Crystallographic relations in the Fe-Zn system

Citation for published version (APA):

DOI:
10.1002/crat.19790140412

Document status and date:
Published: 01/01/1979

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 15. Aug. 2019
Crystallographic Relations in the Fe–Zn System

The crystallographic relations between the various Fe–Zn compounds have been investigated by means of single-crystal X-ray diffraction techniques. These techniques were applied to primary single crystals of each compound upon which after cooling a single crystalline layer of the neighbouring compound richer in zinc was grown. In this way it has been possible to determine relationships in the sequence $\alpha - \Gamma' - \Gamma_1' - \delta$:

$[110]_\alpha || [110]_\Gamma' || [110]_\Gamma || [100]_\delta$ ;

$[111]_\alpha || [111]_\Gamma || [111]_\Gamma || (0001)_\delta$.

No crystallographic relationship could be established for $\delta - \zeta$ because it proved impossible to grow a single crystalline layer of $\zeta$ on $\delta$. The apparently bad compatibility of the two lattices was reflected in the nucleation problems which were always encountered during efforts to grow $\zeta$ on $\delta$. The influence of the relationships on the actually observed textures in the $\delta$ and $\zeta$ layers of hot dip galvanized specimens is discussed.

Die kristallographischen Beziehungen zwischen den verschiedenen Fe–Zn Verbindungen sind mittels Einkristall-Röntgenmethoden untersucht worden. Zu diesem Zweck wurden primäre Einkristalle jeder Verbindung hergestellt, worauf durch Abkühlen in manchen Fällen eine einkristalline Schicht der nächsten, mehr Zink enthaltenden, Phase geziichtet werden konnte. Auf diese Weise war es möglich, kristallographische Beziehungen festzustellen in der Reihe $\alpha - \Gamma' - \Gamma_1' - \delta$:

$[110]_\alpha || [110]_\Gamma' || [110]_\Gamma || [100]_\delta$ ;

$[111]_\alpha || [111]_\Gamma || [111]_\Gamma || (0001)_\delta$.

Zwischen $\delta$ und $\zeta$ konnte jedoch keine kristallographische Beziehung festgestellt werden, weil es sich als unmöglich erwies, eine einkristalline Schicht von $\zeta$ auf $\delta$ zu züchten. Die offensichtlich schlechte Passung der Kristallgitter zeigt sich in Keimbildungsschwierigkeiten, mit denen das Wachstum von $\zeta$ auf $\delta$ verbunden ist.

Der Einfluß der gefundenen Beziehungen auf die in der Praxis wahrgenommenen Texturen in den $\delta$ und $\zeta$ Schichten von feuerverzinkten Proben wird diskutiert.

1. Introduction

During hot dip galvanizing of iron a number of diffusion layers are formed parallel to the original iron/liquid Zn interface. In the order of increasing Zn content these are the $\Gamma$, $\Gamma_1$, $\delta$ and $\zeta$ layer. On withdrawal from the bath the whole assembly is covered by a layer of adhering zinc. A lot of research has been done on the kinetics of the layer growth during hot dip galvanizing.

It seems to be well established now that up to 495 °C layer growth follows parabolic kinetics which indicates that the process is diffusion controlled. Between 495 °C and 530 °C, however, a linear time law is obeyed. Above 530 °C, on the other hand, layer growth proceeds again according to a parabolic time law.

According to Horstmann the region of linear growth can be explained by the premature (with respect to temperature) absence of the $\zeta$ layer in the critical tem-
perature trajec. As a matter of fact the $\zeta$ phase should be stable up to 530 °C in the bulk; as a diffusion layer, however, it is already absent from 495 °C on. As a consequence, the $\delta$ layer is in contact with liquid zinc with which it cannot be in equilibrium. According to HORSTMANN the reason for the absence of the $\zeta$ phase must be sought in nucleation difficulties of $\zeta$ on $\delta$ and essentially, this is a crystallographic problem.

Perhaps even more important crystallographic features related to the hot-dip galvanizing process are the textures in the $\delta$ and $\zeta$ layers. It has been shown recently (BASTIN, VAN LOO, RIECK; BASTIN, VAN LOO) that during hot dip galvanizing sharp fibre textures are produced in these layers. About the origin of these textures and those in diffusion grown layers in general little is known with certainty at the moment.

In a number of cases (e.g. HEUMANN, DITTRICH) it is suspected that preferential diffusion in certain crystallographic directions is responsible for the development of a texture. In other cases one could suspect that crystallographic relationships between substrate and/or adjacent layers play an important role.

With these thoughts in mind the present investigation into the orientation relationships between the various Fe–Zn phases has been carried out.

2. General approach

For the determination of orientation relationships use has been made of single crystals of the various phases which were produced by slowly cooling a melt of suitable composition. On further cooling it has been found possible in a number of cases to grow a thin layer of the neighbouring phase, richer in zinc, on these primary crystals.

Single crystal rotation and Weissenberg techniques were subsequently used to establish the nature of the relationship between the two phases in question.

From the rotation patterns information was obtained on which axes of rotation both phases have in common. At the same time the periodicities of both lattices along their coincident zone axes could be determined. The Weissenberg patterns from the same zones were used to gather the supplementary data necessary to establish the full orientation relationship. Not only will such a pattern reveal information about crystallographic planes being parallel; it will at the same time show how parallel planes of both phases fit with respect to their spacings.

3. The Fe–Zn system

3.1. Phase diagram

The phase diagram (Fig. 1) of the Fe–Zn system is mainly based on the work of SCHRAMM (1936–1938). Since then a number of papers (BABLIC, GÖTZL, HALLA; LEHL, DEMEL; LEHL; BUDUROV et al.; GHONIEM, LöHBERG) have been published on this subject. Apart from some alterations in the $\alpha$- and $\gamma$-Fe phase fields (BUDUROV et al.), however, the main outlines of the diagram as given by Schramm remained unchanged. Recently, additional investigations have yielded the incorporation of the previously unknown $I_1'$ phase (BASTIN, VAN LOO, RIECK, 1974) and some modifications of the $\delta$ phase field (BASTIN, VAN LOO, RIECK, 1977).

3.2. Crystallographic data on the various Fe–Zn phases

In Table 1 the unit cell data and space groups of the Fe–Zn phases are given. It will be noted that the $I_1'$ phase is closely related to the $I'$ phase in that both phases are cubic and the unit cell parameter of $I_1'$ is exactly twice that of $I'$. The $I'$ phase, however, has a BCC lattice while that of $I_1'$ is FCC.
Crystallographic Relations in the Fe-Zn System

Table 1
Crystallographic data on the Fe–Zn compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Structure, Space Group</th>
<th>Unit cell parameters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe</td>
<td>Fe</td>
<td>Cubic, BCC</td>
<td>(a = 2.8664 \text{ Å})</td>
<td>ASTM</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>(\text{Fe}<em>2\text{Zn}</em>{18})</td>
<td>Cubic, BCC (I \frac{4}{m} 3 \frac{2}{m} )</td>
<td>(a = 8.982 \text{ Å})</td>
<td>Schramm (1938)</td>
</tr>
<tr>
<td>(\Gamma_1)</td>
<td>(\text{Fe}<em>3\text{Zn}</em>{21})</td>
<td>Cubic, FCC (F 43m) or (F \frac{4}{3} \frac{2}{m} )</td>
<td>(a = 17.963 \text{ Å})</td>
<td>Bastin, van Loo, Rieck (1974), Present investigation</td>
</tr>
<tr>
<td>(\delta)</td>
<td>(\text{FeZn}_{12})</td>
<td>Hexagonal (P6_3mc) or (P6_5/mmc)</td>
<td>(a = b = 12.815 \text{ Å}) (c = 57.35 \text{ Å})</td>
<td>Bastin, van Loo, Rieck (1977)</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>(\text{FeZn}_{13})</td>
<td>Monoclinic (C \frac{2}{m})</td>
<td>(a = 13.424 \text{ Å}) (b = 7.608 \text{ Å})</td>
<td>Brown</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn</td>
<td>Hexagonal (P6_3/mmc)</td>
<td>(a = b = 2.663 \text{ Å}) (c = 4.947 \text{ Å})</td>
<td>ASTM</td>
</tr>
</tbody>
</table>

4. Experimental

As starting materials for the preparation of single crystals use was made of Zn rod (99.9 wt% ; supplied by Merck) and Fe sheet (99.5 wt% ; supplied by Drijfhout, Amsterdam). The metals were weighed in in the proper weight ratio and subsequently sealed in
evacuated (0.05 Torr) silica capsules. For safety reasons the capsules were transferred into steel tubes. Next the specimens were heated at temperatures of 900—1000 °C during several days. For the zinc-rich compositions generally chosen this implied that the alloys were completely liquid.

After homogenization of the melt the temperature was lowered to a value at which, for the given overall composition, the desired primary crystals could be brought into equilibrium with the liquid, iron-saturated, Zn phase. As it turned out a sufficiently thick (10—20 μm) layer of the secondary phase could be obtained in a number of cases by merely quenching the alloy in water. The material thus obtained was next cut, embedded in synthetic resin and ground and polished. After etching with 4 vol% nitric acid in ethanol the specimen was examined under a microscope.

In order to check the composition and homogeneity of the primary and secondary crystals sometimes electron probe microanalyses were performed according to procedures reported before (BASTIN, VAN Loo, RIECK, 1974).

Single crystals were extracted from the Zn-rich matrix by using dilute hydrochloric acid. As the matrix dissolved much faster than the crystals it was easy to remove the latter from time to time. Under a stereo microscope a number of suitable crystals were selected for the single crystal X-ray diffraction procedures.

5. Results

5.1. $\Gamma - \delta$ relationship

For the preparation of $\Gamma$ single crystals 2 different alloys were used. The overall compositions and the thermal treatment were as follows:

Alloy number one: Overall composition 16.00 at % Fe, 5d 1000 °C, 2d 760 °C; 5d 720 °C; quenching in water.

Alloy number two: Overall composition 8.07 at % Fe, 3d 898 °C, 3d 676 °C; quenching in water.

The compositions of the $\Gamma$ crystals as determined by electron probe micro-analysis were: 27.3 at % Fe for the first and 22.0 at % Fe for the second alloy. It will be noted that these compositions are in close agreement with the results of SCHRAMM. In fact, the whole $\Gamma/\Gamma + L$ boundary in the phase diagrams has been accurately redetermined in the present investigation and excellent agreement with the results of SCHRAMM has been obtained. The results have been incorporated in Figure 1.

![Fig. 2. Part of a $\Gamma$ crystal coated with a layer of $\delta$](image)

Microscopic examination of the quenched alloys learned that the dimensions of the primary $\Gamma$ crystals were about 0.1—0.3 mm. The $\delta$ layer which during quenching has grown on top of the $\Gamma$ crystals had a thickness varying between 5 and 15 μm. As Figure 2 shows the $\delta$ layer is bounded by a number of saw-tooths with angles of about 120°. Both the $\Gamma$ and the $\delta$ phase give the impression of being single crystalline in the sense that no grain boundaries could be detected. This impression was confirmed by
oscillation, rotation and Weissenberg patterns taken from a variety of $\Gamma$ crystals. These patterns which were obtained from the principal zone axes of $\Gamma$ will now be discussed in detail.

5.2. [110] zone axis of $\Gamma$

The rotation pattern of this zone axis showed no layer lines of the $\delta$ phase; only those of the $\Gamma$ phase appeared to be present at first sight. The zero level Weissenberg photograph (Fig. 3), however, clearly revealed a diffraction pattern superimposed on

Fig. 3. Zero level Weissenberg pattern of the [110] zone of a $\delta$ coated $\Gamma$ crystal; CoKα radiation

Fig. 4. Zero level Weissenberg pattern of the [100] $(\equiv[010])$ zone of a $\delta$ single crystal; CoKα radiation

that of $\Gamma$. This extra diffraction pattern, which was characterised by an extremely close arrangement of the diffraction spots, is typical for a zero level Weissenberg pattern taken about [100] $(\equiv[010])$ of the $\delta$ phase as Figure 4 shows. This implies that [110] $\Gamma$ and [100] $\delta$ are parallel.

Fig. 5. Zero level reciprocal lattice of $\Gamma$; axis of rotation [110]. The positions of the reciprocal axis of two $\delta$ individuals rotated about [010] have been indicated
At the same time this coincidence explains the absence of extra layer lines in the rotation pattern because the periodicities along both directions are very much alike: 

$$a_0/\sqrt{2} = 12.73 \text{ Å for } \Gamma \text{ and } 12.81 \text{ Å for } \delta.$$ 

When Figures 3 and 4 are compared in more detail it soon becomes clear that in Figure 3 more than one \(\delta\) individual is involved. In fact, the sequence of the \(c^*\) and \(a^*\) axes in the Weissenberg pattern of Figure 3 indicates the presence of two \(\delta\) individuals which make an angle of 70° (or 110°). This can perhaps best be illustrated with the aid of Figure 5 in which the undistorted reciprocal lattice of \(\Gamma\) has been constructed using the data of Figure 3. The positions of the \(c^*\) axes of the two \(\delta\) crystals indicate that the hexagonal axes of these crystals are aligned along the \(\langle111\rangle\) directions in the \(\langle110\rangle\) plane of the \(\Gamma\) crystals. The angle of about 70° we found between the two \(\delta\) crystals arises simply from the fact that this is the angle between the two \(\langle111\rangle\) directions in the \(\langle110\rangle\) plane of a cubic crystal. The reason for the presence of two \(\delta\) individuals is undoubtedly the fact that both \(\langle111\rangle\) directions in the cubic lattice have an equal probability of accommodating the hexagonal axis of a \(\delta\) crystal. The full orientation relationship which can be established from the data of Figure 3 is in general terms:

\[
\begin{array}{c|c}
\Gamma & \delta \\
\{110\} & \{11\overline{2}0\} \\
\{111\} & \{0001\} \\
\{211\} & \{1010\}
\end{array}
\]

5.3. [111] Zone axis of \(\Gamma\)

The rotation pattern of this zone showed, contrary to that of the [110] zone, a large number of extra layer lines which evidently belonged to the \(\delta\) phase. As could be predicted from the foregoing results \([111]\) \(\Gamma\) was found to coincide with [001] \(\delta\). In addition to this the zero level Weissenberg photograph of this zone demonstrated that every diffraction spot of \(\Gamma\) nearly coincided with one of \(\delta\) which can be taken as evidence that the spacings of many \(\Gamma\) and \(\delta\) lattice planes are almost equal. This excellent matching of both lattices is best demonstrated in Figure 6 in which the observed superposition of the reciprocal lattices has been drawn. It is obvious that the lattices match very well in directions perpendicular to [111] \(\Gamma\). In the [111] \(\Gamma\) direction

\[\text{Fig. 6. Observed superposition of the zero level reciprocal lattices of } \Gamma \text{ (axis of rotation [111]) and } \delta \text{ (axis of rotation [001])}. \text{ For reasons of clarity the reciprocal lattice points of } \delta \text{ (at the intersections of the lines } h_\delta = \text{ constant; } k_\delta = \text{ constant) have not been depicted by symbols.}\]
itself, however, this is apparently not the case as a comparison of the periodicities along some principal directions learns:

<table>
<thead>
<tr>
<th></th>
<th>( \Gamma )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[211]</td>
<td>22.05 Å</td>
<td></td>
</tr>
<tr>
<td>[110]</td>
<td>12.73 Å</td>
<td></td>
</tr>
<tr>
<td>[111]</td>
<td>7.79 Å</td>
<td></td>
</tr>
</tbody>
</table>

5.4. [100] Zone axis of \( \Gamma \)

As can be derived from the relationship established so far the (100) \( \Gamma \) planes are not parallel to any low-indices plane of the \( \delta \) phase. The rotation and Weissenberg patterns did not yield additional information on the relationship.

5.5. \( (\Gamma \rightarrow) \Gamma_1 - \delta \) relationship

In order to be able to establish this relationship single crystalline material of the \( \Gamma_1 \) phase had to be prepared. For this purpose two different procedures were followed. In the first procedure a number of \( \delta \) coated \( \Gamma \) crystals of alloy number one (see under \( \Gamma - \delta \) relationship) were heated at 400°C. As an inspection of the phase diagram (Fig. 1) learns the \( \Gamma \) crystals of this particular composition \((27.3 \text{ at}\% \text{ Fe})\) cannot be transformed into \( \Gamma_1 \) crystals upon cooling because the homogeneity regions of these phases do not overlap for this composition. Instead, only a reaction zone \( \Gamma + \delta \rightarrow \Gamma_1 \) can be expected at the \( \Gamma/\delta \) interface and indeed this turned out to be the case. These crystals were used to record the superimposed Weissenberg patterns of the three compounds in one single exposure. In the second procedure the \( \delta \) coated \( \Gamma \) crystals of alloy number two were employed. The composition of these crystals \((22.0 \text{ at}\% \text{ Fe})\) was more favourable for a transformation into \( \Gamma_1 \).

A heat treatment of 33d at 400 °C yielded fully transformed \( \Gamma_1 \) crystals still coated with a single crystalline layer of \( \delta \). These crystals were subsequently used to determine the \( \Gamma_1/\delta \) relationship. Furthermore, some of the crystals were used to collect more detailed crystallographic data on the \( \Gamma_1 \) phase because up to now these data had only been obtained from polycrystalline specimens \((\text{Bastin, van Loo, Rieck, 1974})\). To this end the \( \delta \) layer was etched away. The remaining pure \( \Gamma_1 \) single crystal was aligned along the principal zone axes \( \langle 001 \rangle, \langle 110 \rangle \) and \( \langle 111 \rangle \) and Weissenberg photographs were taken from a number of layer lines (up to the third). The preliminary unit cell data published in the literature were thereby confirmed and also the fact that the lattice is FCC. Apart from the systematic extinction connected with the face-centering translations, however, no additional systematic extinctions could be observed. In conjunction with the observed 4-fold symmetry this leaves as possible space groups for \( \Gamma_1 \): F432, F43m or Fm3m.

At the moment work is in progress to determine the crystal structure of the \( \Gamma_1 \) phase.

As far as the orientation relationships are concerned it was found that in the case of the \( \Gamma/\Gamma_1/\delta \) crystals the original relationship between the \( \Gamma \) and \( \delta \) phase was fully maintained. The newly grown \( \Gamma_1 \) phase adapted itself perfectly to both the \( \Gamma \) and the \( \delta \) lattice by simply extending the existing principal crystallographic directions from the \( \Gamma \) phase throughout the \( \Gamma_1 \) layer to the \( \Gamma_1/\delta \) interface. Similar results were obtained with the \( \Gamma_1/\delta \) crystals: upon transformation the \( \Gamma_1 \) crystals were found to maintain the original orientation of the \( \Gamma \) crystals. Thus the \( \Gamma_1/\delta \) orientation relationship is identical to that of \( \Gamma/\delta \). Undoubtedly, this similarity is caused by the very close relationship between the \( \Gamma \) and \( \Gamma_1 \) phases.
5.6. \( \alpha \)–\( \Gamma \) relationship

For the investigation of this relationship two alloys with overall compositions of 16.35 and 15.52 at % Fe, respectively, were prepared. After homogenizing at 1000 °C for a few days the alloys were equilibrated at 820 °C during several days. The compositions of the \( \alpha \)-Fe crystals were found to be 61.8 and 61.3 at % Fe, respectively, which is in excellent agreement with the results of Budurov et al.

During quenching the primary \( \alpha \)-Fe crystals (dimensions 0.2–0.5 mm) were covered with a thin (2–3 \( \mu \)m) layer of \( \Gamma \) and/or \( \Gamma' \) and a \( \delta \) layer (about 20 \( \mu \)m) which again showed the familiar saw-tooths. A number of \( \alpha \)-Fe crystals were used for single crystal rotation and Weissenberg patterns about \( \langle 110 \rangle \) and \( \langle 111 \rangle \) \( \alpha \)-Fe. The Weissenberg pattern taken about \( \langle 110 \rangle \) \( \alpha \)-Fe had, apart from the \( \alpha \)-Fe diffraction spots, the same general appearance as that shown in Figure 3, in particular the extremely close arrangement of the diffraction spots typical for the zero level Weissenberg photograph of a \( \delta \) crystal rotated about [100]. Hence, between \( \alpha \)-Fe and \( \delta \) the same orientation relationship exists as the one already established for \( \Gamma \)-\( \delta \) and \( \Gamma \)-\( \Gamma' \)-\( \delta \). This was confirmed by the nature of the \( \Gamma \) reflections in the pattern which clearly showed that \( \Gamma' \) had been rotated about \( \langle 110 \rangle \). The relationship between \( \alpha \)-Fe and \( \Gamma \) is thus, like the one between \( \Gamma \) and \( \Gamma' \), very straightforward:

\[
\langle 110 \rangle \text{\( \alpha \)}-\text{Fe} \parallel \langle 110 \rangle \text{\( \Gamma \)}; \quad \langle 111 \rangle \text{\( \alpha \)}-\text{Fe} \parallel \langle 111 \rangle \text{\( \Gamma \)}.
\]

This relationship was substantiated by the Weissenberg pattern about \( \langle 111 \rangle \text{\( \alpha \)}-\text{Fe} \). Both Weissenberg patterns, however, indicated that the misfit between the \( \alpha \)-Fe and \( \Gamma \) lattices is somewhat larger than that between the \( \Gamma \) and \( \Gamma' \) lattices which was negligible. Calculations showed that in the present case the misfit is about 2%.

Of course, this misfit is not correct for hot dip galvanizing temperatures (usually 450–460 °C) at which temperatures the iron can only dissolve 3.8% Zn instead of 38%. A rough estimate through linear interpolation of the lattice parameter of \( \alpha \)-Fe shows that in this case the misfit is doubled.

5.7. \( \delta \)–\( \zeta \) relationship

The experimental technique so successfully applied to obtain coated single crystals of the \( \alpha \), \( \Gamma \) and \( \Gamma' \) phases proved unsuccessful to produce \( \zeta \) coated \( \delta \) crystals. It was observed that on the \( \delta \) crystals, grown during equilibration within the \( \delta \)-\( L \) phase field, no \( \zeta \) layer would nucleate on cooling, not even after cooling very slowly. Instead, the \( \zeta \) phase preferred to nucleate between the \( \delta \) crystals in the zinc-rich matrix. Efforts to obtain a \( \zeta \) layer on the \( \delta \) crystals by keeping the latter in a supercooled zinc-rich liquid also failed; the only result of this procedure was that the \( \delta \) crystals were badly attacked by the liquid Zn. This attack proceeded preferably in directions perpendicular to the hexagonal axis of \( \delta \). The \( \delta \) crystal disintegrated thereby gradually into segments perpendicular to the hexagonal axis. Exactly the same observations were made during etching of \( \delta \) crystals in dilute hydrochloric acid and during attack by zinc vapour. This can be taken as evidence that Zn (and also acid) has easier access to the \( \delta \) crystals in directions perpendicular to the hexagonal axis than along this axis. Most probably this points to a layer structure of the \( \delta \) phase.

Another effort to produce \( \zeta \) coated \( \delta \) crystals consisted of heating the \( \delta \) crystals in a solidified zinc-rich matrix at 375 °C. Through the solid state diffusion process which has to take place in this case the \( \zeta \) phase has no choice than to grow on \( \delta \). Even so the growth of \( \zeta \) proved very laborious: after 0.5 h at 375 °C no sign of \( \zeta \) was visible yet. Only after about 1 h the first nuclei of \( \zeta \) were observed and these were then found to grow rapidly until after about 2 h a reasonable layer of \( \delta \) had been transformed into \( \zeta \) (Fig. 7). Apparently the \( \zeta \) phase needs an incubation time to form the first nuclei.
On microscopic examination the $\zeta$ phase eventually grown gave the impression of being polycrystalline. This was confirmed by rotation patterns which gave continuous Debye-Scherrer rings superimposed on the single crystal pattern of $\delta$.

For the last method which was tried in order to obtain a single crystalline $\zeta$ layer on top of a $\delta$ crystal use was made of zinc transfer through the vapour phase. In this experiment two $\delta$ single crystals together with a grain of Zn (carefully kept separated from the $\delta$ crystals) were brought into a silica capsule which was then evacuated and sealed. The capsule was subsequently held at 450 °C during 47 h. One of the crystals was afterwards used for rotation patterns. These patterns clearly showed Debye-Scherrer rings thus indicating the polycrystalline nature of the $\zeta$ phase grown on the $\delta$ crystal. Next the crystal was embedded and ground parallel to the hexagonal axis. Figure 8 shows a micrograph of this section. Apparently under the attack of gaseous zinc the $\delta$ crystals has been split up into lamellae perpendicular to the hexagonal axis, similar as during the attack of $\delta$ by liquid zinc mentioned before.

Furthermore, it is obvious from Figure 8 that nucleation of $\zeta$ has taken place only locally and that the $\zeta$ phase which eventually forms is polycrystalline.

Summarizing the results on the $\delta$—$\zeta$ relationship it would seem that all the observations made so far on the growth of $\zeta$ on $\delta$ point to a certain incompatibility of the crystal lattices of the $\delta$ and $\zeta$ phases. The reluctant growth of $\zeta$ on $\delta$ is apparently a symptom of this incompatibility.

6. Discussion

The crystallographic relationship observed between the cubic Fe-Zn compounds $\alpha$, $\Gamma$ and $\Gamma_1$ may not be surprising at first sight in that the indices of parallel planes and directions are simply the same in all cases.

It is remarkable, though, that this relationship applies in spite of the fast growing complexity of the structures: $\alpha$: Fe, 2 at/cell; $\Gamma$ (Fe$_9$Zn$_{10}$), 52 at/cell; $\Gamma_1$ (Fe$_9$Zn$_{11}$), probably 416 at/cell. This is even more so if one takes into consideration that a number of these relationships are established under circumstances which can hardly be considered ideal, i.e. during quenching. Nevertheless unique relationships were observed and this can be taken as evidence that there are large similarities between the structures of e.g. the $\Gamma$ and $\Gamma_1$ phases.
The unique relationship found between $\Gamma$ and $\delta$ (and through the relationships between the cubic phases between $\alpha$ and $\delta$) may be of immediate practical importance because here the relationship between the iron substrate and one of the major constituents of the coating formed during hot dip galvanizing, is involved. Whether this relationship has a major influence on the nature of the texture formed in the $\delta$ layer or that other factors play a role has to be determined yet.

A most striking observation in this respect is the fact that the $\delta$ crystals have been found to be so much more vulnerable in directions perpendicular to the hexagonal axis than along this axis. The easy access which Zn atoms apparently have in the former directions corresponds very well with the texture observed in the $\delta$ layer: in all cases the hexagonal axes of the $\delta$ crystallites were found to be perpendicular to the direction of diffusion (BASTIN, VAN Loo, RIECK, 1976). Undoubtedly, hot dip galvanizing experiments carried out which iron single crystals of various orientations can decide in favour of one of the possibilities; work to this effect will be carried out in the future.

Characteristic for the $\Gamma-\delta$ (or $\alpha-\delta$) relationship is the astonishing ease with which it is established: during quenching fully adapted single crystalline layers of $\delta$ with thicknesses of up to 20 $\mu$m were obtained. Evidently this points to similarities between the $\Gamma(\Gamma')$ and $\delta$ phases.

Quite contrary to the ease with which the relationships discussed sofar seem to be established are the troubles which apparently accompany the nucleation of $\zeta$ on $\delta$. The fact that under none of the applied practical circumstances a single crystalline layer of $\zeta$ on $\delta$ could be obtained must be taken as evidence for a bad compatibility of the two crystal lattices. In particular the delayed nucleation with incubation times of approx. 0.5 h points in that direction. Although these results are in full agreement with those of HÖRSTMANN it is hard to see why these nucleation problems are responsible for the premature absence of $\zeta$ in the critical temperature range of hot dip galvanizing.

It has namely been shown (ALLEN, MACKOWIAK) that also in specimens, in which a fully coherent $\zeta$ layer is produced by galvanizing below the critical temperature range, this $\zeta$ layer nevertheless disappears during subsequent further galvanizing in the critical temperature range. This means that although $\zeta$ nuclei were originally present these cannot prevent the disappearance of the $\zeta$ layer.

Concerning the origin of the texture found in the $\zeta$ layer of hot dip galvanized specimens it must be stated that this texture is obviously not caused by a crystallographic relationship between the $\delta$ and $\zeta$ layers as apparently such a relationship does not exist. In this case it is most probably appropriate to assume preferential diffusion of Zn atoms in a certain crystallographic direction as has been pointed out before (BASTIN, VAN Loo 1978).

References

ASTM: X-ray Powder Data File (inorganic volume) (1967) no. 6 - 696 for $\alpha$-Fe; no. 4 - 831 for Zn
BABLIK, H., GöTZL, F., HALLA, F.: Z. Metallkde. 30, 249 (1938)
BASTIN, G., VAN Loo, F.: Z. Metallkde. 69, 540 (1978)
GHONIEM, M., LÖHBERG, K.: Metall 26, 1026 (1972)
Crystallographic Relations in the Fe–Zn System

Heumann, T., Dittrich, S.: Z. Metallkd. 50, 10 (1959)
Lihl, F.: Z. Metallkd. 46, 434 (1955)
Schramm, J.: Z. Metallkd. 29, 222 (1937)
Schramm, J.: Z. Metallkd. 30, 122 (1938)

(Received October 31, 1978)

Authors’ address:
Dr. Ir. G. F. Bastin, J. C. Verplanke, F. J. J. van Loo
University of Technology
Dept. of Physical Chemistry
P. O. Box 513
Eindhoven/Netherlands