

The sensitivity of each dendrite arm's diffusion layer gradients to the inlet concentration suggests that convective effects can be significant even at low levels of convective motion. This finding is significant for coarsening studies performed on the ground, for which some level of convective motion is almost assured. The importance of having baseline studies with no convection for these cases is evident.

The authors are grateful to Brent Blaha, Ruben Bons, and Adel Omrani for their assistance in verifying the calculations. This work was supported, in part, by the Microgravity Science and Applications Division, NASA, under Grant No. NAS8-37292.

### NOMENCLATURE

$C$	solute concentration (wt pct H <sub>2</sub> O)
$C_0$	solute concentration of inlet liquid (wt pct H <sub>2</sub> O)
$D$	solubility diffusion coefficient (cm <sup>2</sup> /s)
$E$	dimensionless pressure gradient
$h$	half-spacing between dendrites (cm)
$H$	dendrite surface curvature (1/cm)
$P$	pressure $\left(\frac{\text{dyne}}{\text{cm}^2}\right)$
$Pe$	solubility Peclet number
$r$	dendrite radius (cm)
$r_{\text{bot}}$	dendrite radius at $Y = -1$ (cm)
$r_{\text{top}}$	dendrite radius at $Y = +1$ (cm)
$R$	ideal gas constant (J/mol K)
$T$	temperature (K)
$u$	liquid velocity (cm/s)
$U$	dimensionless liquid velocity
$U_m$	mean liquid velocity (cm/s)
$V^B$	molar volume of solid phase (cm <sup>3</sup> /mol)
$x$	distance along dendrite arm (cm)
$X$	dimensionless distance along dendrite arm (cm)
$y$	distance perpendicular to dendrite arm (cm)
$Y$	dimensionless distance perpendicular to dendrite arm (cm)
$\alpha$	denotes liquid phase
$\nu$	transport coefficient $\left(\frac{\text{cm}^2}{\text{s}}\right)$
$\mu$	dynamic viscosity (g/cm s)
$\Phi$	dimensionless concentration

### REFERENCES

1. M.C. Flemings: *Solidification Processing*, McGraw-Hill, New York, NY, 1974.
2. M.H. McCay, J.A. Hopkins, and T.D. McCay: *J. Cryst. Growth*, 1994, vol. 144, pp. 346-52.
3. M.H. McCay, J.A. Hopkins, and T.D. McCay: *Metall. Mater. Trans. A*, 1995, vol. 26A, pp. 227-29.
4. F. White: *Viscous Fluid Flow*, McGraw-Hill, New York, NY, 1974.
5. W.M. Kays and M.F. Crawford: *Convective Heat and Mass Transport*, McGraw-Hill, New York, NY, 1980.
6. A.W. Al-Khafaji and J.R. Tooley: *Numerical Methods in Engineering Practice*, Holt, Rinehart and Winston, Inc., New York, NY, 1986.

7. R.T. DeHoff: *Thermodynamics in Materials Science*, McGraw-Hill, New York, NY, 1993.
8. M.H. McCay, J.A. Hopkins, and T.D. McCay: *Metall. Mater. Trans. B*, 1993, vol. 24B, pp. 669-75.
9. T.D. McCay, M.H. McCay, and J.A. Hopkins: *J. Mater. Processing Manufacturing Sci.*, 1992, vol. 1 (3), pp. 315-30.

## The Role of Grain Corners in Nucleation

WEIMING HUANG and MATS HILLERT

The driving force for the nucleation of a new phase in a binary alloy at a fixed undercooling depends on the compositions of the two phases. It increases rapidly with the composition difference between the two phases.<sup>[1]</sup> Thus, the driving force for an allotropic transformation is generally weak because the difference in composition is small. The austenite  $\rightarrow$  ferrite transformation in Fe-C alloys is a typical example. Ferrite is almost 100 pct Fe and austenite is typically more than 95 pct Fe. Thus, homogeneous nucleation is not possible and only strong heterogeneities are active at reasonable degrees of undercooling.

Since ferrite is almost pure Fe, the driving force for its nucleation in austenite can be estimated as

$$\Delta G_m = RT \ln (a_{\text{Fe}}/a_{\text{Fe}}^0) \cong RT \ln (x_{\text{Fe}}/x_{\text{Fe}}^0) \cong RT(x_{\text{Fe}} - x_{\text{Fe}}^0)$$

where  $x_{\text{Fe}}$  is the Fe content of the austenite matrix and  $x_{\text{Fe}}^0$  is the equilibrium Fe content of austenite in contact with ferrite.

As shown by Clemm and Fisher,<sup>[2]</sup> grain corners may be very active nucleation sites and they may even give rise to nucleation without any nucleation barrier. Next comes grain edges and then grain faces. It is surprising that there have been very few attempts to test this prediction experimentally. An exception is a series of articles by Aaronson and

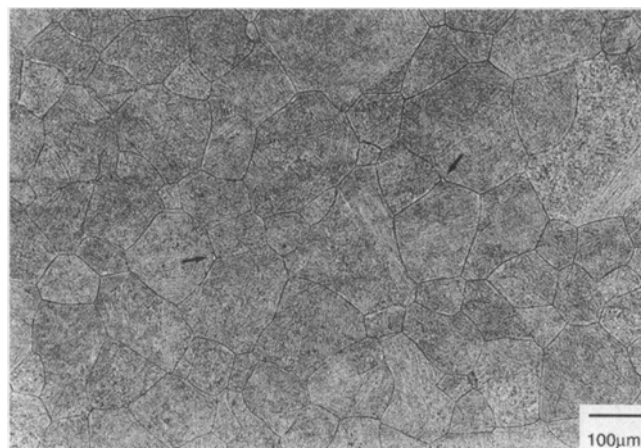


Fig. 1—Microstructure of specimen C.

WEIMING HUANG, Research Associate, and MATS HILLERT, Professor Emeritus, are with the Department of Materials Science and Engineering, Royal Institute of Technology, S-10044 Stockholm, Sweden. Manuscript submitted July 25, 1995.

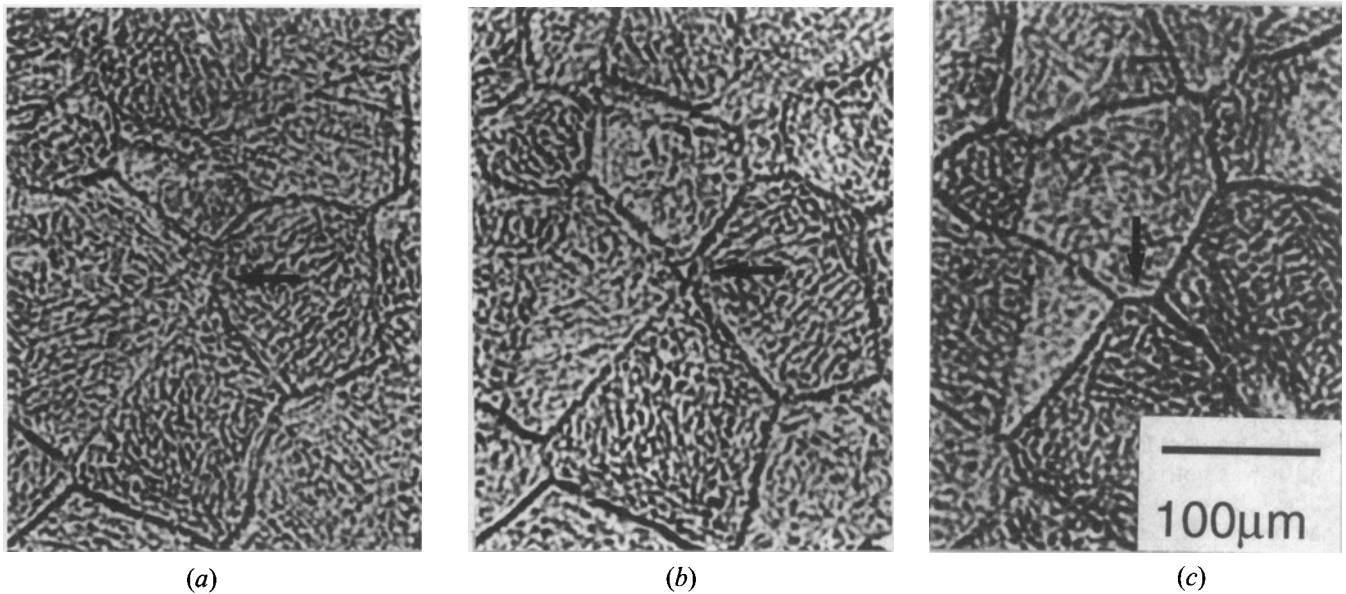


Fig. 2—The appearance and disappearance of an  $\alpha$  particle in the sections through specimen A. The distance between two consecutive sections is 5.3  $\mu\text{m}$ : (a) section 6, (b) section 10, and (c) section 20.

**Table I. Position of  $\alpha$  Nuclei in a Specimen B, Relative to  $\gamma$  Grain Boundaries**

Area	In Corners	On Edges	On Faces
1	4	4	2
2	8	1	0
3	3	1	0
4	8	2	0
5	6	2	0
6	6	3	0
7	5	3	0
8	6	3	0
9	6	1	1
Total	52	20	3
Average	69 pct	27 pct	4 pct

**Table II. Position of  $\alpha$  Nuclei in a Specimen C, Relative to  $\gamma$  Grain Boundaries**

Area	In Corners	On Edges	On Faces
1	4	1	0
2	4	1	0
3	11	2	1
4	5	3	0
5	7	1	0
6	5	1	1
7	5	2	1
8	8	3	2
9	5	1	0
Total	54	15	5
Average	73 pct	20 pct	7 pct

co-workers.<sup>[3-7]</sup> They studied the austenite  $\rightarrow$  ferrite transformation in Fe-C alloys. In their first two articles,<sup>[3,6]</sup> they were mainly interested in obtaining information on the rate of nucleation at grain faces but found that grain edges were so much more effective that only a minority of the ferrite grains nucleated at grain faces, in spite of the fact that they worked with a large austenite grain size. They neglected nucleation on grain corners by referring to the large grain size. In their third article,<sup>[9]</sup> they focused on the effect of grain edges but still neglected grain corners.

In an attempt to test the role of grain corners in the nucleation of ferrite in Fe-C alloys, a collaboration was recently established between the Max-Planck-Institut für Eisenforschung (Düsseldorf, Germany) and the Department of Materials Science and Engineering, KTH (Stockholm, Sweden). The results of the first group are available through an internal report<sup>[8]</sup> and a doctoral thesis.<sup>[9]</sup> The results obtained by the second group will now be presented.

The study was carried out with an Fe-0.51 pct C alloy produced in Düsseldorf from high-purity electrolytic iron by vacuum melting and forging. Specimens of the dimension  $2 \times 13 \times 13 \text{ mm}^3$  were sealed in evacuated silica capsules and austenitized for 15 minutes at 1200 °C. The

capsules were then broken and the specimens transferred to a salt bath of a temperature of about 750 °C and then quenched after different, predetermined times. They were finally annealed at about 400 °C in order to make the previous austenite grain boundaries more visible.

The specimens were sectioned and prepared metallographically. It was found that a volume fraction of 0.3 pct ferrite (specimen A) gave particle sizes too large to distinguish clearly where they had nucleated. The main work was thus done on two specimens with 0.05 (specimen C) and 0.12 pct ferrite (specimen B), obtained after 1 and 3 minutes at 749 °C in the salt bath. Figure 1 shows the microstructure of one of them. It was taken with an objective of 10 times.

Nine areas of each specimen were photographed in a light microscope. Then, five microhardness marks were made with a Vicker diamond using a weight of 300 g. The sizes of the indentations were measured in the microscope. The diagonal was about 39  $\mu\text{m}$ .

Then, the specimens were ground by hand with a Streuer 1000 silicon carbide paper, applying a light pressure and eight strokes. It was then polished with Streuer DP-heavy diamond paste of 2.5  $\mu\text{m}$  for 30 minutes. The indentations

Table III. Observation on the Fe-0.51 Pct C Specimens

Specimen	°C	Min	$f_v$ (Pct)	Examined Volume (mm <sup>3</sup> )	$\alpha$ Particles/mm <sup>3</sup>	$\alpha$ Particle per Corner
B	749	3	0.12	0.95	168	0.070
C	749	1	0.05	0.95	106	0.044

were finally measured again and the diagonal was about 15  $\mu\text{m}$ . This decrease in size corresponds to a removal of about 3  $\mu\text{m}$  of the surface layer. The specimens were then etched for about 3 minutes in 4 pct picral mixed with 20 pct water. After drying, the etching products were removed by attaching Scotch tape and stripping. The etching and cleaning were repeated four times. The indentations were smaller than before etching, but the edges were less distinct and it was not possible to measure their size with any accuracy. It is thus uncertain how much of the surface layer had been removed between the first examination of the microstructure and the next one, but it is certainly somewhat more than 3  $\mu\text{m}$ .

The same areas were photographed again and the procedure was repeated 15 times. Afterward, the decreased thickness of the specimen was measured with a micrometer, and it was found that on the average a surface layer of 5.3  $\mu\text{m}$  had been removed each time.

The micrographs were studied in detail. The ferrite particles, visible in the first section, were not studied any further. Each ferrite particle which appeared later was followed through the subsequent sections, and the austenite grain structure around the particle was studied. A particularly clear case is shown in Figures 2(a) through (c). It is evident that there has been a short horizontal grain boundary on one side of the particle and a short vertical grain boundary on the other side. This is thus a case where it is most probable that the nucleation site was a grain corner. It should be noted that the resolution of the enlarged micrographs in Figures 2(a) through (c) is not very high, the reason being that these micrographs were taken with an objective of 5 times and before it could be expected that the enlarged region would be of special interest.

In other cases, it was necessary to study the grain boundaries in contact with a ferrite particle and to extrapolate them into the particle. It was then more difficult to establish whether there had been a grain corner or a grain edge at the point of nucleation. The results reported in Tables I and II are thus subject to some uncertainty. Only those particles are included that both appeared and vanished again in the series of sections.

The results are rather similar for the two specimens. It may be concluded that most of the ferrite particles have nucleated at grain corners, some at grain edges, and very few on grain faces. No ferrite particle was observed to have nucleated inside a grain. The same conclusion was reached by the Düsseldorf group who worked with a very advanced apparatus for automatic inspection of the microstructure, recording on videotape and electronic pattern analysis.

The dominance of grain corners as nucleation sites is so strong that it may even be suggested that the nucleation recorded as taking place at grain edges may actually have occurred at special points which are energetically similar to grain corners. For instance, it seems possible that such a

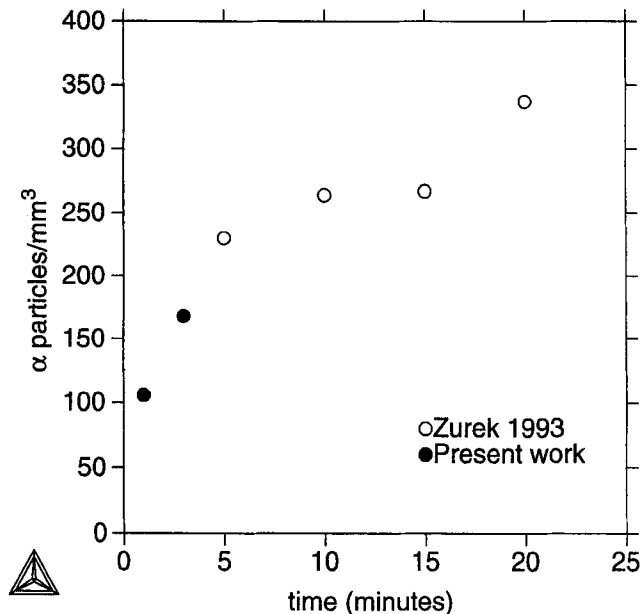


Fig. 3—Number of ferrite particles as a function of time at 749 °C.

point may appear where a twin boundary intersects with a grain edge, in particular, if there is a step in the otherwise flat twin boundary. It should be noticed that annealing twins are very common in this material.

Some of the present results are summarized in Table III, and the total number of ferrite particles (including those that did not vanish before the last sectioning) appearing per mm<sup>3</sup> of specimens B and C is compared with the corresponding data from the Düsseldorf group in Figure 3. The uncertainty of the Düsseldorf data was given as about  $\pm 40$ , but the impression is that the majority of the ferrite particles form before the volume fraction exceeds 1 pct (it is 1.28 pct at 15 minutes). It should also be emphasized that the real number of particles at sort times could be larger than according to the observations, because some particles may be easily missed because of their small size. To the present authors, it makes more sense to assume that all the particles form at an early stage and to talk about the number of nuclei rather than the rate of nucleation which was used by Aaronson and co-workers.

The Düsseldorf data contain information on four specimens from different times at 749 °C. In order to further test whether they contained approximately the same number of ferrite particles, the rate constant in a parabolic growth law was evaluated by calculating  $(3f_v^2/4\pi N_v)^{2/3}$ , which corresponds to  $R^2/t$  assuming radial growth. Here,  $f_v$  represents the volume fraction of ferrite and  $N_v$  represents the number of particles per mm<sup>3</sup>. Almost the same values were obtained for the four specimens, indicating that the number of ferrite particles did not vary more than shown by the measured data.

It should also be interesting to evaluate the number of ferrite particles in relation to the total number of grain corners. To this end, the Düsseldorf group counted the number of austenite grains and the number of grain corners as they worked their way through a specimen quenched directly from 1200 °C. They found  $400 \pm 80$  grains per  $\text{mm}^3$  and  $1600 \pm 120$  grain corners per  $\text{mm}^3$ . That means that each grain should have 16 corners on the average, which seems a little low. The more reasonable value of 24 would yield 2400 grain corners for the number of grains observed. That value was used to obtain the results given in Table III. This evaluation was based on all the ferrite particles observed, independent of their nucleation site.

The results indicate that no more than about 5 to 7 pct of the grain corners were active nucleation sites in the Fe-0.51 pct C alloy at 749 °C. From a practical point of view, it thus seems reasonable to approximate the number of nuclei during the formation of ferrite allotriomorphs as a fraction of the grain corners. The fraction does not seem to vary much with time after an initial period, but of course, it varies with temperature. However, a much more detailed investigation is required in order to determine that dependency. The amount of work in a future study may be reduced if it is accepted that most of the ferrite particles form at an early stage. The main experimental difficulty would be to produce specimens transformed isothermally to a low enough volume fraction of ferrite. At short times and a low heat treatment temperature, it may also be difficult to distinguish between allotriomorphs and Widmanstätten ferrite.

---

A research grant from Volkswagenstiftung is gratefully acknowledged.

#### REFERENCES

1. M. Hillert: *Acta Metall.*, 1953, vol. 1, pp. 764-66.
2. P.J. Clemm and J.C. Fisher: *Acta Metall.*, 1955, vol. 3, pp. 70-73.
3. W.F. Lange III and H.I. Aaronson: *Metall. Trans. A*, 1979, vol. 10A, pp. 1951-52.
4. M. Enomoto and H.I. Aaronson: *Metall. Trans. A*, 1986, vol. 17A, pp. 1385-97.
5. M. Enomoto, W.F. Lange III, and H.I. Aaronson: *Metall. Trans. A*, 1986, vol. 17A, pp. 1399-1407.
6. W.F. Lange III, M. Enomoto, and H.I. Aaronson: *Metall. Trans. A*, 1988, vol. 19A, pp. 427-40.
7. M. Enomoto, N. Nojiri, and Y. Sato: *Mater. Trans. JIM*, 1994, vol. 35, pp. 859-67.
8. C. Zurek, E. Sachova, and H.P. Hougardy: *Abschluss- und Jahresbericht 1992/1993, Projekt COSMOS*, Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany, 1993.
9. C. Zurek: Ph.D. Thesis, RWTH, Aachen, Germany 1993.

## Structural Characterization of Martensitic Iron-Carbon Alloy Films Electrodeposited from an Iron(II) Sulfate Solution

MASANOBU IZAKI and TAKASHI OMI

We have devised a new electrolyte formulation<sup>[1]</sup> and reported that the electrodeposited Fe-1.04 mass pct C alloy films up to 200  $\mu\text{m}$  in thickness<sup>[2]</sup> show a micro-Vickers hardness of around HV800.<sup>[3]</sup> Since the hardness is above twice those of the industrially employed Fe electrodeposits<sup>[4]</sup> and corresponds to those of the carburized or nitrided steels,<sup>[5]</sup> the film is under industrial evaluation<sup>[6]</sup> as hard coating or an alternative of the thermal surface hardening processes. During the evaluation, there arose a demand for low-carbon Fe-C alloy films from the ductility point of view.

In this article, we report structural characterizations of the 100- $\mu\text{m}$ -thick Fe-C alloy films of 0.43 to 1.26 mass pct C electrodeposited by 20 to 700  $\text{A m}^{-2}$  electrolysis in the original electrolyte.

Fe-C alloy films were prepared from the original electrolyte composed of 40  $\text{kg m}^{-3}$  iron(II) sulfate, 1.2  $\text{kg m}^{-3}$  citric acid, and 3.0  $\text{kg m}^{-3}$  L-ascorbic acid kept at 323 K. The Fe film was prepared from a 250  $\text{kg m}^{-3}$  iron(II) sulfate solution kept at 308 K. All solutions were prepared with distilled water and reagent grade chemicals. Stainless-steel sheet cathodes (Japanese Industrial Standard (JIS) No. SUS304) of size 20  $\times$  20  $\times$  0.3 mm were degreased in an electrolyte containing 60  $\text{kg m}^{-3}$  KOH and 30  $\text{kg m}^{-3}$   $\text{K}_4\text{P}_2\text{O}_7$ , and were washed with distilled water prior to electrodeposition. Two plain steel sheets (JIS SPCC) were used as active anodes. Electrodepositions were carried out galvanostatically using a Potentiostat/Galvanostat without stirring, until the deposited alloy films grew to 100  $\mu\text{m}$ . Carbon and oxygen contents in the films were determined by the evolved gas analysis method. Electron spectroscopy for chemical analysis (ESCA) measurements were performed using monochromated Al  $K_\alpha$  radiation under operating pressures of less than  $10^{-6}$  Pa. Electron binding energies were referenced to that of C1s line (285.0 eV). Ion etchings were performed using a differentially pumped ion gun. X-ray diffraction measurements were performed using monochromated Cu  $K_\alpha$  radiation. The diffraction angles were referenced to those from a high-purity Si powder. The profiles of diffracted X-ray lines for calculating unit cell parameters were obtained with step scans performed at a step width of 0.02 deg and a holding time of 100 seconds.

Figure 1 shows the effects of cathodic current density on carbon and oxygen contents in Fe-C alloy films. Carbon content in the films increased from 0.43 to 1.26 mass pct with the increase in cathodic current density. Although the oxygen contents were nearly constant at about 0.01 mass

---

MASANOBU IZAKI, Senior Research Fellow, is with the Department of Inorganic Chemistry, Osaka Municipal Technical Research Institute, Osaka 536, Japan. TAKASHI OMI, Associate Professor, is with the College of Engineering, University of Osaka Prefecture, Osaka 593, Japan. Manuscript submitted April 21, 1995.