Textures in Carburized and Decarburized Steels*

By Kunio ITO**

Synopsis

Iron sheets prepared by decarburizing low carbon steel sheets were carburized in H_2 -CO-CO₂ atmosphere and decarburized in an N_2 -H₂-H₂O atmosphere again. Changes of the texture in the process were determined by an X-ray diffraction method.

The carburization brought about no preferred orientations in the sheets. Columnar grains in the decarburized ferrite zone of the previously carburized sheet showed a relatively sharp [110] fibre texture, whereas the decarburized ferrite zone showed a weak [731] texture when the surface layer of the carburized specimen was polished off prior to the decarburization.

The kinetics of the growth process of the ferrite zone by decarburization was measured directly by a high temperature X-ray diffraction technique. The kinetics was found to be much slower in the carburized sheet than in the specimen whose surface layer was polished off prior to the decarburization. It depended scarcely, however, on the orientation of either gamma matrix or ferrite nucleus.

It appeared that the origin of the preference of the orientation in columnar ferrite crystals should be searched mainly in the dependence of the nucleation frequency on the orientation of the nucleus.

I. Introduction

Many investigations have been reported on the preferred orientations of the columnar crystals grown either by solidification or by electrolytic deposition.¹⁾ It was known that columnar grains grow also in the decarburized zone of steel,²⁾ but no detailed investigations had been made on their preferred orientations.

The author carried out a series of investigations on the textures of the columnar ferrite crystals developed in 0.2 to 0.8 wt% C steels by decarburization at 740° to 880°C in H_2 -N₂ atmosphere containing water vapour.³⁾ The results are summarized as follows:

(1) When the carbon content of the steel is higher than 0.3 wt%, a weak simple fibre texture aligned in [731] orientation is obtained only by decarburizing at temperatures between (A_3+40°) and 860°C. The axis density figure of this texture is shown in Fig. 1. Hereafter this type of the preferred orientation will be called "the [731] preferred orientation" for short.

(2) The temperature (A_3+40°) is higher than 860°C in the case of 0.2 wt% C steel. Columnar crystals grown in this steel take a [100] fibre texture after the decarburization at 860° and 880°C.

(3) For the [731] preferred orientation to be obtained, it is necessary to austenitize the steel completely prior to the decarburization. In the growth process of the columnar crystals, no selection of orientation is done: the preferred orientation has been developed at the specimen surface during the gamma to alpha transformation.

Aspden⁴⁾ also observed a (100) [uvw] preferred

Fig. 1. Sheet surface normal density of the 0.3 wt% C steel decarburized at 860°C for 0.5 hr

orientation in iron sheets after annealing in hydrogen atmospheres in the gamma region and cooling slowly to alpha region.

In the present investigation, iron sheets prepared by decarburizing plain carbon steel sheets were first carburized and then decarburized again. The texture variation in the process was determined by an X-ray diffraction method. The growth rate of the ferrite zone by the decarburization was also measured by a high temperature X-ray diffraction technique and from metallographs.

The decarburized structure has been investigated by Pennington,²⁾ but not the growth rate of the ferrite band. The X-ray diffraction method employed in this study permits of a direct measurement of both the time elapses before ferrite crystals form on the specimen surface and the initial growth rate of the ferrite zone. Another characteristics of this method consists in the fact that the dependence of the kinetics of the transformation near the surface on the orientation of both gamma and alpha phases can be revealed.

II. Experimental Procedures

1. Preparation of Specimens

Material Sheet

Low carbon steel sheets cut from commercial hot rolled strips, 2.3 mm in thickness, were cold rolled to 1 mm, annealed at 920°C for 5 min in hydrogen, cold reduced to 0.6 mm, annealed at 920°C for 5 min in hydrogen, and decarburized at 740°C for 18 hr in wet hydrogen. The chemical composition of the finally

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** Department of Metallurgy and Materials Science, The University of Tokyo, Bunkyo-ku, Tokyo 113.

decarburized sheet was as follows: Si 0.01; Mn 0.31; P 0.009; S 0.016; C 0.001 in wt%.

Carburization

Hydrogen stream passed through a methanol-water mixture bath kept at a prescribed temperature was cracked into the carburizing atmosphere in an alumina tube of the first electric furnace kept at a prescribed temperature.

Each specimen was laid in the second furnace and heated in dry hydrogen. When the temperature of the second furnace reached the pre-set level, the atmosphere of the second furnace was replaced with the decarburizing one coming from the first furnace.

Carbon contents of the sheets were controlled by the ratio of methanol to water of the bath, its temperature, and the temperatures of the first and the second furnaces. For example, 0.8 wt% C was attained under the following conditions: the bath was of 100% methanol and kept at 0°C, the temperature of the first furnace was 860°C, and the iron specimen was held at 860°C for 13 hr in the carburizing atmosphere. The flow rate of hydrogen was controlled between 0.5 and 1.0 Nl/min.

Decarburization

A mixture of hydrogen and nitrogen (1:1), which was passed through water kept at 25°C, was used for the decarburization (where P_{H_2O}/P_{H_2} is equal to 0.06). The flow rate of the gas was controlled to 2 to 4 Nl/min, and the cross section of the alumina tube was 11.4 cm².

Two modes of time-temperature cycle were employed. In the cycle 1, specimens were furnace cooled in hydrogen to the decarburizing temperature after the carburization, then the atmosphere was changed to decarburizing. In the cycle 2, specimens were pulled out into the cold chamber after the carburization to cool to room temperature in hydrogen. Then the specimens were pushed again into the hot zone now kept at the decarburizing temperature and heated in hydrogen. The atmosphere was changed to decarburizing after 10 min. The sheets were cooled in hydrogen after the decarburization.

The phase transformation does not occur in the former cycle between carburization and decarburization, whereas specimens transform from gamma phase to alpha on cooling and reversely on heating during the

latter cycle. The texture of the gamma phase prior to the decarburization can thus be different if the carburization brings about a preferred orientation in the gamma phase and if the orientation changes irreversibly by the transformation.

2. Determination of Preferred Orientations

Pole Density Distribution Curves

The specimen surface was etched in a solution of $H_3PO_4-H_2O_2$ (1:1) to remove 0.05 mm prior to the measurement unless stated otherwise. Pole figures were determined by Schulz's reflection method from 0° to 60°C of the tilting angle α from the sheet surface normal. The average intensity $I(\alpha)$ on the small circle of angle α expressed in random unit was plotted against α .

For measurements of the (110) and (200) poles CoK_α was used, and their intensities were measured by a G-M counter. MoK_α and a scintillation counter were used for the (222) pole.

Axis Density Figures

Axis densities of the sheet surface normal in the standard stereographic triangle were computed from three pole density distribution curves based on the principle of Jetter's method.⁵⁾ The triangle was divided into 64 sub-triangles. The angle α was divided by 2 deg. step. Sixty-four axis densities were computed from 90 pole densities by the least squares method.

3. Determination of the Growth Rate of the Ferrite Zone

Direct Measurement by a High Temperature X-ray Diffraction Technique

A specimen set on a high temperature stage of the goniometer was heated in dry hydrogen from room temperature to the decarburizing temperature in 10 min. The atmosphere was changed to decarburizing after 15 min of holding. The peak intensity $I(t)$ was measured against decarburizing time t .

The thickness of the ferrite zone $\xi(t)$ was calculated from the following equations* by the ratio of intensities, R :

$$R^{\gamma}(t) = I^{\gamma}(t)/I^{\gamma}_{\text{initial}},$$

$$R^{\alpha}(t) = I^{\alpha}(t)/I^{\alpha}_{\text{final}},$$

* When a layer of the alpha phase with a thickness ξ covers the gamma phase, each of the incident and the reflected X-ray beam is reduced by $\exp(-\mu\xi/\sin\theta)$ through the alpha phase in the experimental arrangement of the diffractometer. The diffracted intensity from the gamma phase under the layer of the alpha phase is therefore expressed as follows:

$$I^{\gamma}(\xi) = I^{\gamma}_0 \exp(-2\mu\xi/\sin\theta).$$

By definition R^{γ} should correspond to $I^{\gamma}(\xi)/I^{\gamma}(0) = \exp(-2\mu\xi/\sin\theta)$.

The diffracted intensity from a volume element of the alpha phase between x and $x+dx$ is similarly expressed as follows:

$$dI^{\alpha} = I^{\alpha}_0 \exp(-2\mu x/\sin\theta) dx,$$

where x is the distance from the surface. The total diffracted intensity from a layer of the alpha phase with a thickness ξ is obtained by integration from $x=0$ to $x=\xi$:

$$I^{\alpha}(\xi) = I^{\alpha}_0 (2\mu/\sin\theta) \{1 - \exp(-2\mu\xi/\sin\theta)\}.$$

The R^{α} should correspond to $I^{\alpha}(\xi)/I^{\alpha}(\infty) = 1 - \exp(-2\mu\xi/\sin\theta)$.

$$\xi^{\gamma}(t) = -\sin \theta \cdot \ln (R^{\gamma}(t)) / 2\mu,$$

$$\xi^{\alpha}(t) = -\sin \theta \cdot \ln (1 - R^{\alpha}(t)) / 2\mu.$$

Where the superscripts α and γ denote alpha and gamma phases, respectively; I_{initial} is the intensity prior to the decarburization, and I_{final} , that after a sufficiently long time; μ , the linear absorption coefficient of iron; and θ , the Bragg angle.

The time required for the ferrite zone to thicken to 0.5 micron (μ), i.e. t for $\xi=0.5 \mu$, was denoted by $t_{0.5\mu}$, and was arbitrarily used to designate the period of time elapsed before the change in the diffraction intensity due to the phase transformation became detectable. The $t_{0.5\mu}$ will conventionally be called the incubation period hereafter. The average growth rate $\langle V_{1,5} \rangle$ was defined by the following equation:

$$\langle V_{1,5} \rangle = 4/(t_{5\mu} - t_{1\mu}) \text{ } (\mu/\text{sec}),$$

the $t_{5\mu}$ and $t_{1\mu}$ being the time required for ξ to reach 5 and 1 μ , respectively, and the $\langle V_{5,10} \rangle$ was defined in the same manner.

Though, strictly speaking, the relation between ξ and t should have been expressed by continuously curved line, inasmuch as the curvature of such curves was large in the range of smaller ξ 's and they became fairly linear as ξ increased, two average rates were deemed satisfactory. The $t_{0.5\mu}$, $\langle V_{1,5} \rangle$, and $\langle V_{5,10} \rangle$ were used to show in somewhat phenomenological manner the dependence of the transformation kinetics on the surface orientation of both gamma and alpha phases.

Diffraction lines from gamma phase were measured by CoK_{α} , whereas those from alpha phase by either CoK_{α} or MoK_{α} . Mean values and confidence intervals for confidence coefficient of 95% were calculated from three measurements each.

Measurement on Metallographs

As the thicknesses of the ferrite zone beyond about 15 μ were not measurable by the X-ray diffraction technique, those ranging from 40 to 100 μ were measured on photomicrographs of the section of the decarburized sheets. The ξ^2 's were plotted against t , from which $(d\xi^2/dt)^{1/2}$ was obtained as the inclination of the curve.

4. Electron Diffraction from the Specimen Surface

Electron diffraction patterns from the surface were taken at beam acceleration of 80 kV with two carburized specimens, one of which was as carburized, whereas the surface layer of the other had been polished off. Both specimens had been annealed at 800°C for 10 min, then pulled out into the cold chamber to cool to room temperature in hydrogen prior to the diffraction experiment.

III. Experimental Results

1. Preferred Orientations

Figure 2 shows (200) pole density distribution curves of a carburized and cooled specimen. It was concluded from these results and the intensities from gamma phase spectral lines as revealed by the high temperature

1: at the specimen surface;
2: as 0.1 mm etched off the surface

Fig. 2. (200) pole density distribution of the sheet carburized at 860°C for 13 hr to 0.8 wt% C

1: by the time-temperature cycle 1; 2: by the cycle 2

Fig. 3. (200) pole density distribution of the sheet carburized at 860°C for 7 hr to 0.3 wt% C and decarburized at 860°C for 2.5 hr

X-ray diffraction that no clear preferred orientation was formed in gamma phase by the carburization.

Figure 3 shows (200) pole density distribution curves of two specimens, one decarburized in the cycle 1 and the other in the cycle 2. The axis density figure of the specimen decarburized in the cycle 2 is shown in Fig. 4. Both cycles result in the formation of [110] preferred orientation in the columnar ferrite crystals.

Figure 5 shows (200) pole density distribution curves of two specimens after decarburization. The surface layer of one specimen was polished off on the metallographic buff after the carburization. The other specimen, whose surface layer had been polished off after the first carburization, was annealed once again in the same carburizing atmosphere, then finally decarburized. It will be seen in the figure that, while the

Fig. 4. Sheet surface normal density of the steel whose (200) pole density distribution is shown in Fig. 3, curve 2

1: carburized at 860°C for 13 hr to 0.8 wt% C, surface layer polished off, annealed as the first carburization, and decarburized at 800°C for 3 hr
2: carburized at 860°C for 7 hr to 0.3 wt% C, surface layer polished off, and decarburized at 860°C for 2.5 hr

Fig. 5. (200) pole density distribution of decarburized sheets

former has resulted in the [731] preferred orientation, the latter has given rise to the [110] preferred orientation. This [731] preferred orientation is the same as that was obtained by decarburizing carbon steels that were not treated in the carburizing atmosphere.³⁾ The results show that the [110] preferred orientation originates not in the autonomous transformation from alpha to gamma phase by carburization but in the properties of the specimen surface that have been given birth to by annealing in the carburizing atmosphere.

Hereafter the carburized specimen whose surface layer was polished off prior to the decarburization will be called "the polished off specimen," whereas that which was left as carburized will be called "the carburized specimen."

Pole densities were measured for the specimens carburized to 0.8 wt% C at 800° to 930°C and decarburized at 740° to 880°C, and for the specimens car-

burized to 0.3 wt% C at 860° to 930°C and decarburized at 860°C. The [110] preferred orientation was always observed in these specimens. Sharper textures were brought about by carburizing at lower temperatures and decarburizing at medium temperatures.

2. Growth Rate of the Ferrite Zone

Decarburization Rate Measured by the High Temperature X-ray Diffraction

Photographs 1 (a), (b), (c), and (d) show changes in $(311)_\gamma$ and $(110)_\alpha$ intensities during the decarburization. It will be observed in the photographs (a) and (c) that the peak of the diffraction lines from the gamma phase shifts according to the change in lattice constant by the decarburization. In the case of the carburized specimen the peak shift was followed by repeatedly scanning in the early period for several minutes, then the counter was moved by the angle, which was determined taking further shift into account and fixed thereat, as shown in Photo. 1 (c). In the case of the polished off specimen, on the other hand, the counter was fixed during the whole decarburizing time at this predetermined angle. In this case the original off-set in the counter position is cancelled by the progressive shift of the peak, and the recorded intensity increases at first as shown in Photo. 1 (a).

The $t_{0.5\mu}$'s, $\langle V_{1,5} \rangle$'s, and $\langle V_{5,10} \rangle$'s calculated from the diffraction data recorded on charts are shown in Figs. 6 and 7. It will be seen that the rate of the decarburization in the early stage is very much different between the polished off and the carburized specimens. The differences in the kinetics due to diffraction indices are, however, in the natural scatter range of the measurements. The time elapses before the atmosphere within the furnace has been changed from dry hydrogen to decarburizing by turning the switch cock was estimated less than 5 to 6 sec from the observation of the peak shift of the diffraction lines from the polished off specimen. The net $t_{0.5\mu}$'s must therefore have been smaller by several seconds than those in Figs. 6 and 7.

Growth Rate of the Ferrite Zone Determined from Photomicrographs

Photographs 2 (a), (b), and (c) show the ferrite zones developed by the decarburization. The values of $(J_z^2/Jt)^{1/2}$ determined from photomicrographs are tabulated in Table 1 (p. 93). The difference in the growth rate between the polished off and the carburized specimens is less for thicker ferrite zone.

The average diameter of the columnar crystals was comparable to that of the gamma matrix, and the interface between alpha and gamma phases was jaggy in the early stage of the decarburization, though it became smooth after the former has grown to a certain thickness.

3. Electron Diffraction Patterns from the Specimen Surface

The carburized specimen always showed distinct rings as shown in Photo. 3 (a), whereas the polished off specimen showed only diffuse patterns as shown in Photo. 3 (b). Strong lines in Photo. 3 (a) are those from the cubic magnetite (Fe_3O_4),⁶⁾ and weak lines are

Photo. 1.

Changes in peak intensities during the decarburization as observed by high temperature X-ray diffraction

(a) and (b) From the polished off specimen with 0.8 wt% C

(c) and (d) From the specimen carburized at 860°C for 13 hr to 0.8 wt% C

Fig. 6. Decarburization kinetics of the polished off 0.8 wt% C specimen determined by high temperature X-ray diffraction. The dependence of the kinetics on diffraction index and on temperature was measured at 805°C and by the (111) γ diffraction, respectively. Indices with * mark were measured by MoK α and the others by CoK α .

Fig. 7. Decarburization kinetics of the carburized 0.8 wt% C specimen determined by high temperature X-ray diffraction. Notations are the same as Fig. 6.

from the hexagonal hematite (α -Fe $_2$ O $_3$)⁽⁶⁾ and the cementite (Fe $_3$ C).⁽⁷⁾

It was concluded that a thin oxide film consisted of a thin α -Fe $_2$ O $_3$ layer and a thicker Fe $_3$ O $_4$ layer^{(8),(9)} was formed on the surface of the carburized specimen

during cooling, and with the polished off specimen, on the other hand, the oxide film did not develop so fully that sharp diffraction patterns were not obtained. These results demonstrate an aspect of the differences in the surface properties between the polished off and the carburized specimens.

4. Effect of Composition on the Preferred Orientations

In the previous experiment,⁽³⁾ the angle α repre-

Photo. 2. Sections of decarburized sheets

- (a) Both the upper and the lower are the polished off 0.8 wt% C steel decarburized at 790°C for 2 min ($\times 600$) ($\times 2/3$)
- (b) Both the upper and the lower are the steel carburized at 860°C for 13 hr to 0.8 wt% C and decarburized at 790°C for 10 min in the time-temperature cycle 2 ($\times 600$) ($\times 2/3$)
- (c) The specimen and the process are the same as (b) except decarburizing time: the upper was decarburized for 40 min, whereas the lower for 80 min ($\times 150$) ($\times 2/3$)

senting the peak of pole density distribution curves differed slightly from specimen to specimen. As it was then thought that the difference in the texture was caused by the difference in the composition of the steel, the effects of silicon and manganese on the texture have been examined in the present study.

Specimens were prepared from an electrolytic iron melted in vacuum by high frequency induction, and silicon and manganese were added so that compositions ranging from 0.005 to 0.31 wt% silicon and from 0.005 to 0.22 wt% manganese would result.

As shown in Fig. 8, as the content of silicon increases the peak of the pole density distribution curve shifts several degrees for the case of [731] preferred orientation, but manganese has no effect on it. The [110]

Photo. 3. Electron diffraction patterns from the specimen surface

- (a) Carburized at 860°C for 13 hr to 0.8 wt% C, then prior to the diffraction annealed at 800°C for 10 min and cooled in hydrogen
- (b) Carburized likewise, but the surface layer of the specimen was polished off prior to annealing

texture, on the other hand, has the tendency to become sharper, the larger the ratio of manganese to silicon, as shown in Fig. 9.

IV. Discussion of Results

1. Decarburization Rate

The kinetics of the decarburization of the steel has in many cases¹⁰⁾⁻¹²⁾ been calculated by solving the diffusion equation of carbon under the boundary condition of the constant concentration at the specimen surface on the assumption that the chemical reaction rate at the surface is large enough. Some investigators¹³⁾⁻¹⁵⁾ reported, however, that the decarburization rate depends on the atmosphere used, an observation that probably means that the reaction rate at the gas-metal interface affects the decarburization kinetics.

If the reaction rate at the surface is assumed to be independent of the carbon concentration after Doehle-mann,¹⁵⁾ at least in the range where the surface concentration C_s in Fig. 10 (a) is larger than C° in (c), which depicts a schematical phase diagram, the flux of carbon at the surface J can be put as constant, and the concentration profile $C(x,t)$ in Fig. 10 (a) may be expressed by the following equation for a semi-infinite slab and a constant diffusivity of carbon in gamma iron D_c^γ :

$$C(x, t) = C_0 - 2 \frac{J}{D_c^\gamma} \left\{ \sqrt{\frac{D_c^\gamma t}{\pi}} \exp\left(-\frac{x^2}{4D_c^\gamma t}\right) - \frac{x}{2} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_c^\gamma t}}\right) \right\},$$

Fig. 8. Effects of silicon and manganese on the (200) pole density distribution of the 0.8 wt% C steel decarburized at 860°C for 3 hr

Fig. 9. Effects of silicon and manganese on the (110) pole density distribution of the sheet carburized at 860°C for 13 hr to 0.8 wt% C and decarburized at 860°C for 3 hr in the time-temperature cycle 2

where t is the decarburizing time, and erfc is the complementary error function. The $C_s(t) = C(0, t)$ is then obtained as follows:

$$C_s(t) = C_0 - 2J\sqrt{\frac{t}{\pi D_c^{\alpha}}}$$

The J 's were estimated by substituting average $t_{0.5\%}$'s of Figs. 6 and 7 for t , C_i° for C_s , and 0.79 wt% for C_0 on the assumption that alpha phase nucleates from gamma matrix when C_s reaches C_i° . The D_c^{α} is known as a function of the carbon concentration,¹⁶⁾ and values correspondent with the concentration $(C_0 + C_i^{\circ})/2$ were used in this paper. The J , which is the estimated apparent surface reaction constant, was 0.11 and 0.025 wt% μ /sec at 805°C for the polished off and the carburized specimens, respectively.

When Wagner's¹⁷⁾ equation is applied to the decarburization of the carbon steel with a carbon concentration profile as shown in Fig. 10 (b), where C_s is assumed to be constant in accordance with the phase diagram shown in (c), Eqs. (1) and (2) should hold for a semi-infinite slab and a constant D_c^{α} .

$$\xi = 2\eta\sqrt{D_c^{\alpha}t}, \dots\dots\dots(1)$$

$$C_i^{\circ} - C_a^{\circ} = (C_a^{\circ} - C_s)f(\eta) - (C_0 - C_i^{\circ})g(\eta\sqrt{\phi}), \dots\dots(2)$$

$$(d\xi^2/dt)^{1/2} = 2\eta\sqrt{D_c^{\alpha}}, \dots\dots\dots(3)$$

where, $f(\eta) : \exp(-\eta^2)/(\sqrt{\pi}\eta \text{erf}(\eta))$,
 $g(\eta\sqrt{\phi}) : \exp(-\eta^2\phi)/(\sqrt{\pi}\eta\sqrt{\phi} \text{erfc}(\eta\sqrt{\phi}))$, and
 $\phi : D_c^{\alpha}/D_c^{\gamma}$, and D_c^{α} is the diffusivity of carbon in alpha iron.

By substituting proper values into C_a° ,¹⁸⁾ C_i° ,¹⁹⁾ D_c^{α} ¹¹⁾ and D_c^{γ} ,¹⁶⁾ and letting C_0 and C_s be 0.79 and 0.001 wt%, respectively, Eq. (2) was solved for η by numerical computation. Values of $\langle V_{1,5} \rangle$ and $\langle V_{5,10} \rangle$, which were calculated formally from Eq. (1), and of $(d\xi^2/dt)^{1/2}$ as calculated from Eq. (3) are given in Table 1.

These values show that the growth rate of the columnar ferrite crystals in the early stage of the decarburization is affected by the reaction rate at the surface. For large ξ , the calculated values agree fairly well with the observed ones. Provided that the zone is thick enough, the growth rate of the ferrite zone by the decarburization of gamma phase will become calculable by solving the diffusion equation of carbon under the boundary condition of the constant surface concentration as done by Smith¹¹⁾ for the decarburiza-

Fig. 10. Schematic concentration profiles and phase diagram

Table 1. The growth rates of the ferrite zone, as observed and as calculated. The observed $\langle V_{1,5} \rangle$ and $\langle V_{5,10} \rangle$ are shown in Figs. 6 and 7.

Decarburizing temperature (°C)	Observed $(d\xi^2/dt)^{1/2}$ ($\mu/\text{sec}^{1/2}$)		Calculated values		
	Carburized specimen	Polished off specimen	$(d\xi^2/dt)^{1/2}$ ($\mu/\text{sec}^{1/2}$)	$\langle V_{1,5} \rangle$ (μ/sec)	$\langle V_{5,10} \rangle$ (μ/sec)
790	1.9	2.6	2.83	1.34	0.534
805	2.1	2.2	2.80	1.31	0.521
820	2.3	1.9	2.73	1.24	0.497

tion of two phase alloys of iron and carbon.

2. Formation of the Preferred Orientations

As stated previously, the preferred orientations in the decarburized ferrite zone are developed in the early stage of the formation of ferrite crystals and influenced by the conditions of the specimen surface. The free surface energies, of gamma phase σ_γ and of alpha phase σ_α , are parameters representing the surface properties as well as the surface reaction rate.

As the reaction rate at the gas-metal interface is known to depend at least in some instances^{(20),(21)} on the crystallographic orientation of the metal surface, the possibility of the dependence of the surface reaction rate in decarburization on the orientation of gamma and alpha irons cannot be denied *a priori*. If this happens, the incubation period will depend on the orientation of gamma matrix and the growth rate of columnar crystals on their orientations. The experimental results were, however, that the dependence of the decarburization rate on the orientation of either gamma phase or alpha phase was not very large, if any, as shown in Figs. 6 and 7.

Gamma phase seems not to take clear preferred orientations as mentioned previously. The average diameter of the columnar ferrite grains would be larger by far than that of gamma matrix if the nuclei of alpha phase formed only on specially oriented gamma grains because of the dependence of such factors as surface reaction rate and σ_γ on the surface orientation. Metallographs revealed that such is not the situation.

The concentration distribution in a plane parallel to the surface would be uniformized after certain growth of the ferrite zone unless the difference in the surface reaction rate was extremely large, because the diffusivity of carbon in alpha iron would surely be large in comparison with the reaction rate. The dependence of the reaction rate on the orientation of alpha phase thus probably has little effect on the relative growth rate of nuclei.

The reason for the formation of the preferred orientation in the decarburized columnar ferrite crystals must thus be searched mainly in the difference in the dependence of the nucleation rate on the orientation of the nucleus, this, in turn, is probably attributable to the dependence of σ_α on the surface orientation. When the interfacial energy between alpha and gamma

Fig. 11. A mutual encroachment of nuclei by impingement

phases depends on the relative orientation between alpha nucleus and gamma matrix, this is very likely,⁽²²⁾ then the texture of alpha phase will be affected by that of gamma phase. When gamma phase has no preferred orientation, as is the case of this experiment, this will make the texture of alpha phase diffuse.

Nuclei must encroach upon each other in the process of the growth. A kind of impingement can be analyzed in the following manner: Let the triple point P in Fig. 11 move towards P' . When the direction of PP' or the angle θ is calculated on the principle that the maximum free energy drop be gained at a constant transforming volume by the migration of the interface between alpha and gamma phases, Eq. (5) is obtained under inequality (4):

$$\sin^2 \theta_0 > \frac{|\sigma_{\alpha_2/\gamma} - \sigma_{\alpha_1/\gamma}|}{\sigma_{\alpha_1/\alpha_2}}, \dots\dots\dots(4)$$

$$\sin \Delta\theta = \frac{\sigma_{\alpha_2/\gamma} - \sigma_{\alpha_1/\gamma}}{\sin \theta_0 \sigma_{\alpha_1/\alpha_2}}, \dots\dots\dots(5)$$

Then θ is calculated from the following equations: $\theta = \theta_0 + \theta_2 - \Delta\theta$ and $\theta_0 = \pi/2 - (\theta_1 + \theta_2)/2$. The $\sigma_{\alpha_1/\gamma}$, $\sigma_{\alpha_2/\gamma}$, and $\sigma_{\alpha_1/\alpha_2}$ are the interfacial energy between α_1 and γ , α_2 and γ , and α_1 and α_2 , respectively. Inequality (4) may in actuality hold always.

The probability that θ_1 is larger than θ_2 must be high when σ_{α_1} is larger than σ_{α_2} if θ_1 and θ_2 satisfy the equation, $(\sigma_\gamma - \sigma_\alpha)/\sigma_{\alpha_1/\gamma} = \cos \theta$, according to the heterogeneous nucleation model. When θ_1 is larger than θ_2 , α_1 can go round ahead of α_2 even if $\sigma_{\alpha_2/\gamma}$ is equal to $\sigma_{\alpha_1/\gamma}$, i.e. $\Delta\theta = 0$. If $\sigma_{\alpha_2/\gamma}$ is larger than $\sigma_{\alpha_1/\gamma}$, α_1 goes further round ahead of α_2 . The $\Delta\theta$ is large when θ_0 is small as shown in Eq. (5). It will be that the encroachment of this type is therefore to occur only near the surface, for θ_1 and θ_2 approach to zero with the thickness of the ferrite zone as is observed in metallographs. On the basis of this analysis that the grains left on the surface tend to take orientations near (100)⁽³⁾ can be explained because the free surface energy of a (100) plane is relatively low.^{(23),(24)}

The grains with small σ_α are thus concluded to tend to be left on the surface by the impingement of nuclei. It may be due to the small orientation dependence of the free surface energy σ_α that with the polished off specimen the texture after the decarburization is diffuse and the preferred orientation is difficult to be considered coincident with the orientation of the minimum σ_α . By the carburized specimen, on the other hand,

the texture is sharp, and the preferred orientation can reasonably be considered to be the orientation of the minimum σ_α .²³⁾ As shown by the experimental results of this study the difference in the properties of the surface between the polished off specimens and the carburized ones is very large. The dependence of σ_α on the orientation, therefore, must also be significantly different.

V. Summary

Iron sheets carburized in H_2 -CO-CO₂ atmosphere to 0.3 to 0.8 wt% C were decarburized in an N_2 - H_2 -H₂O atmosphere.

The changes in texture were determined by the X-ray diffraction method. The carburization brought about no preferred orientations in the sheets. Columnar grains in the decarburized ferrite zone of the sheet, previously carburized, showed a relatively sharp [110] fibre texture, whereas the decarburized ferrite zone showed the [731] texture, a texture which was already reported by the author in other steels when the surface layer of the carburized specimen was polished off prior to decarburization.

The kinetics of the gamma to alpha transformation in the early stage of decarburization was directly measured by the high temperature X-ray diffraction technique. The observed kinetics showed that the reaction at the surface offers resistance to the flux of carbon atoms. The estimated flux for the polished off specimen was larger than that for the carburized specimen by a factor of 3 to 5. The dependence of the decarburization rate on the orientation of either gamma phase or alpha phase was found to be not very large, if any.

The electron diffraction patterns from the specimen surface also showed the difference between the polished off specimens and the carburized ones.

Both [110] and [731] preferred orientations developed in the early stage of the formation of the ferrite zone. The reason for the preference of the orientations in columnar crystals should be searched mainly in the dependence of the nucleation frequency on the orientation of the nucleus. It is very likely that the free surface energy of (110) plane is so small in the carburized specimen that the ferrite grains attain the sharp [110] texture. The [731] preferred orientation in the polished off specimen, which is hardly related

to a plane of a low surface energy, however, could hardly be considered to be formed by the difference in the nucleation frequency only.

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REFERENCES

- 1) G. Wassermann and J. Grewen: *Texturen Metallischer Werkstoffe*, (1962), 122, 139, Springer.
- 2) W. A. Pennington: *Trans. ASM*, **37** (1946), 48.
- 3) Hideo Abe and Kunio Ito: *J. Jap. Inst. Met.*, **32** (1968), 927.
- 4) R. G. Aspden, J. A. Berger, and H. E. Trout: *Acta Met.*, **16** (1968), 1027.
- 5) L. K. Jetter, G. J. McHargue, and R. O. Williams: *J. Appl. Phys.*, **27** (1957), 368.
- 6) Shizuo Miyake: *Sc. Pap. I.P.C.R.*, **31** (1937), 161.
- 7) Shigemaro Nagakura: *J. Phys. Soc. Japan*, **14** (1959), 186.
- 8) Takeo Iimori: *Sc. Pap. I.P.C.R.*, **34** (1938), 60.
- 9) E. A. Gulbransen and J. W. Hickman: *Trans. AIME*, **171** (1947), 1.
- 10) J. K. Stanley: *Iron Age*, **151** (1943), Jan. 21 p. 31, Jan. 28 p. 36, Feb. 4 p. 49.
- 11) R. P. Smith: *Trans. AIME*, **224** (1962), 105.
- 12) J. H. Swisher: *Trans. AIME*, **242** (1968), 763.
- 13) J. R. Low, Jr. and H. Gensamer: *Trans. AIME*, **158** (1944), 207.
- 14) R. M. Hudson: *Trans. AIME*, **227** (1963), 695.
- 15) E. Doehlemann: *Z. Elektrochem.*, **42** (1936), 561.
- 16) C. Wells, W. Batz, and R. F. Mehl: *Trans. AIME*, **188** (1950), 553.
- 17) C. Wagner: see W. Jost: *Diffusion in Solids, Liquids, and Gases*, (1960), 69, Academic Press, New York.
- 18) J. K. Stanley: *Trans. AIME*, **185** (1949), 752.
- 19) R. F. Mehl and C. Wells: *Trans. AIME*, **125** (1937), 429.
- 20) H. Leidheiser, Jr. and A. T. Gwathmey: *J. Amer. Chem. Soc.*, **74** (1948), 1200.
- 21) A. Rönquist and H. Fischermeister: *J. Inst. Metals*, **89** (1960/1961), 65.
- 22) Pierre Guiraldenq and Paul Lacombe: *Mem. Sci. Rev. Metal.*, LXII, No. 3 (1965), 215.
- 23) B. E. Sundquist: *Acta Met.*, **12** (1964), 67.
- 24) C. G. Dunn and J. L. Walter: *Trans. AIME*, **224** (1962), 518.