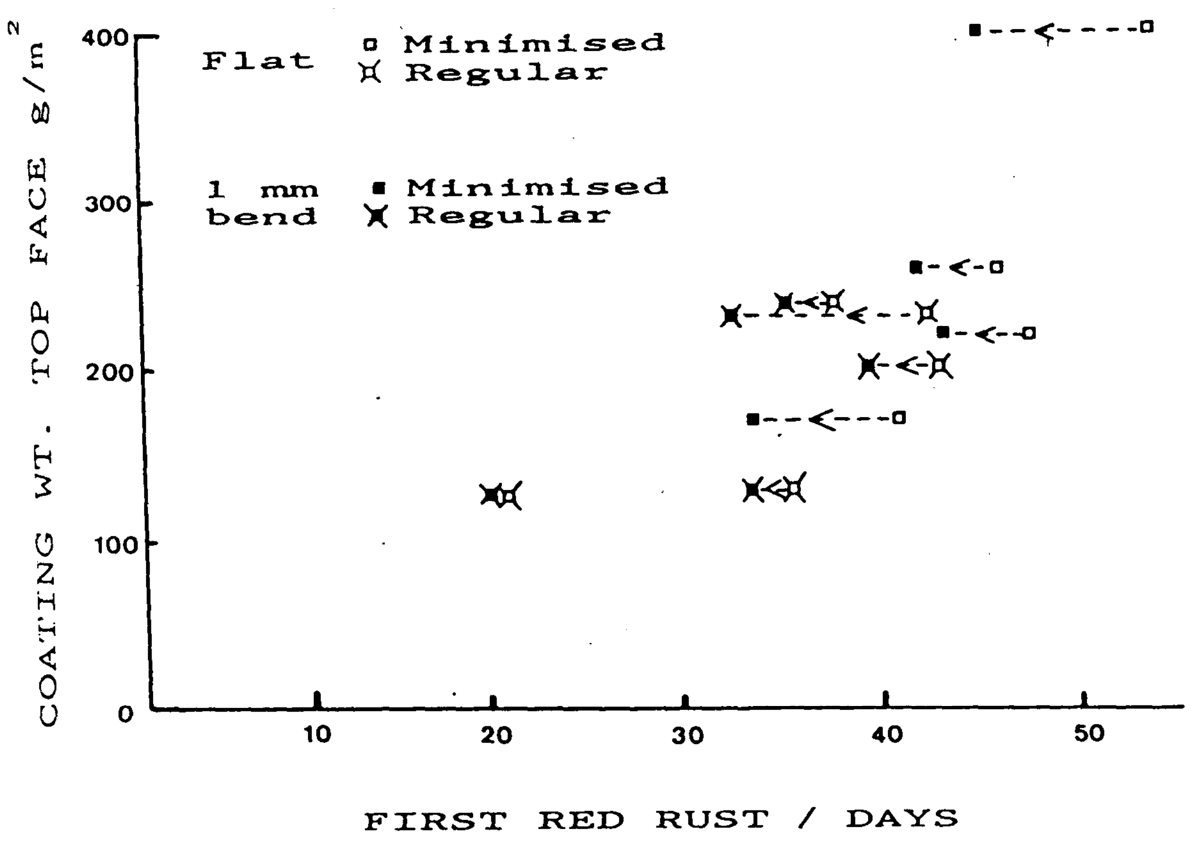
FIGURE 2

INTENSITY / %

Plane	Ideal Random	Regular Galv.	Min. Galv.	Low Lead	E.G.	Galfan
0002	1.72	45.0	75.2	16.9	6.5	11.8
$10\bar{1}0$	5.17	7.3	13.1	14.2	-	6.4
$10\bar{1}1$	10.34	11.0	2.9	17.9	5.3	5.6
$10\bar{1}2$	10.34	11.0	2.5	-	-	3.9
$10\bar{1}3$	"	3.5	3.4	16.9	6.4	3.4
$11\bar{2}0$	"	-	-	-	-	2.4
$11\bar{2}1$	"	-	1.4	-	-	-
$11\bar{2}2$	"	3.0	1.0	11.9	75.0	66.4
$20\bar{2}1$	"	22.4	2.4	-	-	-
$10\bar{1}4$	"	-	-	21.9	6.7	-
$10\bar{1}5$	"	3.8	-	-	-	-

INTENSITY OF OCCURRENCE OF PLANES PARALLEL TO THE SURFACE IN COATED STEEL.

FIGURE 3



CHANGE OF SALT SPRAY CORROSION RESISTANCE OF GALFAN WITH DEFORMATION.

FIGURE 4

GALFAN WILL HAVE <u>BETTER</u> FORMING PROPERTIES THAN GALV. BECAUSE:

(i) Its preferred orientation provides more plasticity in the plane of the sheet to ηZn.

(ii) The $5\%^{+}$ aluminium-rich phase is likely to be intrinsically more ductile than ηZn.

(iii) The thinner alloy layer is less effective in nucleating intragranular cracks in Galfan.

FIGURE 5

Structural Variations in [illegible] near Eutectic Zn-Al Alloys

1. Hypoeutectic alloys have primary Zn solid solution (β) + eutectic. Increasing cooling rate decreases size of β crystals and refines eutectic.

2. Microstructure of hypereutectic alloys governed by cooling rate and aluminium content. Depending on %Al, increased cooling rate may change the constitution of the microstructure from primary α' + eutectic to wholly eutectic or even to primary β + eutectic. The constituents will also be refined as the cooling rate increases.

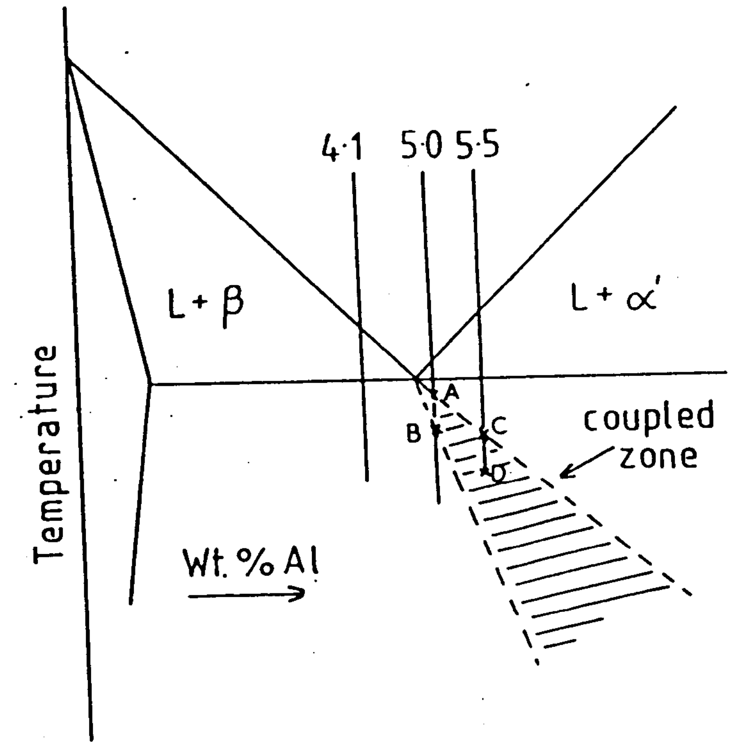
3. The addition of Titanium, at concentrations as low as 0·01% causes the following changes:

   (i) In hypereutectic alloys, nucleation of both the primary α' crystals and etuectic grains is enhanced.

   (ii) In hypoeutectic alloys, nucleation of the eutectic grains is enhanced but that of the β primary crystals appears to be unaffected.

FIGURE 6

STRUCTURAL VARIATIONS IN NEAR-EUTECTIC Zn-Al ALLOYS



Schematic diagram of the suggested location of the coupled zone of eutectic growth for the Zn–Al system.

FIGURE 7

STRUCTURAL STUDIES OF STEEL - MELT REACTIONS

1. During hot dipping of pure iron into Zn - 3Al and Zn - 6Al melts, a thin (<o.5μm) layer rich in aluminium formed on the steel initially.

2. Abnormal and localised growth of this layer took place at slightly longer dipping times. The onset of abnormal growth depends on Al content. The higher the Al content, the lower the time to initiate abnormal growth.

3. The abnormal growth is accompanied by irregularities in the form of zinc-rich layers within the inter-metallic layer.

4. The aluminium depletion at sites near the localised growth of the inhibiting layer changed the solidification characteristics of the last liquid to those associated with a lower aluminium content.

5. At lower dipping times a fibre-like or columnar growth morphology developed. This had a structure isomorphous with Fe_3Al (complex monoclinic) with a composition $Fe(Al_{0.85}-Zn_{0.15})_3$.

FIGURE 8

REACTION INHIBITION BY SILICON IN ZINC - ALUMINIUM BATHS

First established by Mann and Hunt (BNF ~ 1960)

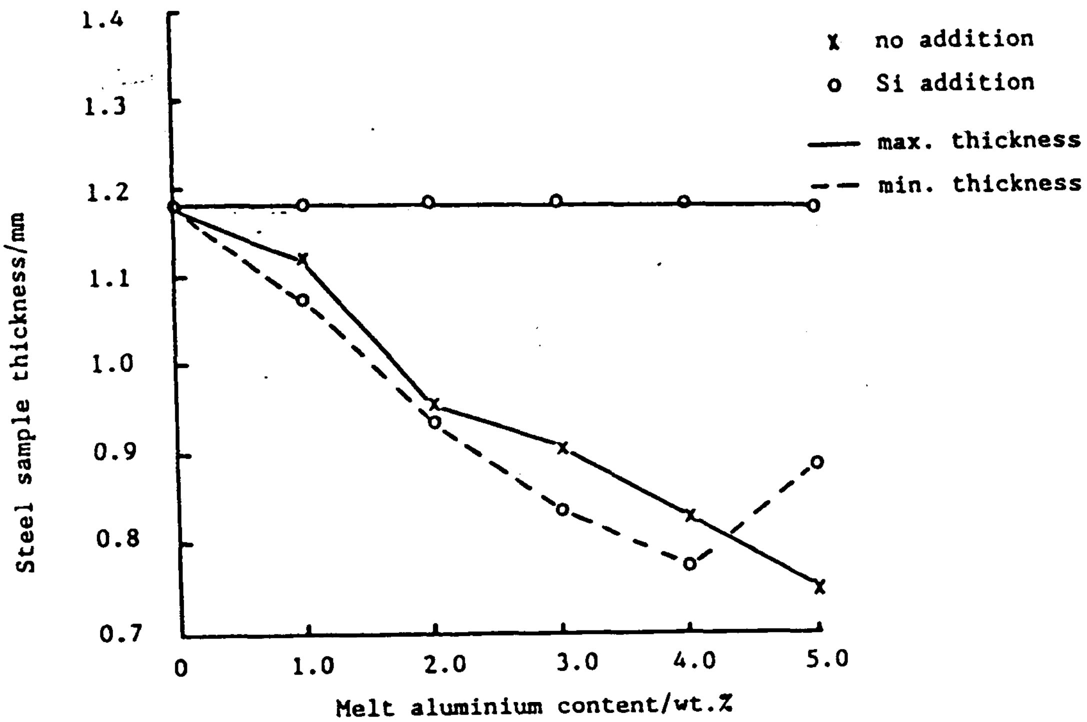
Examined in more detail by Neemuchwalla and Hershman (also BNF) and reported in 7th Intergalva. They claimed that silicon acted as a "Getter" in removing iron from solution in the galvanizing bath. Iron-saturated baths promoted rapid alloy layer growth whereas low-iron baths produced thin alloy layers - possibly because dissolution was faster.

We have found evidence for a thin (3μm) inhibiting layer rich in silicon and aluminium forming on the steel.

Don't rush to saturate your baths with silicon just yet - it promotes embrittlement in zinc - 12% aluminium casting alloys!

(Thompson and Niessen, J. Mat. Sci, 1986, 21, 2565)

FIGURE 9



INFLUENCE OF A SATURATION (0.035% ?) SILICON ADDITION ON THE THICKNESS OF STEEL REMAINING AFTER 2 HOURS IMMERSION AT 470°C.

FIGURE 10

FLUXING STUDIES

Originally developed 'Unigalva' process so that steel could be coated with scrap zinc (typical composition: 4.01% Al, 0.82% Cu, 0.46% Pb, 0.174% Mg) works well for this material and coating has better salt spray durability than conventional Galv. of same thickness.

Use of lead salt in pretreatment may prevent its use for Galfan although Cu, Mg components in scrap must help in controlling its adverse effect.

UNIGALVA METHOD

Cathodically electropickle the steel substrate in a solution of hydrochloric acid containing lead ions.

Active constituent is lead chloride which is present in the dried deposit as an array of angular crystals.

Process works for zinc or zinc-aluminium alloys on batch basis (using barrelling) or continuous basis (pilot wire line has produced zinc and zinc-aluminium coated wire).

FIGURE 11

UNIVERSITY OF WALES, CARDIFF

"GALFAN-RELATED" RESEARCH

[illegible]NATION STUDIES

STRUCTURAL STUDIES OF STEEL / MELT REACTIONS.

FLUXING STUDIES.

DEFORMATION STUDIES

Galfan studied as one of a large group of coated steel products which includes: Galvalume, hot dip galvanized, electrozinc (incl. some EZ 'alloys'), hot dip aluminised.

MAIN FINDINGS

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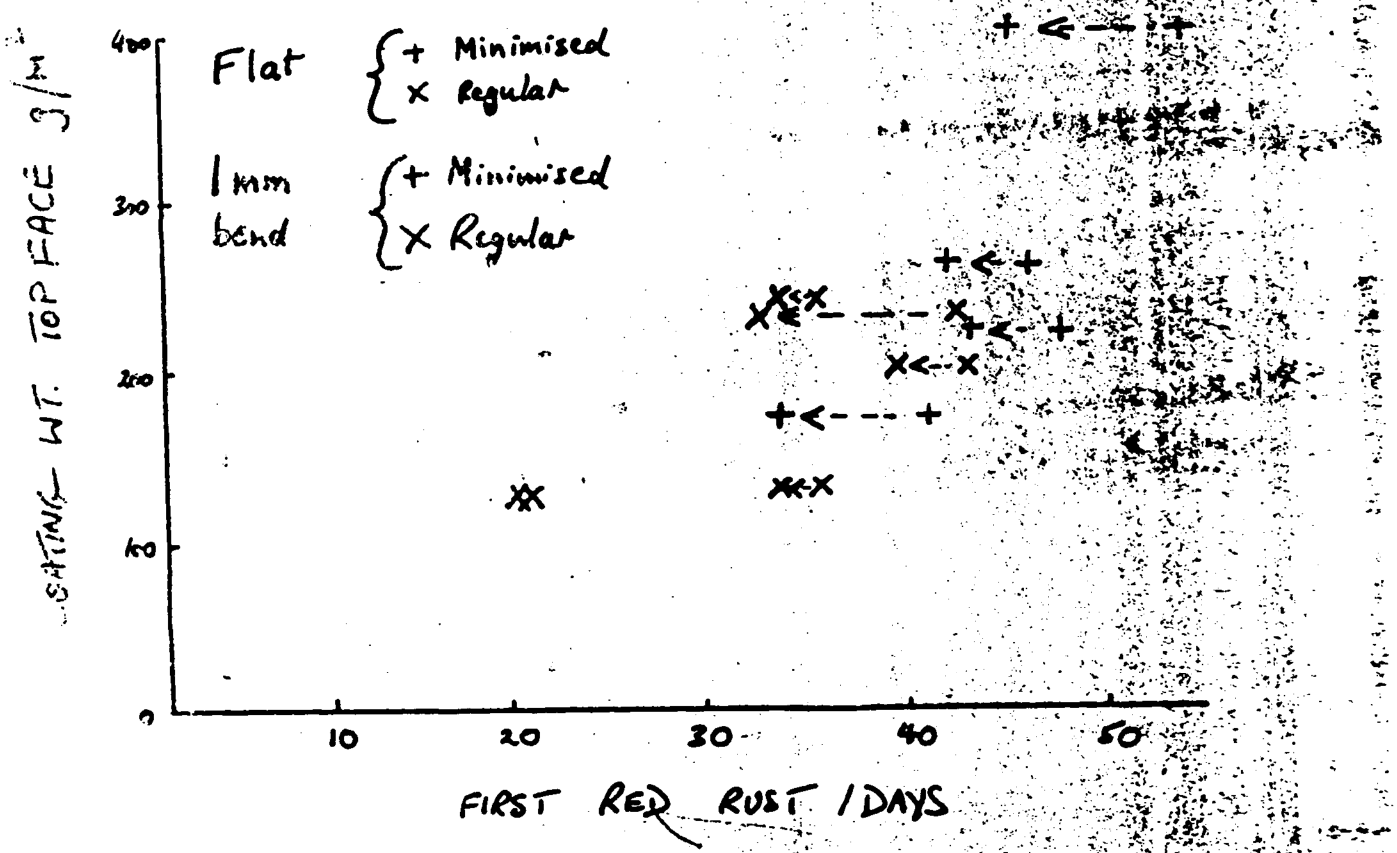
PLANE	INTENSITY / %					
	IDEAL RANDOM	REGULAR GALV.	MIN. GALV.	LOW LEAD	E.G.	GALFAN
[illegible]	1.72	45.0	75.2	16.9	6.5	11.8
[illegible]	5.17	7.3	13.1	14.2	—	6.4
[illegible]	10.54	11.0	2.9	17.9	5.3	5.6
[illegible]	10.34	11.0	2.5	—	—	3.9
[illegible]	"	3.5	3.4	16.9	6.4	3.4
[illegible]	"	—	—	—	—	2.4
[illegible]	"	—	1.4	—	—	—
[illegible]	"	3.0	1.0	11.9	75.0	66.4
[illegible]	"	22.4	2.4	—	—	—
[illegible]	"	—	—	21.9	6.7	—
[illegible]	"	3.8	—	—	—	—

INTENSITY OF OCCURRENCE OF PLANES PARALLEL TO THE SURFACE IN COATED STEEL



CHANGE OF SALT SPRAY CORROSION RESISTANCE OF GALFAN WITH DEFORMATION

GALFAN WILL HAVE BETTER FORMING PROPERTIES THAN GALV. BECAUSE:

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ii) The 5%+ aluminium-rich phase is likely to be intrinsically more ductile than η Zn.

iii) The thinner alloy layer is less effective in nucleating intragranular cracks in Galfan.

STRUCTURAL VARIATION IN NEAR EUTECTIC Zn-Al ALLOYS

1. HYPOEUTECTIC ALLOYS HAVE PRIMARY Zn SOLID SOLUTION (β) + EUTECTIC. INCREASING COOLING RATE DECREASES SIZE OF β CRYSTALS AND REFINES EUTECTIC.

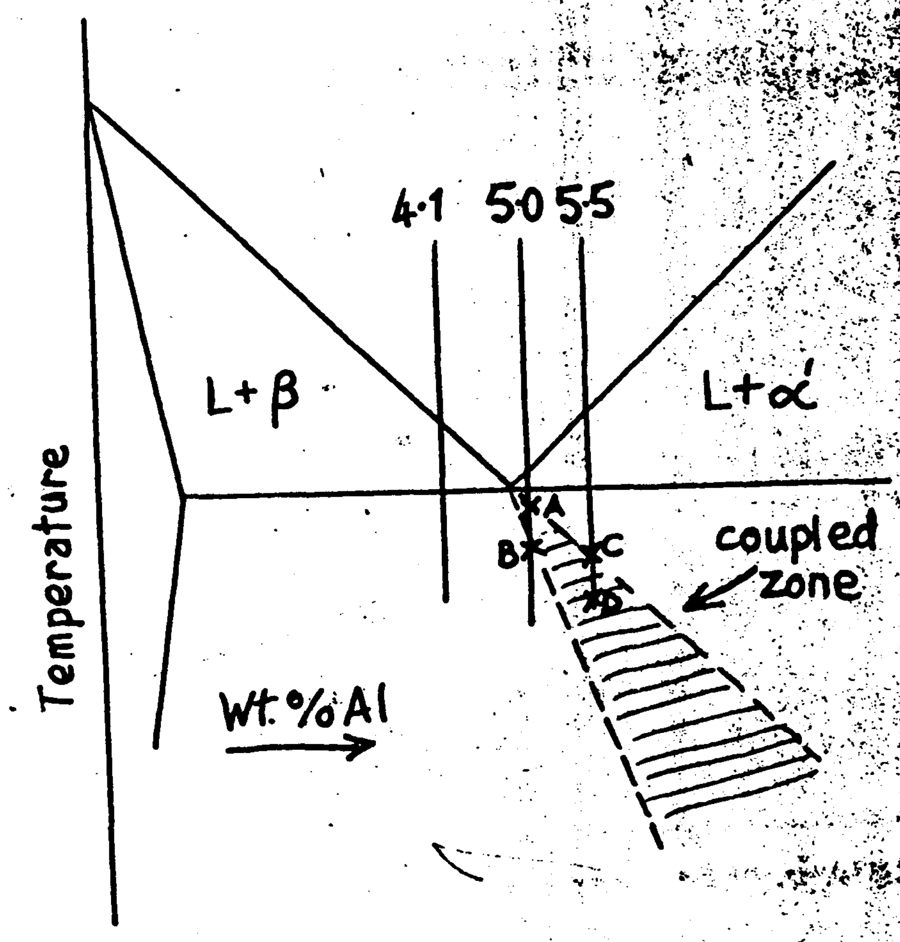
2. MICROSTRUCTURE OF HYPEREUTECTIC ALLOYS GOVERNED BY COOLING RATE AND ALUMINIUM CONTENT. DEPENDING ON % Al, INCREASED COOLING RATE MAY CHANGE THE CONSTITUTION OF THE MICROSTRUCTURE FROM PRIMARY α' + EUTECTIC TO WHOLLY EUTECTIC OR EVEN TO PRIMARY β + EUTECTIC. THE CONSTITUENTS WILL ALSO BE REFINED AS THE COOLING RATE INCREASES.

3. THE ADDITION OF TITANIUM, AT CONCENTRATIONS AS LOW AS 0.01% CAUSES THE FOLLOWING CHANGES:

   (i) IN HYPEREUTECTIC ALLOYS, NUCLEATION OF BOTH THE PRIMARY α' CRYSTALS AND EUTECTIC GRAINS IS ENHANCED

   (ii) IN HYPOEUTECTIC ALLOYS NUCLEATION OF THE EUTECTIC GRAINS IS ENHANCED BUT THAT OF THE β PRIMARY CRYSTALS APPEARS TO BE UNAFFECTED.

STRUCTURAL VARIATION IN NEAR-EUTECTIC Zn-Al ALLOYS



TRUCTURAL STUDIES OF
TEEL - MELT REACTIONS.

...RING HOT DIPPING OF PURE IRON INTO Z-3Al ... Zn-6Al MELTS A THIN ($<0.5\ \mu m$) LAYER ... N ALUMINIUM FORMED ON THE STEEL INITIALLY.

...RMAL AND LOCALISED GROWTH OF THIS LAYER ... PLACE AT SLIGHTLY LONGER DIPPING TIMES. ... SET OF ABNORMAL GROWTH DEPENDS ON ... CONTENT. THE HIGHER THE AL CONTENT, THE ... ER THE TIME TO INITIATE ABNORMAL GROWTH.

...HE ABNORMAL GROWTH IS ACCOMPANIED BY ... ULARITIES IN THE FORM OF ZINC-RICH ... WITHIN THE INTERMETALLIC LAYER.

... ALUMINIUM DEPLETION AT SITES NEAR THE ... LISED GROWTH OF THE INHIBITING LAYER CHANGED ... SOLIDIFICATION CHARACTERISTICS OF THE LAST ... TO SOLIDIFY. TO THOSE ASSOCIATED WITH A ... ALUMINIUM CONTENT.

... LONGER DIPPING TIMES A FIBRE-LIKE OR ... MNAR GROWTH MORPHOLOGY DEVELOPED. THIS HAD ... RUCTURE ISOMORPHOUS WITH Fe_3Al (COMPLEX ... CLINIC) WITH A COMPOSITION $Fe(Al_{0.85}Zn_{0.15})_3$

REACTION INHIBITION BY SILICON IN ZINC - ALUMINIUM BATHS

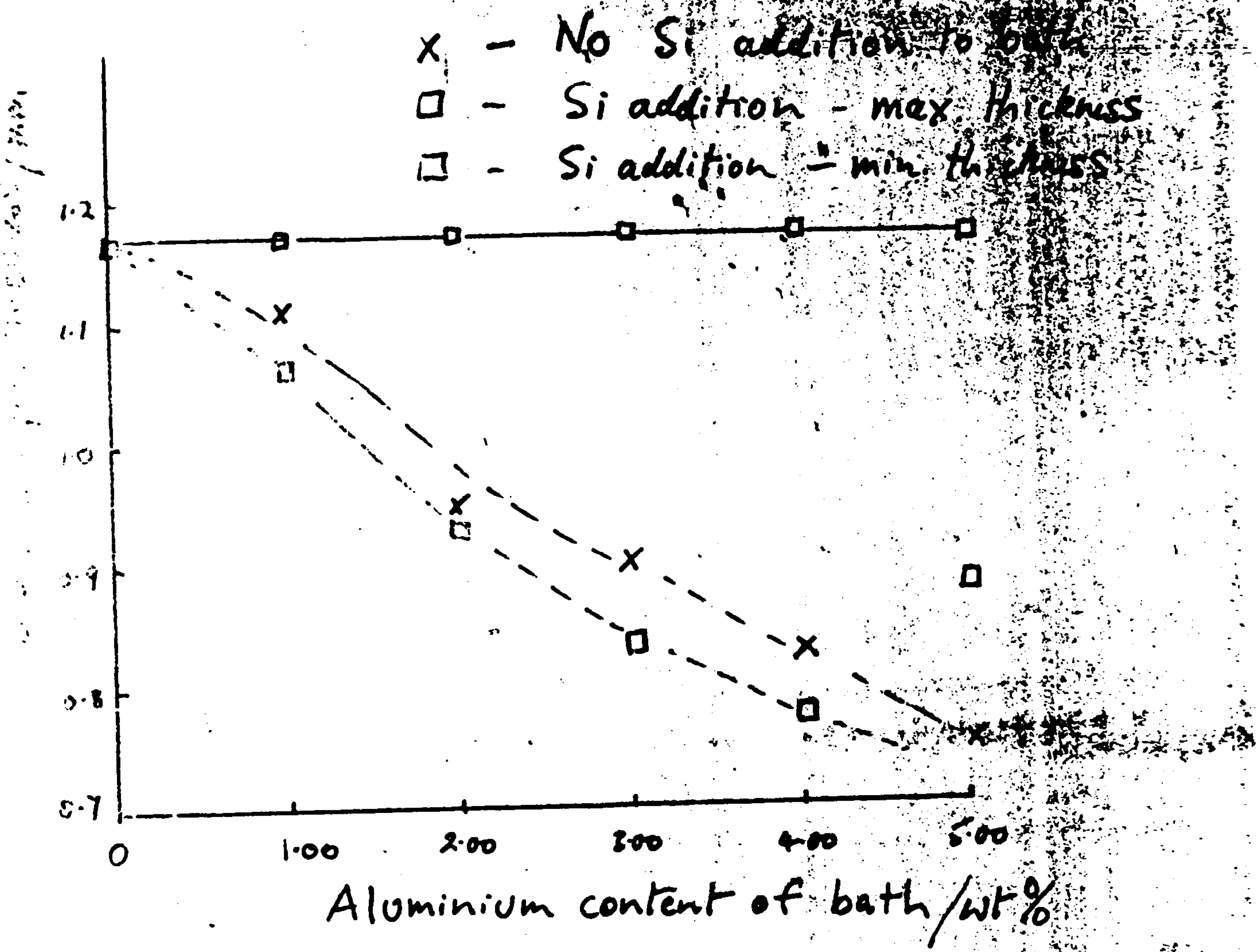
FIRST ESTABLISHED BY MANN AND HUNT (BNF ~1960)

EXAMINED IN MORE DETAIL BY NEEMUCHWALLA AND HERSHMAN (ALSO BNF) AND REPORTED IN 7TH INTERGALVA. THEY CLAIMED THAT SILICON ACTED AS A "GETTER" IN REMOVING IRON FROM SOLUTION IN THE GALVANIZING BATH. IRON-SATURATED BATHS (PROMOTED RAPID ALLOY LAYER GROWTH WHEREAS LOW-IRON BATHS PRODUCED THIN ALLOY LAYERS - POSSIBLY BECAUSE DISSOLUTION WAS FASTER.

WE HAVE FOUND EVIDENCE FOR A THIN (3 μm) INHIBITING LAYER RICH IN SILICON AND ALUMINIUM FORMING ON THE STEEL.

DON'T RUSH TO SATURATE YOUR BATHS WITH SILICON JUST YET — IT PROMOTES EMBRITTLEMENT IN ZINC - 12% ALUMINIUM CASTING ALLOYS

(THOMPSON AND NIESSEN, J. MAT SCI, 1986, 21, 2565)



INFLUENCE OF A SATURATION (0·035%?) SILICON ADDITION ON THE THICKNESS OF STEEL REMAINING AFTER 2 HOURS IMMERSION AT 470°C

FLUXING STUDIES

ORIGINALLY DEVELOPED 'UNIGALVA' PROCESS SO THAT STEEL COULD BE COATED WITH SCRAP ZINC (TYPICAL COMPOSITION

4.01% Al, 0.82% Cu, 0.46% Pb, 0.174% Mg)

WORKS WELL FOR THIS MATERIAL AND COATING HAS BETTER SALT SPRAY DURABILITY THAN CONVENTIONAL GALV. OF SAME THICKNESS.

USE OF LEAD SALT IN PRETREATMENT MAY PREVENT ITS USE FOR GALFAN ALTHOUGH Cu, Mg COMPONENTS IN SCRAP MUST HELP IN CONTROLLING ITS ADVERSE EFFECT.

UNIGALVA METHOD

CATHODICALLY ELECTROPICKLE THE STEEL SUBSTRATE IN A SOLUTION OF HYDROCHLORIC ACID CONTAINING LEAD IONS. *

ACTIVE CONSTITUENT IS LEAD CHLORIDE WHICH IS PRESENT IN THE DRIED DEPOSIT AS AN ARRAY OF ANGULAR CRYSTALS.

PROCESS WORKS FOR ZINC OR ZINC-ALUMINIUM ALLOYS ON BATCH BASIS (USING BARRELLING) OR CONTINUOUS BASIS (PILOT WIRE LINE HAS PRODUCED ZINC AND ZINC-ALUMINIUM COATED WIRE).

11th Galfan Meeting, Reims, January '88
Research Session
HOESCH STAHL investigations reported by W. Schwarz

Corrosionstests

In order to prove that GALFAN can be used with a lower coating mass than that of HDG to obtain the same corrosion protection, samples of both materials have been exposed at four German sites having rural, industrial, and severe marine atmospheres. The sites are at

Olpe
Kreuztal-Eichen
Dortmund
Baltrum (North Sea, 20 m from the shore).

Samples, both bare and coil coated with silicone polyester and PVDF, have been tested. The coating weights of the GALFAN samples are 95, 140, 185, and 255 g/m^2, resp.. The HDG samples have the same coating thickness.

Fig. 1 shows the weight loss after a 2 year exposure. After this short time GALFAN behaves already better than HDG. After finishing the tests (in 1 or 2 years time) we will contact the German authorities for the building industries (IfBt, Berlin) in order to get an approval.

Deformations behavior

The study of the deformation behavior of GALFAN compared with competitive products is very important, because there are advantages especially in this matter. The first tests with a so called hat profile (Fig. 2) had demonstrated the qualitative differences between GALFAN and HDG, but we could not yet get quantitative results. On the HDG coating single particles broke out whereas the GALFAN coating were rubbed of. These studies will be continued in a ring test of the German IDDRG section including additional laboratories and improved testing facilities. In these studies also other materials, e.g. cold rolled, electro-galvanized and galvannealed sheet are involved. The build-up of the coating at the tool as well as wear of the tool are tested.

Joining techniques

This year we will have a manual published on the joining practice of GALFAN with instructions for welding and other possible procedures.

In Fig. 3 joining methods for GALFAN are compared with those for HDG. Not mentioned in this list is clinching, which should be recommended for coated products of either kind when mechanical fastening seems favorable.

Annealing behavior

When annealing GALFAN, e.g. with intended over-aging treatments or hardening of the material, but also at higher temperatures during coil coating or in case of heavy sunshine on walls and roofs, structure changes of the metal coating can appear. This can result in change of the volume, which might be disadvantageous for the formability and the adhesion of the GALFAN coating.

Samples of zinc aluminium-alloys with 4.8, 3.5, and 1.1 % Al have been annealed in the Dilatometer at temperatures between 50 and 450 °C and over 10 min to 20 hr. Between 50 and 250 °C changes of the volume occured, which could be registrated by contraction and re-extension of the samples. The degree of contraction depends on the Al content. The highest contraction could be determined with an 4.8 % Al alloy near the eutectic composition. This may be because of the stabilisation of the Al-rich phase. The precipitations within the -phase occur later and result in the re-extension of the samples.

The same procedure could be found at the GALFAN coatings. The consequence for the industrial practice is the possibility of more or less fast transformations of structure and volume of GALFAN coatings depending on the temperature used. The formabilitity of GALFAN may be changed by these influences as a function of the time of manufacturing.

This investigation will soon be published.

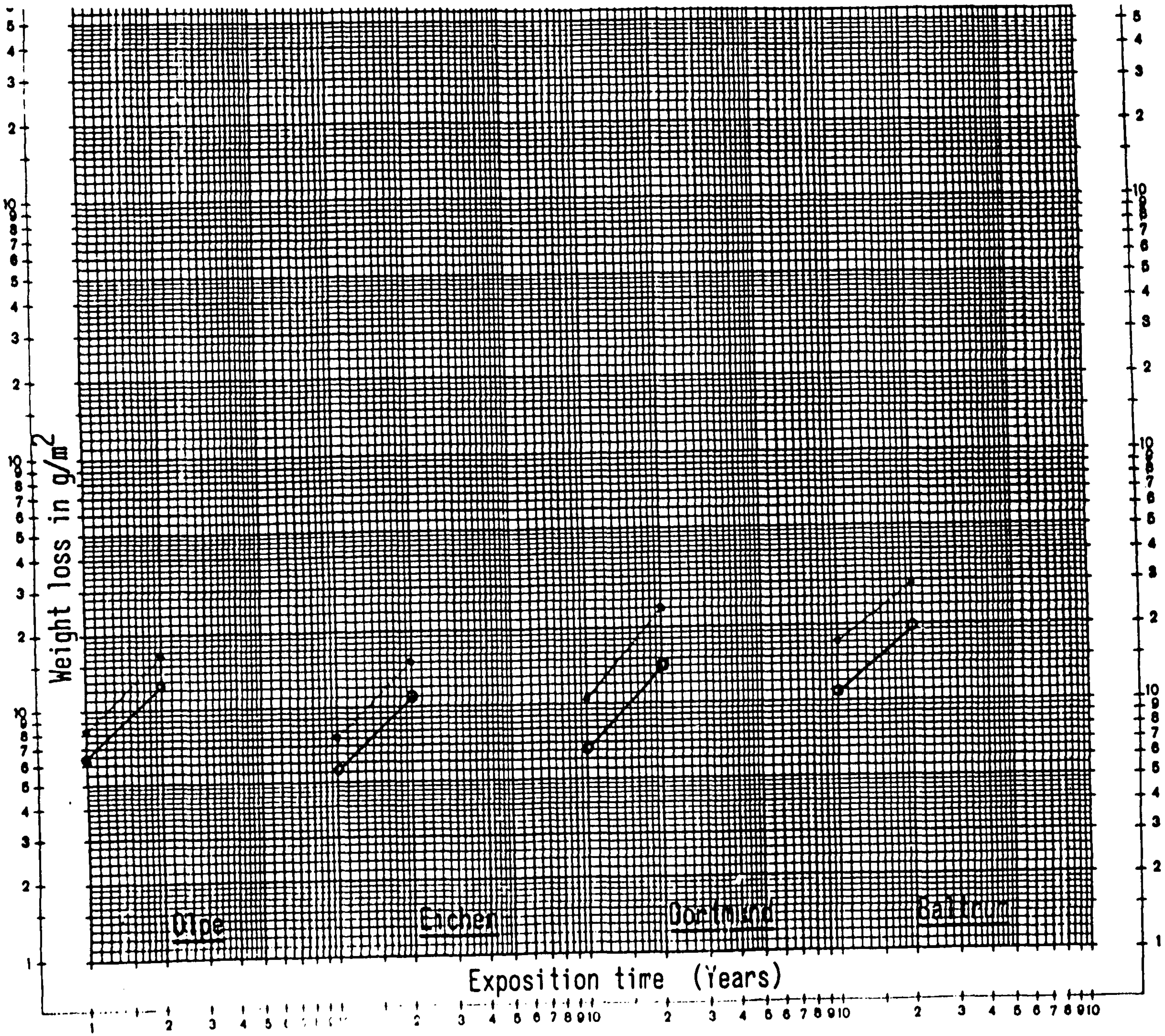
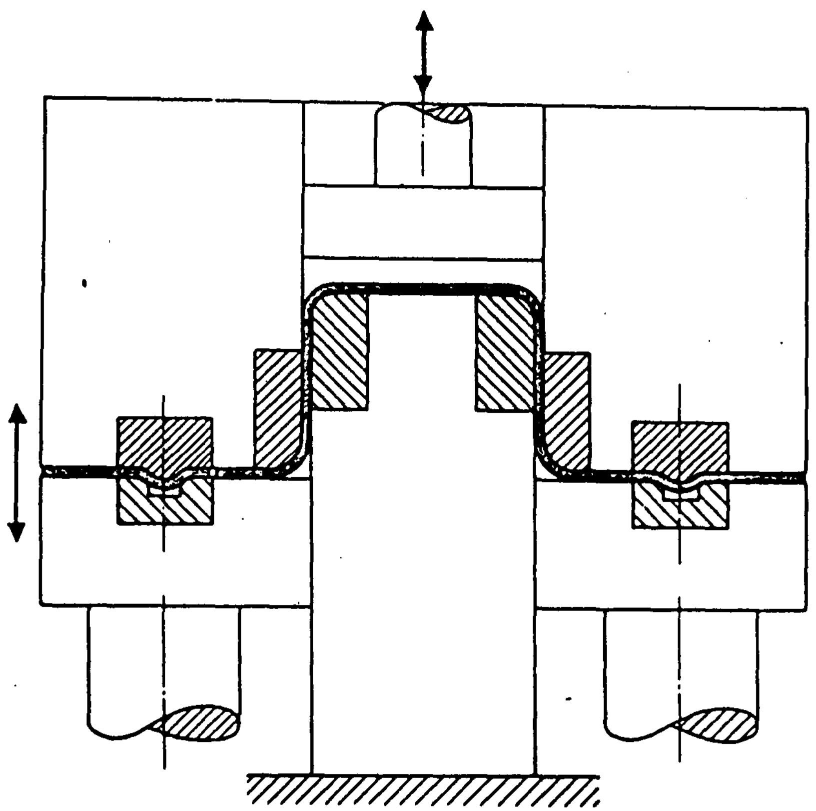
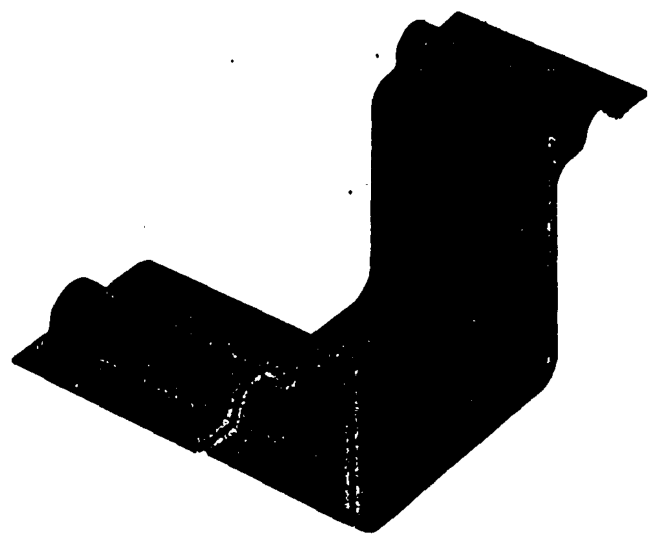

Weight loss in g/m2
Exposition time (Years)
Olpe
Eichen
Dortmund
Baltrum

Fig. 1



Werkzeug

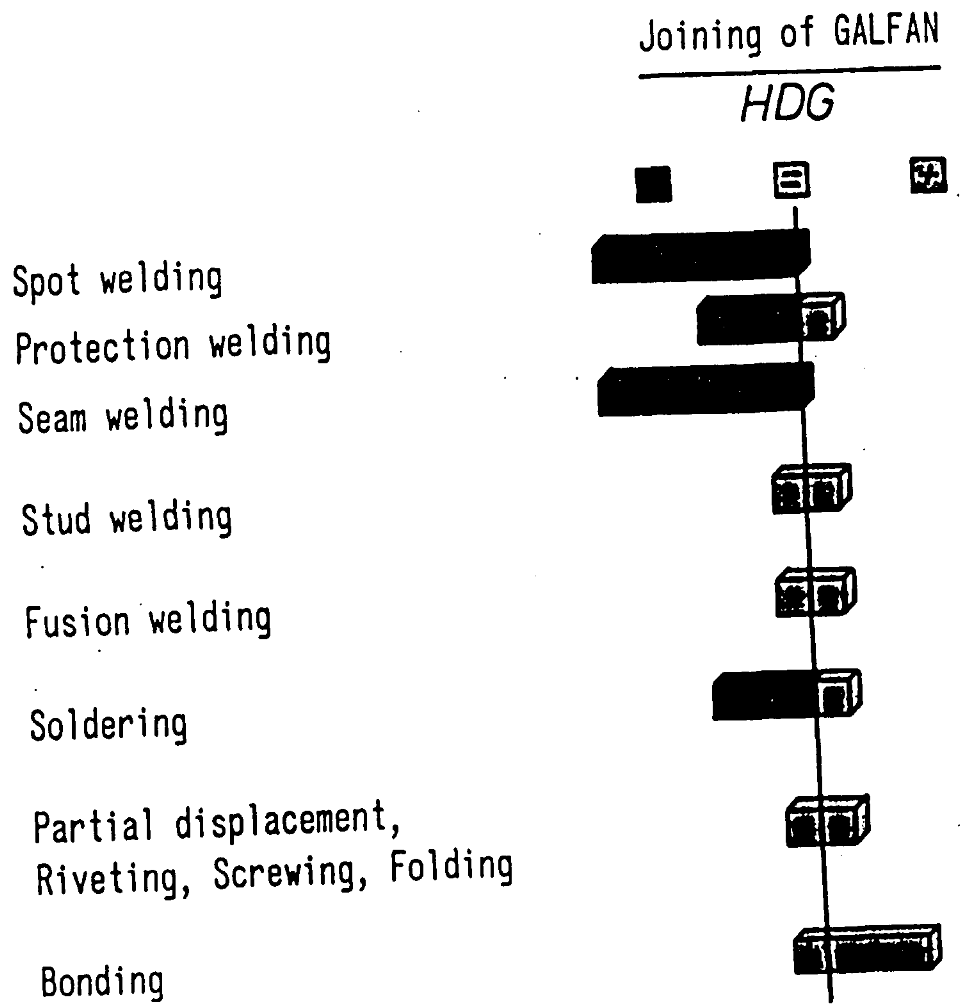
tool



Werkstück

work piece

Fig 2


Joining of GALFAN
HDG
Spot welding
Protection welding
Seam welding
Stud welding
Fusion welding
Soldering
Partial displacement,
Riveting, Screwing, Folding
Bonding

Influence of annealing on the structure of GALFAN

Temp. range	:	50 - 450 °C
Time range	:	10 min - 20 h
Al	:	4,8 - 3,5 - 1,1 Weight-%
Used methods	:	normal metallography SEM TEM EMPA DILATOMETER
Observed effects	:	contraction - re-extension precipitation in η-phase coarsening of structure

Investigation including explanation of the effects is not yet completed

MPK

iv

FORMATION OF INTERMETALLIC LAYER IN GALFAN COATING PROCESS

JAN. 1988

SUMITOMO METAL IND., LTD.

MATERIAL USED

· CHEMICAL COMPOSITION

C	Si	Mn	P	S	Sol.Al
0.06	0.01	0.23	0.020	0.014	0.025

· TEST PIECE SIZE

06×50×200 mm

CHEMICAL COMPOSITION OF BATH

Al	La	Ce	Fe	Pb	Zn
4.5	0.02	0.02	0.03	0.003	balanced

HOT-DIP COATING CONDIDIONS

ANNEALING CONDITION ------- 720°C×10sec

ANNEALING ATMOSPHERE ------ N_2+20%H_2

INLET TEMPERATURE --------- 480~580°C

BATH TEMPERATURE ---------- 460~500°C

IMMERSION TIME ----------- 4sec

COATING WEIGHT ----------- 250g/m^2

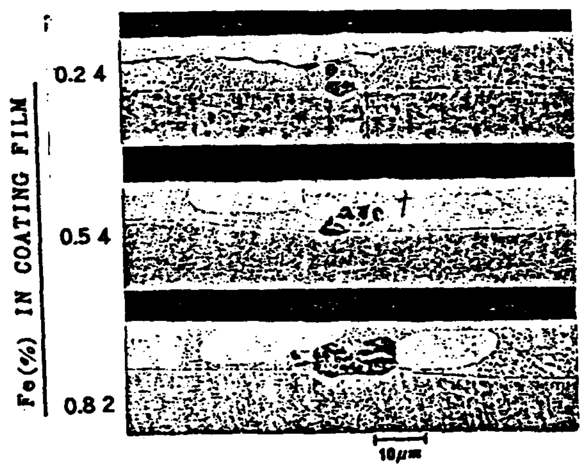


Fig 1-a EXAMPLES OF INTER METALLIC LAYER

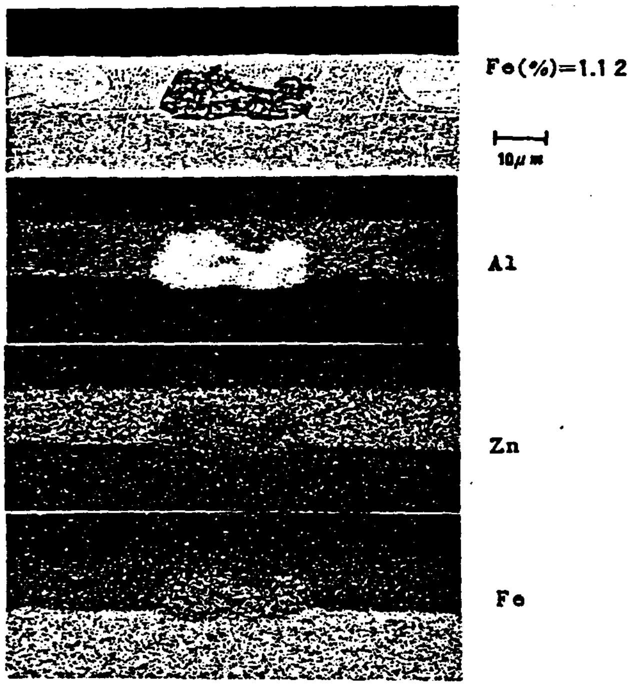


Fig1-b EPMA IMAGE OF Al,Zn AND Fe

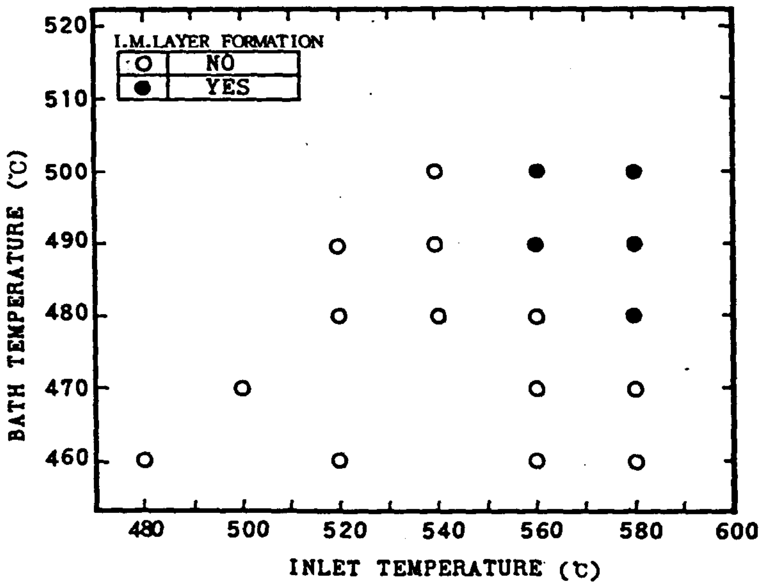


FIG.2 EFFECT OF HOT-DIP COATING CONDITIONS ON THE FORMATION OF INTERMETALLIC LAYER

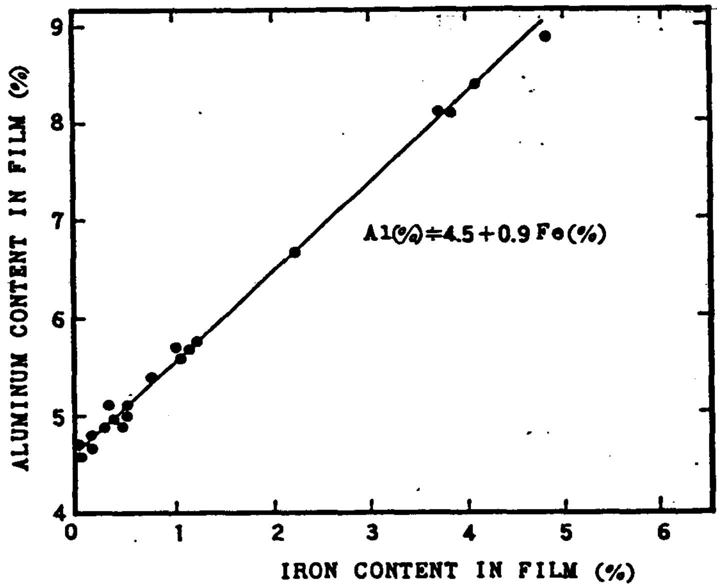


FIG. 3 CORRELATION BETWEEN IRON CONTENT AND ALUMINUM CONTENT IN FILM

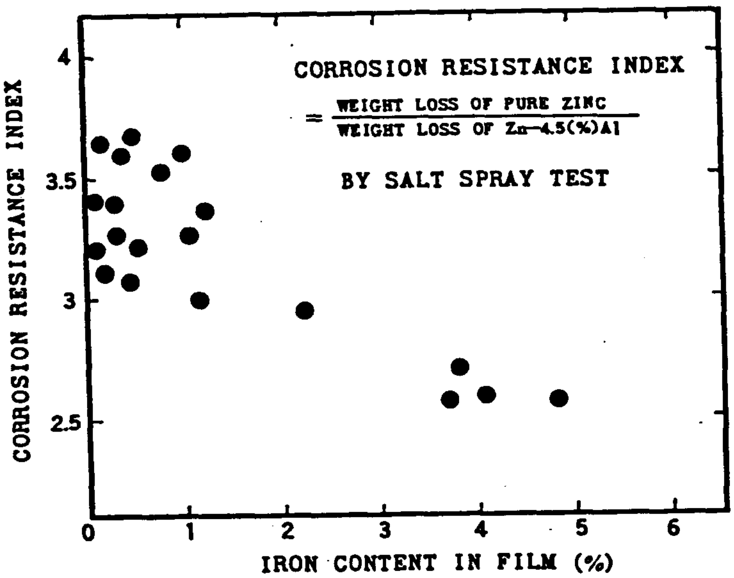


FIG. 4 EFFECT OF I. M. LAYER FORMATION ON CORROSION RESISTANCE

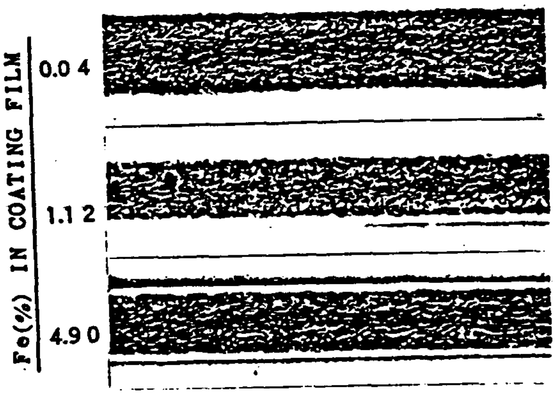


Fig.5 OUTLOOK AFTER OT BEND TEST

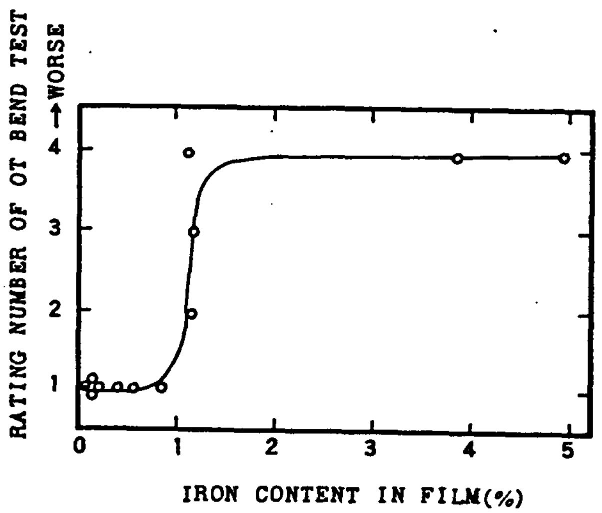


Fig.6 EFFECT OF I.M. LAYER FORMATION ON DUCTILITY

EFFECTS OF Mg-ADDITION ON THE PROPERTIES OF GALFAN COATINGS

by

Yusuke Hirose, Nisshin steel Co.,Ltd.

Study was made on the effects of Mg-addition to Galfan coatngs on their performance of Galfan coated steel sheets with and without organic paints.

Chemical compositions of coatings are shown in Table 1(plain Galfan) and Table 2(painted Galfan) respectively. Pre-treatment and painting conditions are shown in Fig.3.

Test results are summerized as follows;

1) Mg in Galfan alloy precipitates on Al-rich phase in Zn-Al eutectic structure (Photo.1). With increased Mg content, the Al-rich phase is coagulated and its shape becomes grobular, which leads to increase the volume of β-Zn phase in the coating structure (Photo.2, Fig.2). This means that the addition of Mg has an effect of shifting the eutectic point to higher Al content.

2) Mg-addition to Galfan coatings improves their corrosion resistance, and its effect is saturated at the Mg content of 0.1% (Fig.2, Photo.3). The optimum content of Mg is from 0.05 to 0.1%.

3) The addition of Mg reduces the ductility of coatings. Although Mg-containing Galfan coatings are finely cracked by severe bending, it is not harmful in practical use (Photo.4).

4) In cyclic corrosion test, Mg-containing Galfan coatings have better performance in the growth of blister on painted panels (Fig.4, Fig.5). Same effects of Mg-addition are also found in 3-year atmospheric exposure test (Fig.6, Photo.5).

5) At 2T-bended portion of painted Galfan panels, red-rusting is not observed after 3-year exposure (Photo.6).

Table 1 Specimen used for the investigation on the properties of plain GALFAN coated steel sheets

Specimen		Chemical composition of coating (wt.%)						Coating weight (g/m²)	
		Al	Mg	Fe	Pb	MM	Zn	light coating	heavy coating
1	Free-Mg	4.25	0.002	0.08 ~ 0.13	0.002 ~ 0.003	0.009 ~ 0.015	bal.	86	185
2	0.01%-Mg	4.28	0.009					91	193
3	0.03%-Mg	4.28	0.032					88	190
4	0.05%-Mg	4.23	0.051					93	186
5	0.1%-Mg	4.25	0.099					90	189
6	0.3%-Mg	4.29	0.305					87	192

Base steel: Al-killed (0.35 mmt) MM: mishmetal

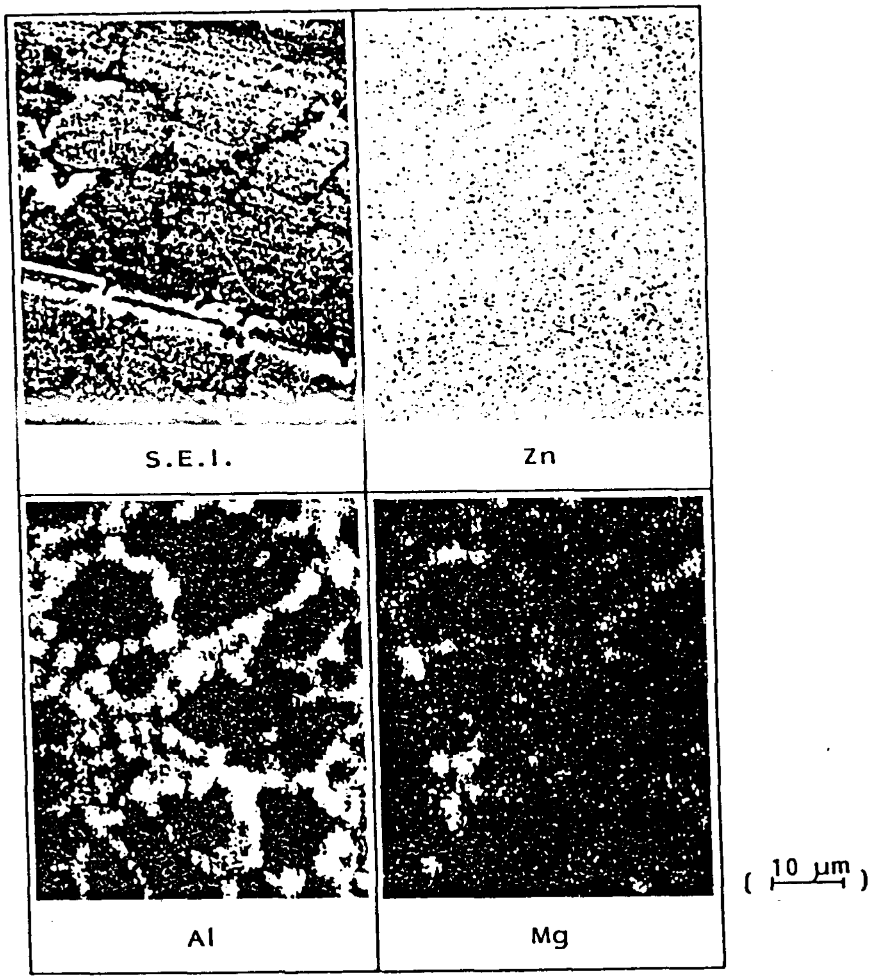
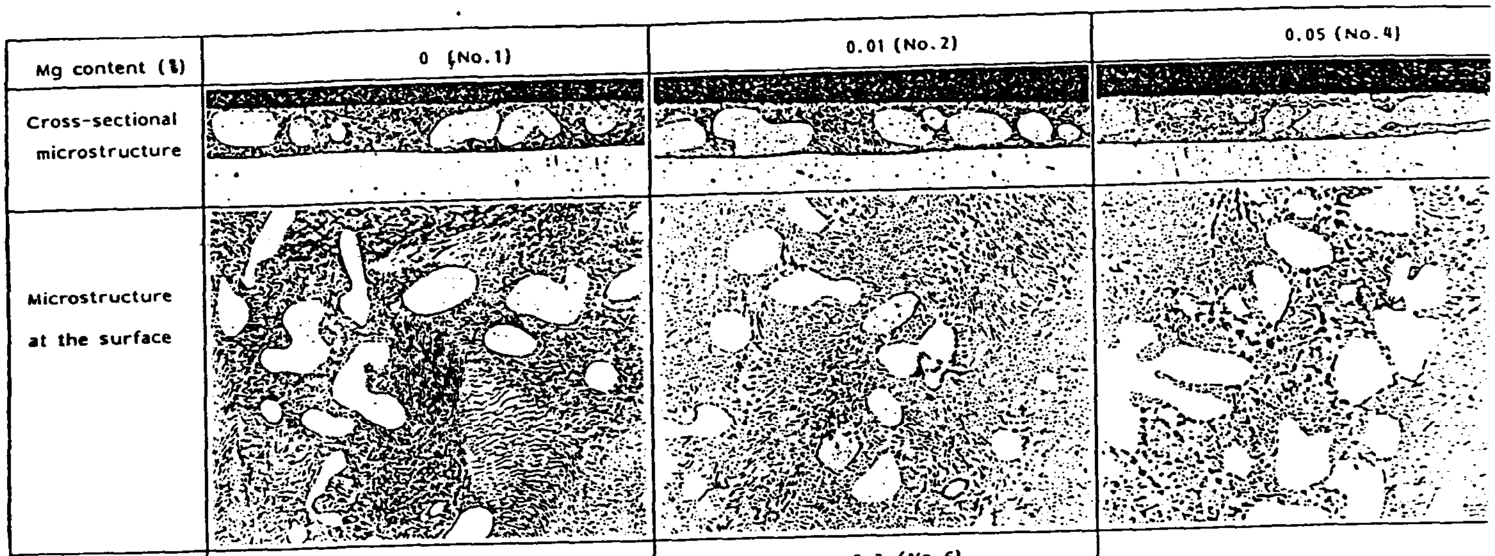


Photo.1 X-ray images of Al,Mg and Zn at the surface of Mg-added GALFAN coatings (by XMA)
Specimen: No.5 (0.1%-Mg)



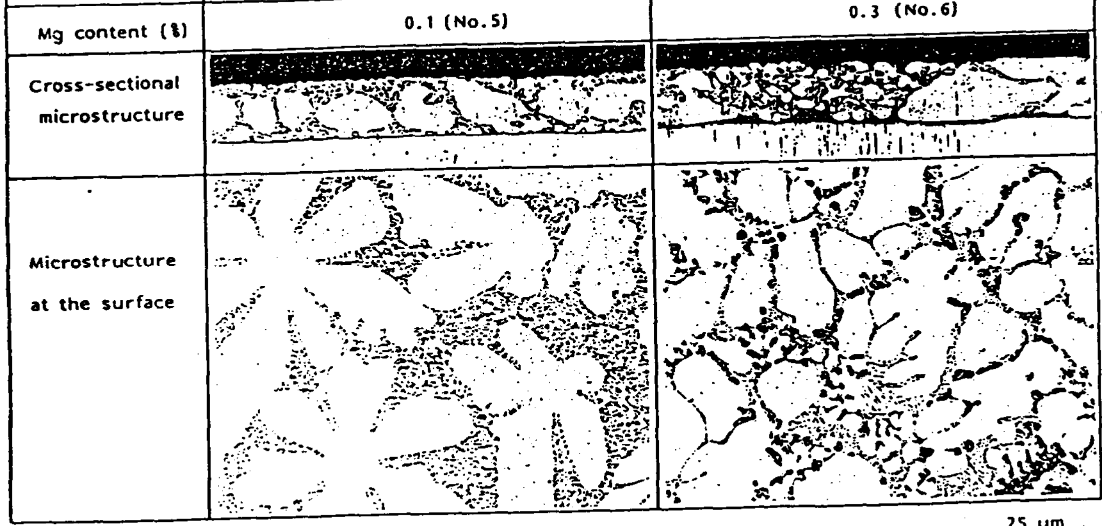


Photo.2 Effects of Mg-addition on the microstructure of GALFAN coatings
(coating weight: 185 ~ 193 g/m²)

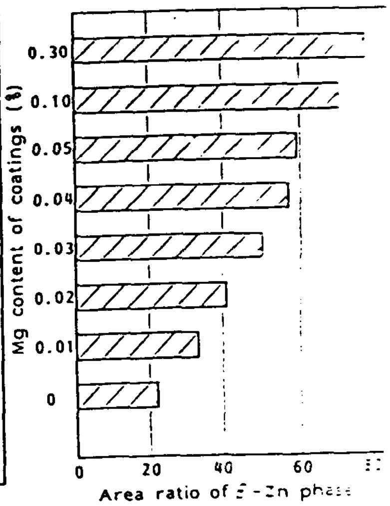


Fig.1 Change of area ratio of [illegible] phase by Mg-addition to [illegible] coatings

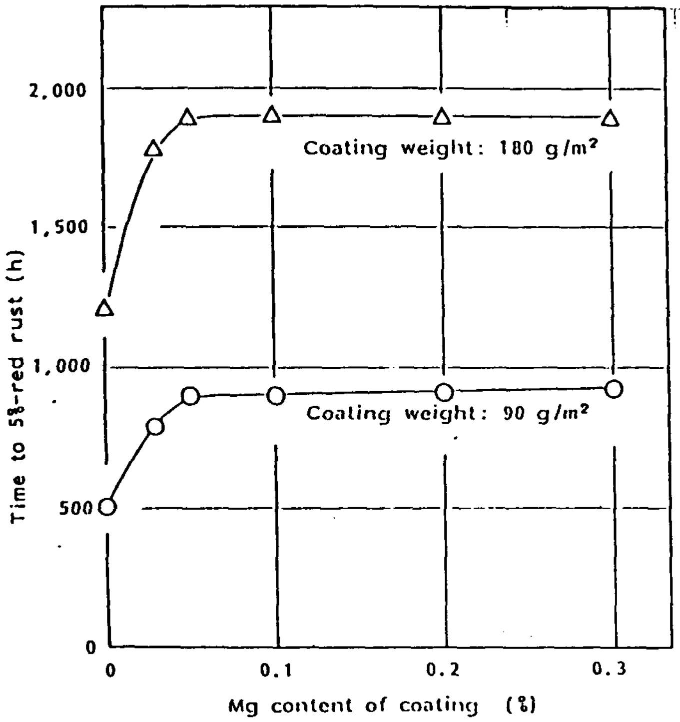


Fig.2 Effects of Mg-addition on corrosion resistance of GALFAN coatings (by salt spray test)

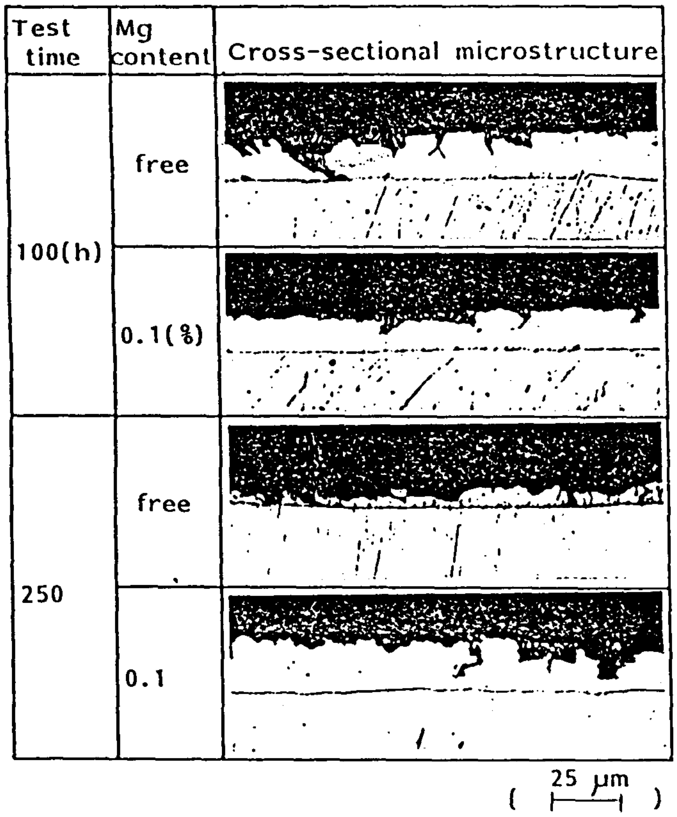


Photo.3 Cross-sectional microstructures of Mg-added GALFAN coatings at the test time of 100 and 250 hours (by salt spray test)

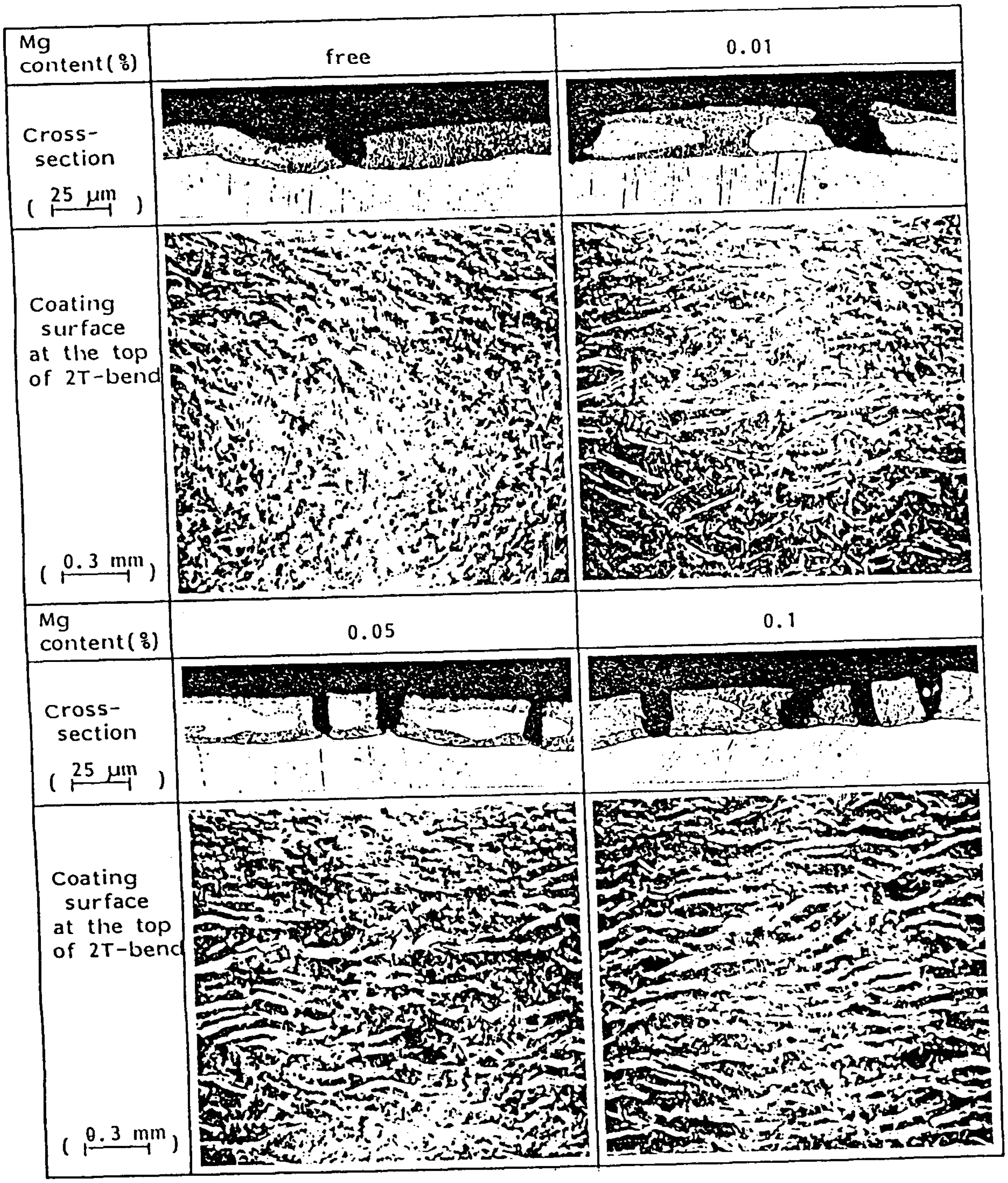


Photo.4 Effects of Mg-addition on ductility of GALFAN coatings (by 2T-bend)

Table 2 Specimen used for the investigation on corrosion resistance of painted GALFAN steel sheets

<table>
<tr><th colspan="2" rowspan="2">Specimen</th><th colspan="6">Chemical composition of coating (wt.%)</th><th rowspan="2">Coating weight (g/m^2)</th></tr>
<tr><th>Al</th><th>Mg</th><th>Fe</th><th>Si</th><th>Pb</th><th>MM</th></tr>
<tr><td>1</td><td>4%Al-MM</td><td>4.25</td><td>0.001</td><td rowspan="2">0.08 ~ 0.11</td><td>—</td><td rowspan="3">0.002 ~ 0.003</td><td rowspan="2">0.011 ~ 0.018</td><td>140</td></tr>
<tr><td>2</td><td>4%Al-0.1%Mg-MM</td><td>4.28</td><td>0.094</td><td>—</td><td>134</td></tr>
<tr><td>3</td><td>Zn(HDG)</td><td>0.41</td><td>—</td><td>0.06</td><td>—</td><td>—</td><td>141</td></tr>
<tr><td>4</td><td>55%Al-Zn(Galvalume)</td><td>54.1</td><td>0.007</td><td>0.89</td><td>2.7</td><td>0.002</td><td>—</td><td>82</td></tr>
</table>

Base steel: Al-killed (0.35 mmt) MM: mishmetal

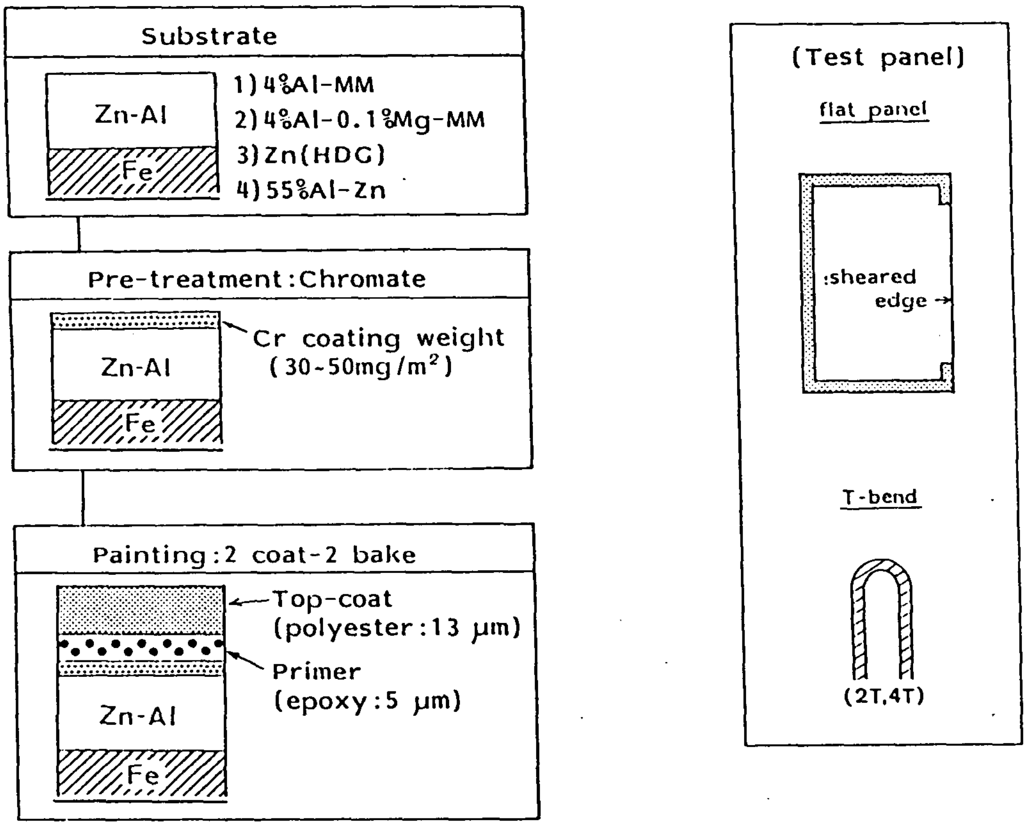


Fig. 3 Painting condition

Condition of cyclic corrosion test

Salt spray	Dry	Humidity	Dry
35°C x 4h 5%-NaCl	60°C x 2h	50°C x 16h 98%R.H.	60°C x 2h

(24 h/cycle)

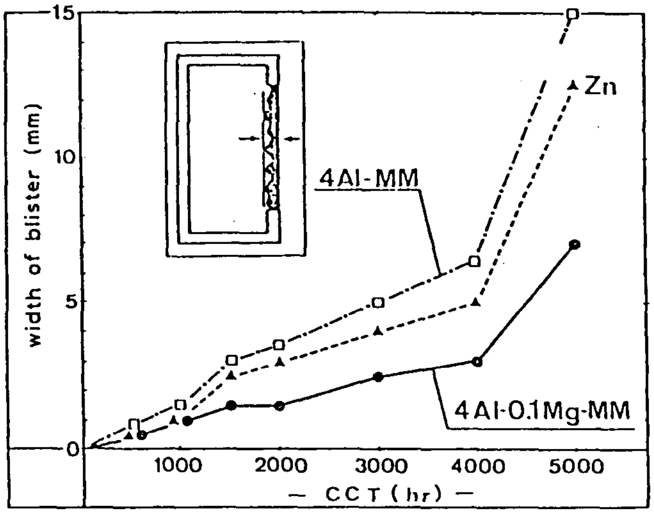


Fig.4 Blister formation at sheared edges of painted steel sheets in the cyclic corrosion test

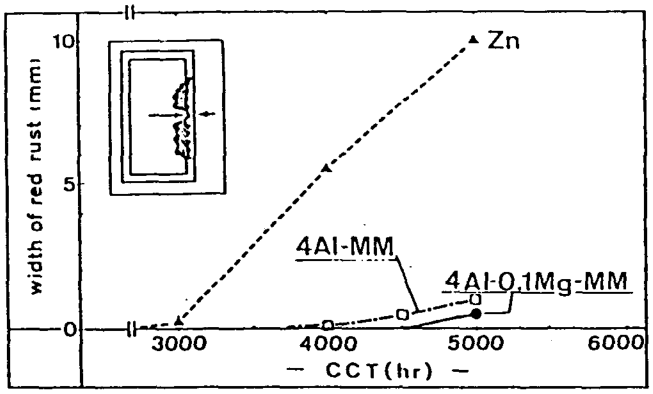


Fig.5 Growth of red-rust at sheared edges of painted steel sheets in the cyclic corrosion test

Table 3 Exposure sites and their environmental conditions

Exposure site		Location
Ichikawa-shi (Chiba-ken)	1	Industrial environment 5m from coastline of Tokyo Bay
	2	Industrial environment 800m from coastline of Tokyo Bay
Kiryu-shi (Gunma-ken)		rural area surrounded by the green field

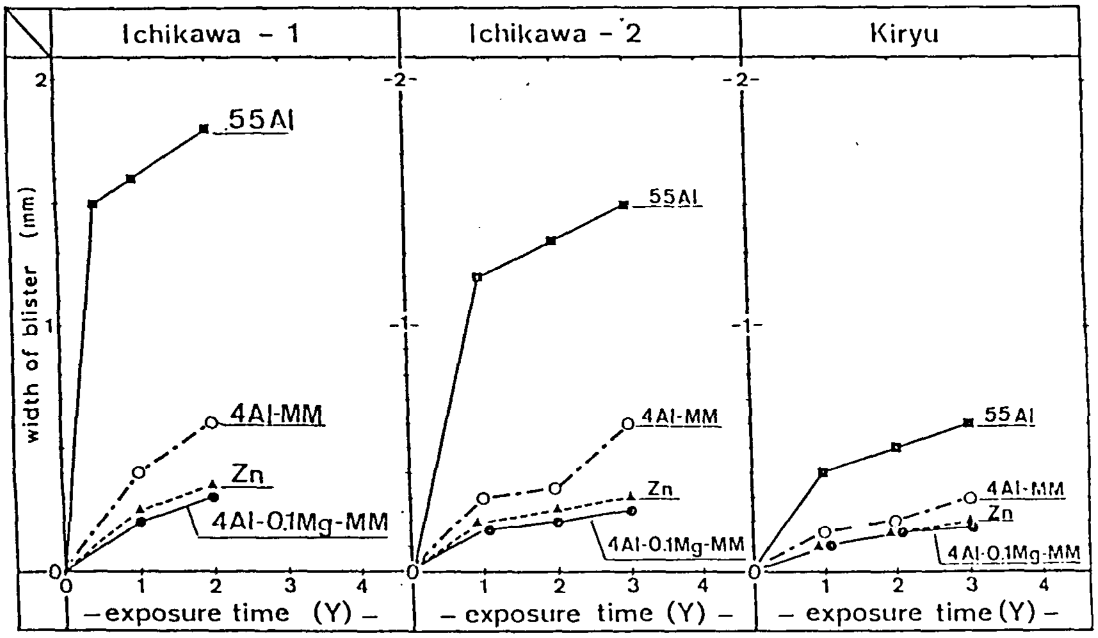


Fig.6 Blister formation at sheared edges of painted steel sheets in the atmospheric corrosion test

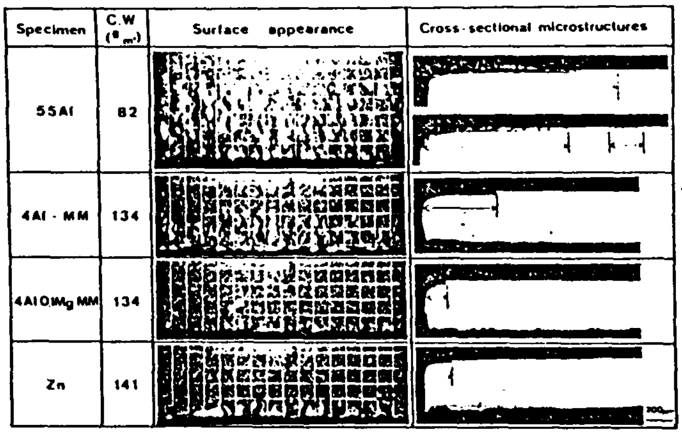


Photo.5 Blister formation at sheared edges of painted steel sheets at 3-year exposure in Ichikawa-2

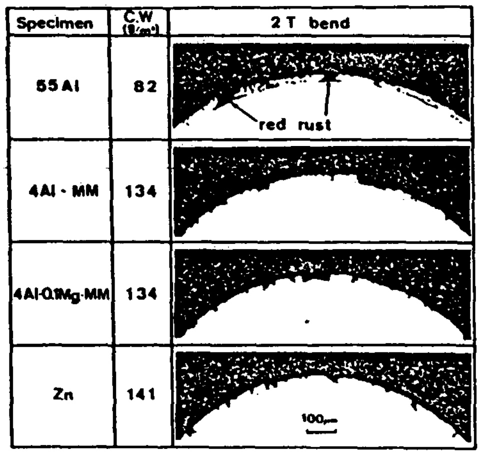
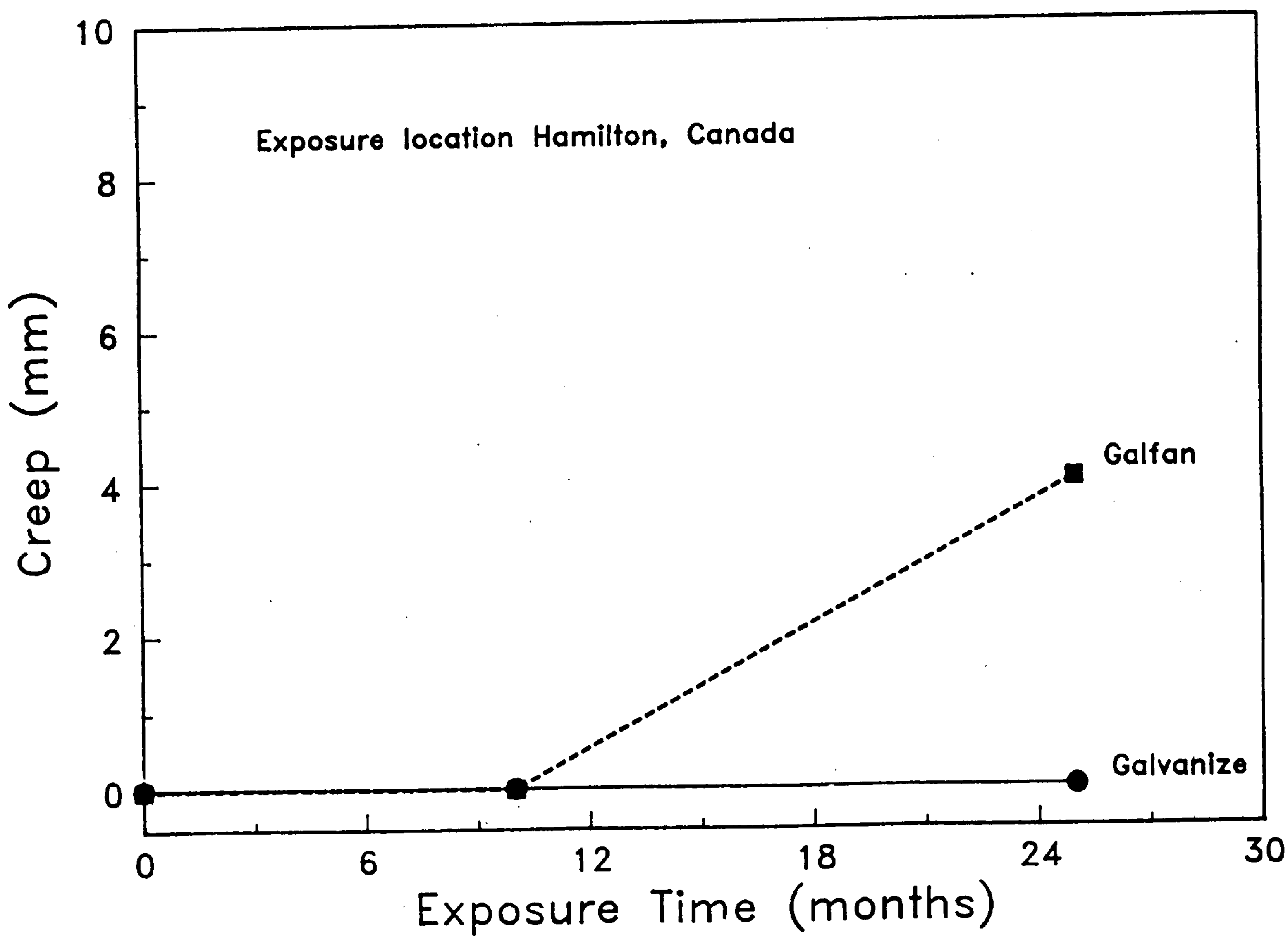


Photo.6 Cross-sectional microstructures at 2T-bended portion of painted steel sheets exposed for 2 years in Ichikawa-1

/fwh/galfan/ed_creep_5000.grf

Zinc Coating Edge Creep
Silicone-modified Polyester System



stelco

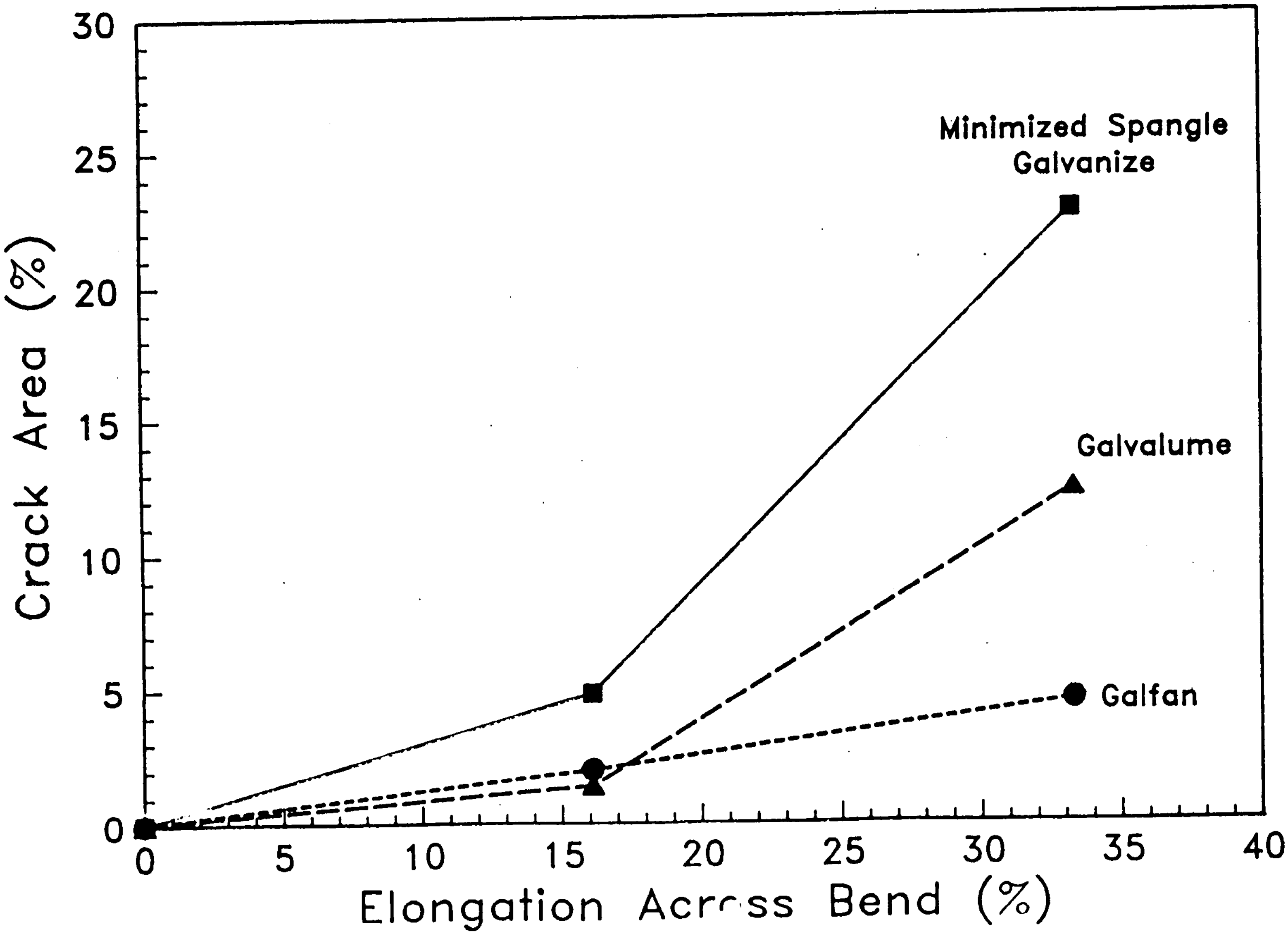
/fwh/galfan/crack_txt.grf

Stelco Procedure for Quantifying Tension Bend Cracking

Image analysis of high-contrast back-scattered electron micrograph on Hitachi S-570 SEM with Link Systems AN 10000 Digipad image analysis program

/fwh/galfan/ten_bend_crack.grf

Zinc Coating
Tension Bend Formability



stelco

11th Galfan Licencess Meeting, Reims, January '88
Marketing Session
HOESCH STAHL report by W. Schwarz

As we mentioned yesterday at the operation session, Galfan sheet production at HOESCH STAHL AG has developed continuously from 550 (metric) tons in 1983 to 15,580 tons last year. In January 1988 we have produced additional 5,920 tons and we expect a total of about 20,000 tons in 1988. This will be facilitated by the quick-change multipurpose equipment with two ceramic pots and by improved coating, wiping, and skin-passing techniques as Dr. Furken already explained yesterday.

Till fall '88 we will have at least two further campaigns. We look forward ro stimulating the market by additional domestic competition.

In order to make the product GALFAN known to a larger circle of customers we have made various deliveries of trial quantities to various European users.

We are awaiting a feed-back within short.

The German Galvanizers Association (DVV), Düsseldorf, representing the German captive sheet galvanizers and steel coil coaters, runs technical and market promotion committees. A detailed brochure on "Characteristic features of Galfan hot-dip coated sheet steel" was first published in 1987. This user's manual provides information on availability, forming grades, coating weights, surface conditions, tolerances, testing, handling and fabrication guidelines, etc.. Standardized coating masses are lower by about 6 percent compared with zinc-coating of the same thickness.

A second, revised edition of this brochure is in preparation and will be soon available, because the first editions has almost been sold out on account of the heavy demand. In the new edition steel grades and coating weights are to be in full accordance with the recent proposals of the new Euronorm EN 10 142 for HDG.

For both materials we now have the 06 grade (extra deep-drawing quality). The term S for skinpassed has been cancelled.

Galfan is generally considered to have distinct advantages over galvanized sheet in case of increased product performance, e.g., improved corrosion resistance combined with superior formability. Typical applications include deep-drawn automotive "underhood" parts. The major acceptance of Galfan in prepainted form (more than 75 % of the total production) can be explained by its enhanced suitability for coil coating, facilitated by the choice of conventional pretreatment and primer systems. This material has been successfully adopted for pre-engineered building components (roofing, walling, sandwich panels) including officially approved structural thin-walled panels.

In the domestic appliances market we aspect a breakthrough of prepainted GALFAN, especially as a replacement of porcelain-coated sheet in case of dishwasher wrappings. The major advantage over HDG is the improved detergent resistance.

Other case histories are available for window-frames section and waste-can lids.

The prospects look promising. Galfan offers both traditional and new customers the technical and economic advantages of the precoated sheet concept resulting in even wieder use of zinc coating.

encls. Galfan sheet production
Prepainted Galfan sheet

Galfan sheet production at Hoesch Stahl, F.R.G.

Year	No. of campaigns	Total production, metric tons
1983	2 (trials)	550
1984	2	4,060
1985	3	8,120
1986	4	14,170
1987	4	15,580
1988	(first)	5,920

Cumulative output, 48,400 tons

Prepainted GALFAN hot-dip coated sheet steel

3 Coil coating lines at Hoesch Stahl

width, 73 in. (1,850 mm) max.

speed, 440 fpm (135 m/min) max.

Pretreatment and primer/top coat systems,

same as with HDG (advantage)

Prepainted GALFAN has been replacing

prepainted HDG in certain cases

(corrosion resistance after severe forming)

Prepainted GALFAN

for captive building products,

but mainly supplied to fabricators of

- window frame sections
- dishwasher wrappings
- cold storage
- waste-can lids

using two-coat high or medium-gloss polyester

and polyurethane coatings, also textured

V. LIST OF PATENTS, TRADEMARKS, AND APPLICATIONS FOR PATENTS AND TRADEMARKS

A. GALFAN Patents Granted

Country	Patent Number	Issue Date
Argentina	227,220	September 30, 1982
Australia	544,400	October 21, 1985
Belgium	882,431	March 25, 1980
Belgium	887,121	January 6, 1981
Canada	1,175,686	October 9, 1984
East Germany	220,342	March 27, 1985
European (EPC)*	0048270	August 14, 1985
Finland	70254	September 15, 1986
New Zealand	199,491	April 9, 1986
Poland	136,815	November 18, 1987
Russia	1,301,320	March 30, 1987
Spain	508,771	May 3, 1983
South Africa	82/0091	November 24, 1982
Taiwan	17,916	November 1, 1982
U.S.A.	4,448,748	May 15, 1984

*France, West Germany, Luxembourg, Sweden, Switzerland, Liechtenstein, United Kingdom, Austria, and The Netherlands.

B. GALFAN Patents Applied For

Country	Serial Number	Filling Date
Brazil	PI 81 07944	November 24, 1981
Czechoslovakia	PV.323-82	January 15, 1982
India	1437/Cal/81	December 21, 1981
Italy	68730-A/81	December 30, 1981
Japan	501400/1981	March 18, 1981
Korea	5,198/1981	December 29, 1981
Mexico	9872	January 15, 1982
Yugoslavia	P-57/82	January 12, 1982
Patent Cooperation Treaty	PCT/US 81/00347	March 18, 1981

C. GALFAN Trademarks Granted

Country	Registration Number	Date
Benelux	375,388	August 4, 1981
Bophuthatswana	84/0177	March 19, 1984
Canada	313,867	April 3, 1987
Finland	92,853	June 5, 1985
France	1,184,193	October 2, 1981
New Zealand	150,709	October 8, 1986
Norway	119,540	March 20, 1985
South Africa	84/0191	May 29, 1985
South West Africa	84/0168 (SWA)	March 14, 1984
Sweden	181,144	April 23, 1982
Transkei	84/0183	May 29, 1985
West Germany	1,049,001	May 30, 1983
U.S.A.	1,414,721	October 28, 1986

D. GALFAN Trademarks Applied For

Country	Serial Number	Filing Date
Austria	4175/86	December 22, 1986
Australia	402,160	July 29, 1982
Brazil	813,489,423	May 26, 1987
Great Britain	1,158,613	July 31, 1981
Italy	22.133 C/81	October 27, 1981
Japan	84488/1981	October 6, 1981
Taiwan	(75) 62,661	December 20, 1986
Venda	84/0173	March 19, 1984
Yugoslavia	Z-66/84	February 17, 1984

ITEM 1 1

August 10, 1987

Explanation

Revision to B750-85, Zinc-5% Aluminum - Mischmetal Alloy (UNS Z38510) in Ingot Form for Hot-Dip Coatings

Further developments in coating technology with the zinc-5% aluminum-mischmetal alloy since original development of this specification have established that the aluminum composition should be broadened to a range of 4.2-6.2% from the prior 4.7-6.2% range. Commercial use has shown that a lower aluminum level can facilitate production of a product with desired characteristics while laboratory investigations has found no reduction in properties, per the attached letter from Dr. F. Goodwin. In fact, four companies are now producing commercial product with an aluminum level below that given in B750-85. Accordingly, a reduction in the minimum aluminum content to 4.2% is warranted.

Proposed Revision to B750-85, Standard Specification for Zinc-5% Aluminum-Mischmetal Alloy (UNS Z38510) in Ingot Form for Hot-Dip Coatings

Section	Change
Table 1	Aluminum Composition Range to 4.2-6.2% (from 4.7-6.2%)

INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION, IN

2525 MERIDIAN PARKWAY
POST OFFICE BOX 12036
RESEARCH TRIANGLE PARK, N.C.
TELEPHONE
TELEX
FACSIMILE

August 7, 1987

Dr. Richard F. Lynch
Zinc Institute, Inc.
292 Madison Avenue
New York, NY 10017

RE: ZM-285 GALFAN - ASTM Specifications

Dear Rich:

Based on further developments in GALFAN coating technology since the groundwork for the first ASTM GALFAN specifications was laid, producers have extended the range of aluminum content below its presently specified minimum of 4.7%. Four producers are now selling commercial product with levels down to 4.2%. Experimentation on this material and user experience to date show no reduction in properties, as shown in Exhibits 1-9. I believe that this provides technical and commercial justification for lowering the minimum specified aluminum limit in B750 to 4.2%, and ask you and your subcommittee to kindly revise the specification accordingly. Please advise me if clarifying information is needed.

Yours sincerely,

Frank E. Goodwin, Sc.D.
Vice President, Materials Sciences

cc: Y. Hirose, Nisshin Steel Corp.

Schedule of Exhibits:

1. Effect of aluminum content on corrosion properties per ASTM B117 salt spray test (Source: Sumitomo Metal Industries report to GALFAN licensees, December 1986).

2. Effects of aluminum content on corrosion properties per ASTM B117 salt spray test (Source: Nisshin Steel Corp. report to GALFAN licensees December 1985).

3. Effect of aluminum content on T-bend cracking of coating (Source: Exhibit 2, op.cit).

4. Effect of aluminum content on coating grain boundary indentation depths (Source: Exhibit 2, op.cit).

Richard F. Lynch
August 7, 1987

Schedule of Exhibits (contd.)

5. Effect of aluminum content on GALFAN coating surface roughness (Source: Report to GALFAN licensees, Centre de Recherches Metallurgiques, May 1987).

6. Effect of aluminum content on coating darkening (Source: Nisshin Steel Corp. report to GALFAN licensees, June 1985).

7. Effect of aluminum content on chromated coating darkening (Source: Exhibit 6, op.cit).

8. Effect of aluminum content on paint edge creepage (Source: Kawasaki Steel Corp., report to GALFAN licensees, November 1984).

9. Photograph of samples used to construct graph in Exhibit 8, showing deterioration of painting properties below 4% aluminum (Source: Exhibit 8, op.cit).

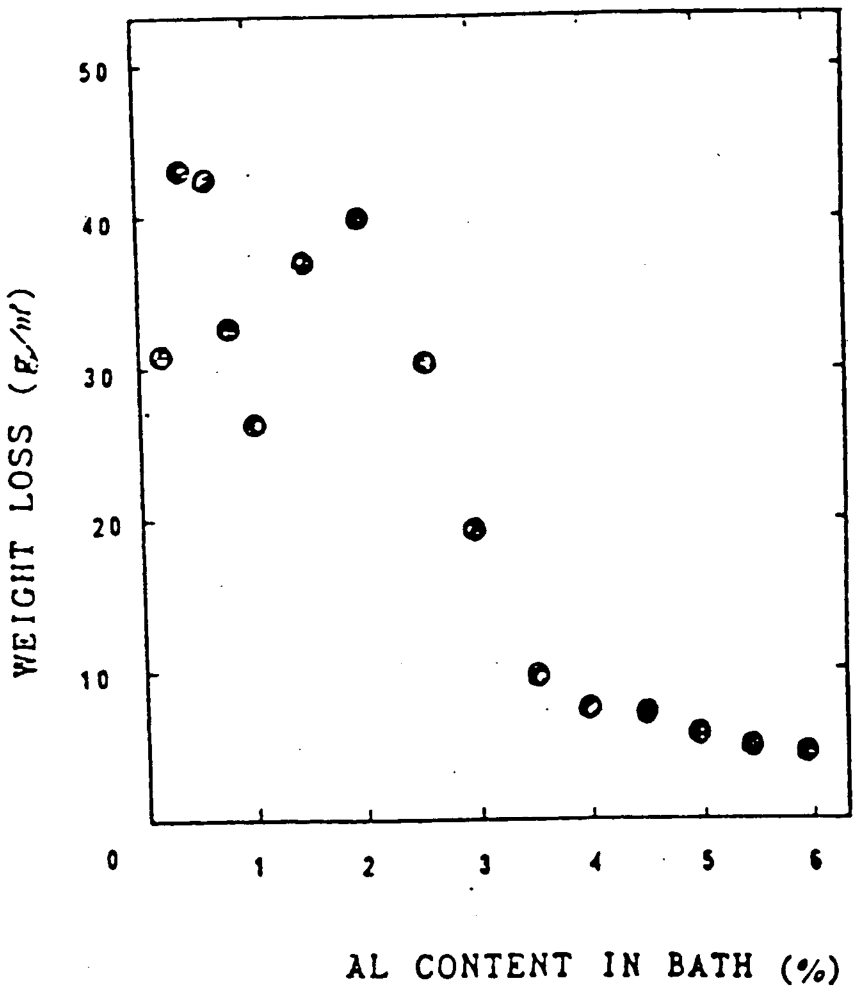


FIG. 2.44 - EFFECT OF AL CONTENTS ON CORROSION RATE OF ZN-AL COATING.
WEIGHT LOSS AFTER 96 HOUR EXPOSURE TO SALT SPRAY.

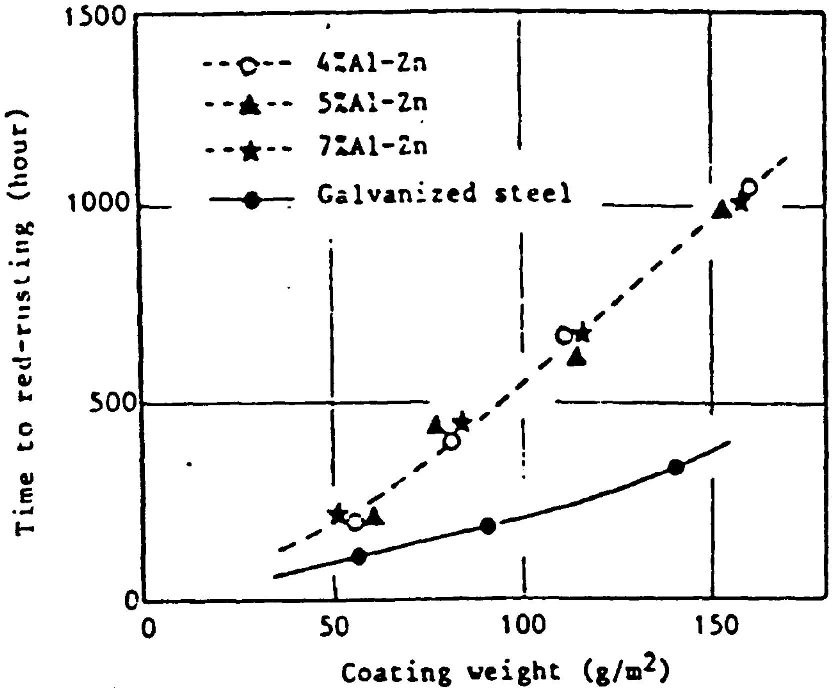
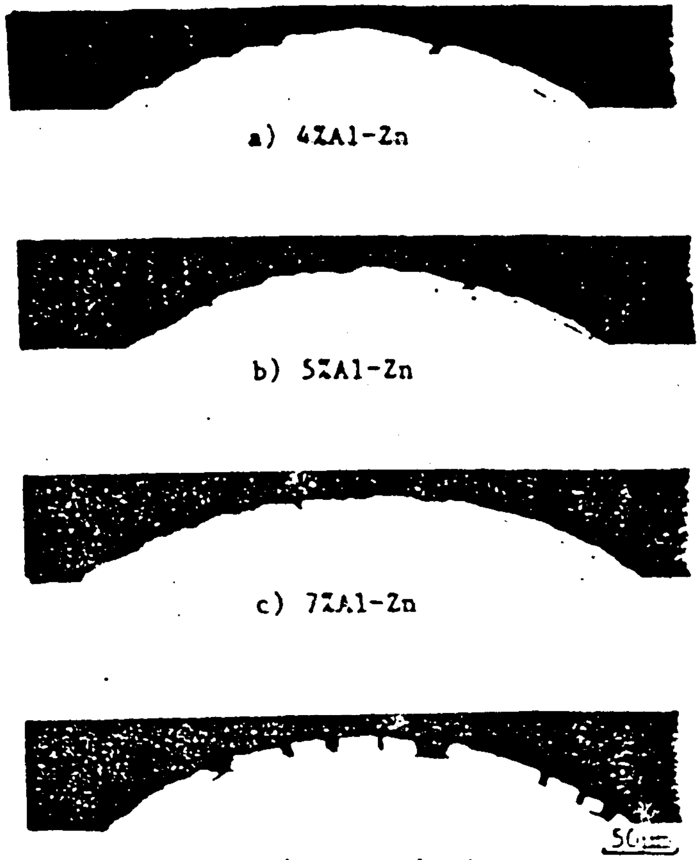


Figure 6 Time to red-rusting in salt spray test

"EXHIBIT 3"



a) 4%Al-Zn

b) 5%Al-Zn

c) 7%Al-Zn

d) Galvanized

Figure 10 Cross-sectional structure of 2T-bended specimens

"EXHIBIT 4"

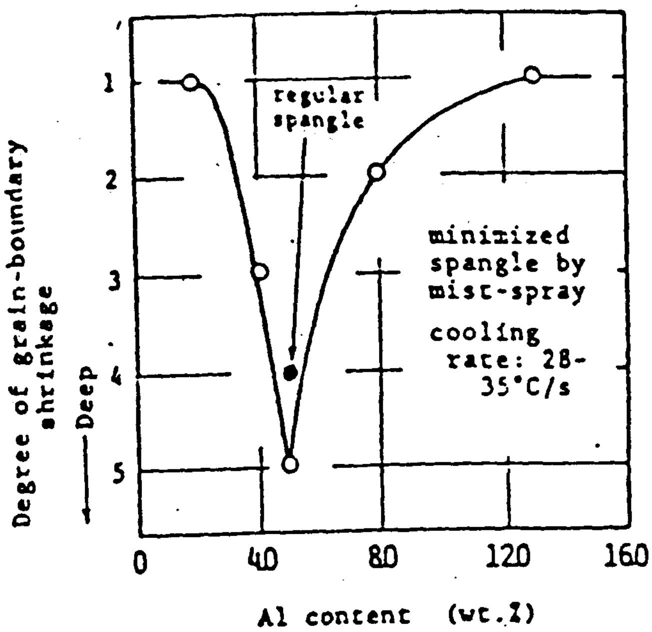


Figure 4 Relation between aluminum contents in the coating and the depth of grain boundary dent

T 23 - GRAIN BOUNDARY DEFECTS

INFLUENCE OF PROCESS PARAMETERS

1. THE ALUMINUM CONTENT OF THE GALFAN BATH.

2. THE COOLING RATE

PRELIMINARY ~~RUGOSITY~~ ROUGHNESS MEASUREMENTS

AL IN THE BATH (%)	4.4 AND 4.8
COOLING RATE (°C/SEC)	2.5 AND 20-30

<u>RESULTS</u> : THE ~~RUGOSITY~~ ROUGHNESS IS HIGHER AT :
(REFER TO T24 AND T25)

- HIGHER AL CONTENTS (4.8%)
- HIGHER COOLING RATES (20-30°C/SEC)

THE PEAKS (THUS THE BOUNDARIES) ARE LARGER AT LOW COOLING RATES.

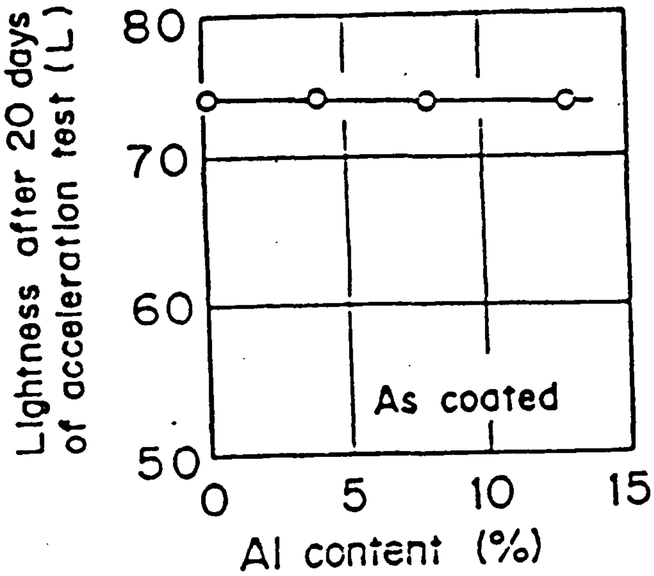


Fig.2 Effects of Al content in coatings on black patina formation

 "EXHIBIT 7"

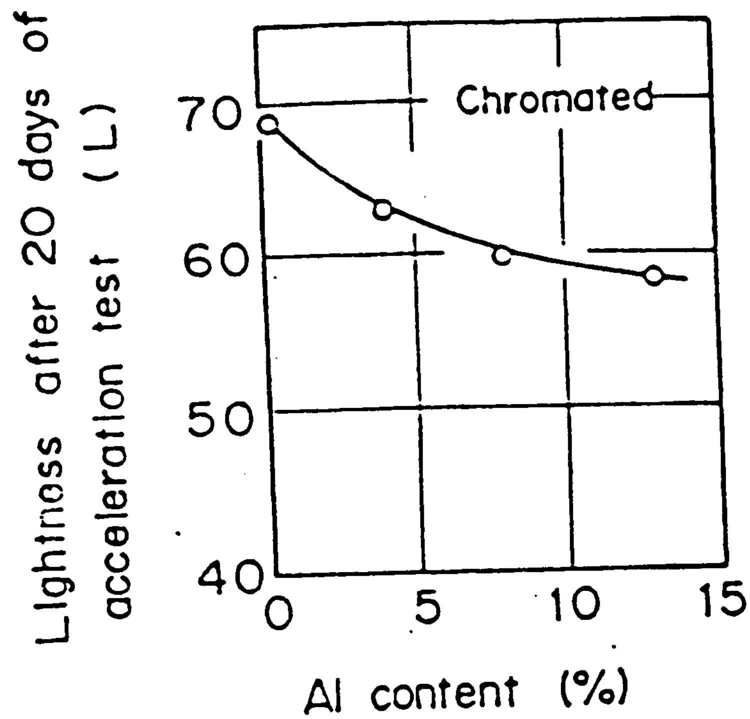


Fig. 3 Effect of Al content in coatings and chromating on black patina formation

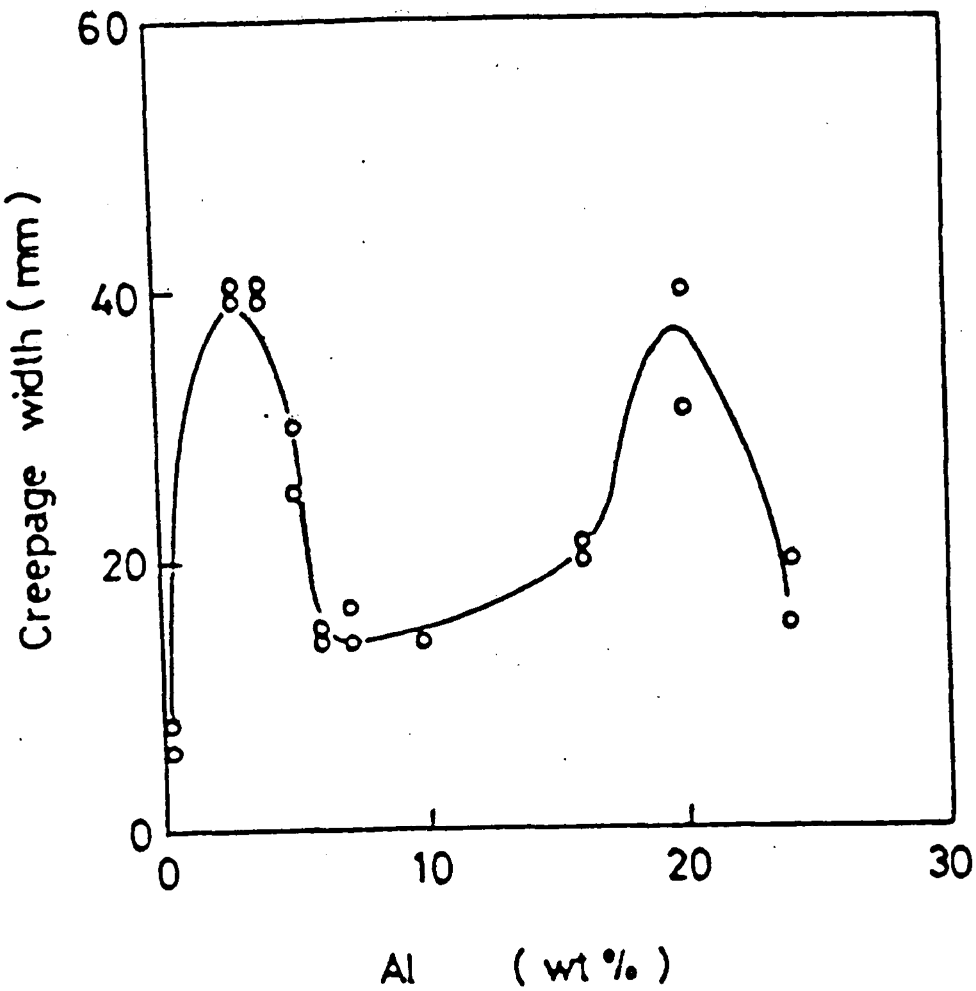


Fig.3 Influence of Al content in molten Zn bath on creepage of painted materials

 "EXHIBIT 9"

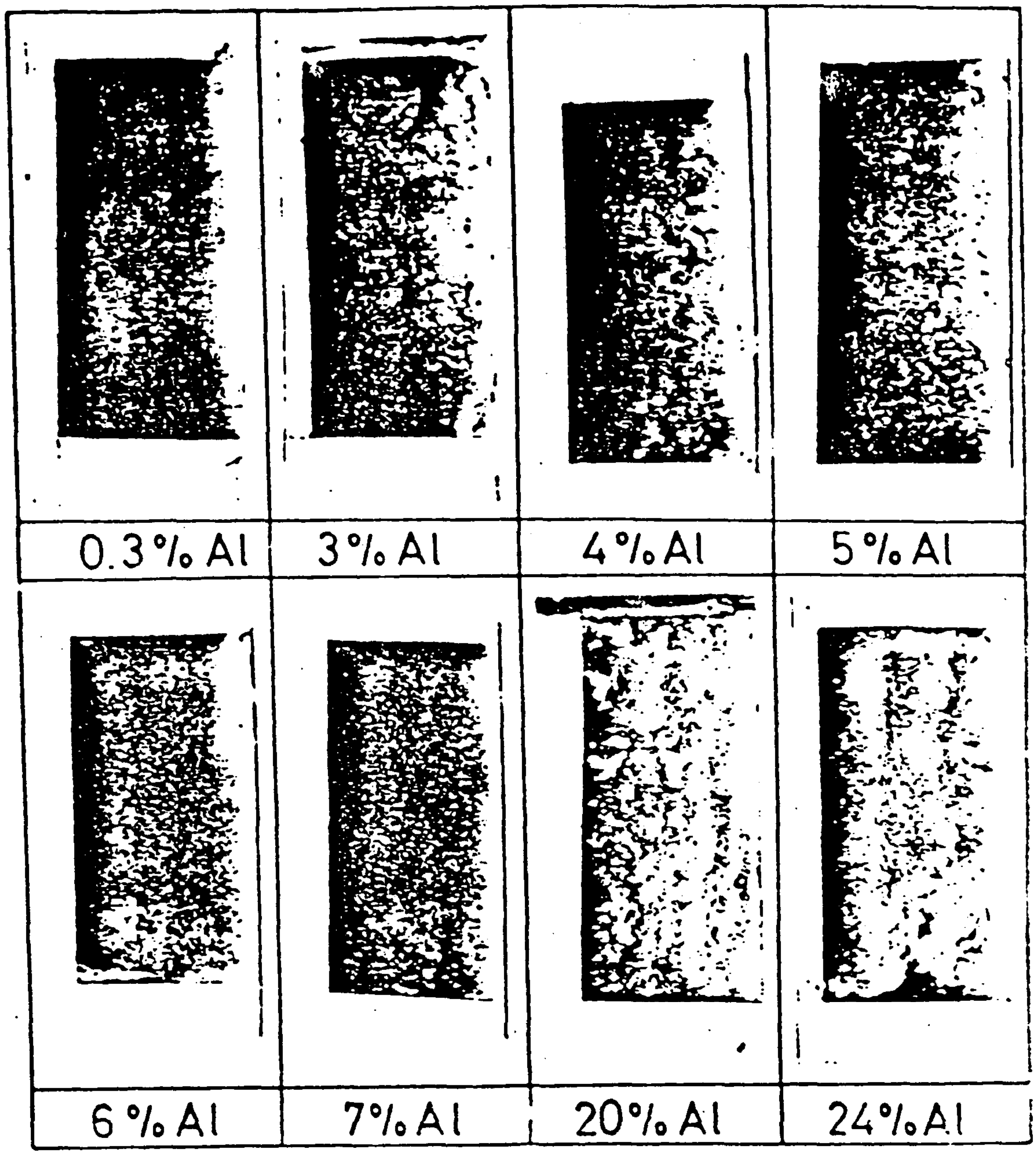


Photo 3 Creepage of painted sheet after salt spraying for 10C