Dissociation and Dissolution of Cementite in Low-carbon Steel by Cold Rolling and Annealing*

By Hideo ABE,** Takeshi SUZUKI** and Jean Jacques LAVIGNE***

Synopsis

Annealing processes in low-carbon aluminium-killed steel sheets after 75% cold-rolling have been studied by means of vector analyses of the thermoelectric power vs. electrical conductivity plots on the basis of the postulates, that the gradient of the vector characteristic to dislocations is $500 \mu V \cdot \mu \Omega \cdot cm \cdot deg^{-1}$ in pure iron but decreases by trapping of carbon atoms, and that the gradient of the vector representing the cementite precipitation at 250°C is $310 \mu V \cdot \mu \Omega \cdot cm \cdot deg^{-1}$. It is speculated that a certain amount of carbon atoms is liberated from cementite and trapped by dislocations during cold rolling. The amount, which depends on the size and morphology of cementite particles, is correlated with the kinetics of recovery and recrystallization.

I. Introduction

Partial dissociation of cementite by cold working and dissolution of cementite into the deformed iron matrix during annealing have been reckoned to be of practical importance, in particular for the control of structure and properties in low-carbon sheet steels. However, only a few studies¹⁻³⁾ have been concerned with these problems.

Part of the carbon atoms liberated from cementite must be trapped by dislocations, while the rest enter the normal interstitial sites of dislocation-free regions in the iron matrix. In order to determine the rate of cementite dissolution in the deformed iron matrix, the amounts of carbon atoms trapped by dislocations and those drifted into the normal interstitial sites should be followed separately. In an interpretation of the thermoelectric power vs. electrical conductivity plot for an annealing process of a low-carbon aluminium-killed steel, the authors⁴⁾ suggested a possibility of semi-quantitative estimation of the amount of carbon atoms liberated from cementite and trapped by dislocations. The present paper presents several additional data and gives more detailed interpretation of cementite dissolution in the early period of annealing. The conclusions described in a recent paper⁵⁾ ought to be revised according to the consequences of the present paper.

II. Experimental

The material and the experimental procedure are the same as described in previous papers.^{4,5)} The material is a hot band of a low-carbon aluminium-killed steel. The chemical composition is given in Table 1. Three specimens, 100 mm long, 30 mm wide, and 2.96 mm thick, prepared from the hot band were referred to as specimens A, B, and C, according

to the additional heat-treatments shown schematically in Fig. 1. The microstructures of these specimens after their respective heat-treatments were as shown in a previous paper;⁵⁾ specimen A included fine spheroidal cementite particles, specimen B large pearlite colonies and eutectoid cementite particles located along grain boundaries, and specimen C very large cementite particles located at the edges or corners of ferrite grains.

These specimens were cold-rolled at room temperature (about 20°C) to 75% reduction in 22 passes through a two-high laboratory mill with working rolls 160 mm in diameter without lubrication. The times between passes were in a range between 20 sec and 30 sec. A large number of test-pieces prepared from the cold-rolled sheets were annealed by immersing for various times in a salt bath kept at $695^{\circ}C \pm 5^{\circ}C$ and subsequently quenched into iced water. Then, the thermoelectric power⁶⁾ and electrical conductivity of each test-piece were measured at 0°C. After that, every test-piece was tempered at 250°C for 50 hr and measurements were made again of the thermoelectric power and electrical conductivity at 0°C. All the data were plotted on the thermoelectric power vs. electrical conductivity graphs. The accuracy in the absolute value of thermoelectric power is at best of the order of $\pm 0.5\%$, but the relative accuracy is of

Table 1. Chemical composition. (wt%)

C	Si	Mn	P	S	sol.Al	insol.Al	sol.N
0.046	0.01	0.35	0.020	0.018	0.030	0.010	0.0060

Fig. 1. Schematic diagram showing the heat-treatments for specimens A, B, and C prior to cold rolling.

* Received March 10, 1980.
** Department of Metallurgy and Materials Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.
*** The Graduate School, The University of Tokyo. On leave from Institut de Recherches de la Sidérurgie Française, 78105 Saint Germain en Laye Cedex, France.

the order of $\pm 0.05\%$.

III. Results and Discussion

Figure 2 summarizes the thermoelectric power *vs.* electrical conductivity plots for specimens A, B, and C, cold rolled to 75% reduction, annealed for various times in a salt bath kept at 695°C and quenched into iced water. As noticed in a previous paper,⁴⁾ a period of about 6 sec was required to heat individual test-pieces up to nearly 695°C throughout the entire thickness. Therefore, the data within the initial period of 6 sec should be regarded as obtained by continuous heating.

The plot for specimen A was interpreted in the previous paper.⁴⁾ Similar but somewhat modified interpretation can be given for the other two specimens. The following discussion is valid for the early stages of annealing.

Shift of every data-point on tempering at 250°C for 50 hr is shown in the upper half of Figs. 3(a), (b), and (c) by the same representation as in the previous paper.⁴⁾ Filled circles attached by a number 1, 2, 3, etc. are respectively the data-points after annealing in the salt bath kept at 695°C for 1 sec, 2 sec, 3 sec, and so on, followed by quenching into iced water. Open circles attached by 1', 2', 3', etc. are the respective data-points after subsequent tempering at 250°C for 50 hr. Some of the corresponding data-points before and after the tempering are connected by solid lines for easy comprehension. The filled circle affixed by 0 is the data-point immediately after cold rolling, and it shifted to the point 0' after annealing at 250°C for 50 hr.

As reported elsewhere,⁵⁾ observation of the annealed structures by optical microscopy showed that primary recrystallization completed at 8 sec in specimen A, at 20 sec in specimen B, and at 12 sec in specimen C. Therefore, the data-point 8' for specimen A, 20' for specimen B, and 12' for specimen C can be regarded as their respective "purest states" in which the dislocation density is lower than 10^8 cm/cm^3 and the dissolved carbon content is very small equal to the equilibrium solubility of cementite at 250°C. Since

data-points 20 and 12, and 20' and 12', for specimen B nearly coincided each other, data-point 12' was taken as the purest state of this specimen.

The chain lines connecting data-points 0', 3', 4', 6', and 8' for specimen A, 5', 6', 8' and 12' for specimen B, and 0', 4', 5', and 12' for specimen C can be regarded as characteristic of dislocations to which carbon atoms have segregated (we call them as "carbon-deposited dislocations"⁴⁾). The gradient *g* of the chain line is 240 in specimen A, 250 in specimen B, and 290 in specimen C in the unit of $\mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$.

The solid lines 88' for specimen A and 12-12' for specimen B or C have exactly the same gradient of $310 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$. These lines can be regarded as representing the cementite precipitation at 250°C.⁴⁾

The thermopower *vs.* conductivity plots shown in Fig. 3 should be interpreted on the basis of the following postulates.

- (1) The gradient characteristic of dislocations in pure iron is $500 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$.^{6)*}
- (2) The gradient characteristic of "carbon-deposited dislocations" is lower than $500 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$ and decreases depending on the concentration of trapped carbon. The minimum gradient in the unit of $\mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$ is 240 of line 8'0' for specimen A, 250 of line 12'-5' for specimen B, and 290 of line 12'-0' for specimen C.
- (3) The gradient of a straight line representing the cementite precipitation at 250°C is $310 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$.⁴⁾

As described in the previous paper,⁴⁾ any straight line connecting two data-points in the thermopower *vs.* conductivity plot can be regarded as a position vector and the concept of vector analysis can be applied for the analysis of the plot. If we take an orthogonal coordinate system (O; $-\Delta S$, $-\Delta\sigma$), Fig. 4, in which the origin O is located at data-point 8' in the case of specimen A, and at data-point 12' in the case of specimen B or C, every data-point can be represented by the coordinates $(-\Delta S, -\Delta\sigma)$. The position vector of each data-point can be resolved into several component-vectors which have simple physical

Fig. 2. Absolute thermoelectric power *vs.* electrical conductivity plots for specimens A (●), B (▲), and C (■), cold rolled to 75% reduction, annealed by immersing for various times in a salt bath kept at 695°C and quenched into iced water.

* According to an unpublished work, the gradient characteristic of "pure dislocations" in the low-carbon aluminium-killed steel would be about $620 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$. The conclusions of the present paper are not affected by this modification.

meanings. The direction of a vector is determined by the gradient $\Delta S/\Delta \sigma$.

Fig. 3. The plots showing shift of data-points on tempering at 250°C for 50 hr and the diagrams showing conductivity differences, for specimens A (Fig. 3(a)), B (Fig. 3(b)), and C (Fig. 3(c)). The broken line designated by D, which has a gradient of $g=500 \mu V \cdot \mu \Omega \cdot \text{cm} \cdot \text{deg}^{-1}$, represents the change in dislocation density. For the details of the figures, see the text.

Fig. 4. The $(O; -\Delta S, -\Delta\sigma)$ coordinate system taken in the thermoelectric power (S) *vs.* electrical conductivity (σ) graph.

There are several kinds of elementary vectors which have simple physical meanings. They are the vector characteristic of "pure dislocations" defined by the gradient of $500 \mu\text{V} \cdot \mu\Omega \cdot \text{cm} \cdot \text{deg}^{-1}$, the vector representing the cementite precipitation at 250°C defined by the gradient of $310 \mu\text{V} \cdot \mu\Omega \cdot \text{cm} \cdot \text{deg}^{-1}$, and an infinite number of vectors characteristic of the "carbon-deposited dislocations", the gradient of which

depends on the concentration of trapped carbon.* Since there can be an infinite number of vectors which have simple physical meanings, we cannot obtain a unique solution of a plot mathematically. However, it is possible to deduce a physically most probable solution after several trial-and-error procedures. The final solution should be self-consistent so that all segments in a S - σ plot can be interpreted without inconsistency.

It was postulated that any position vector before the commencement of recrystallization would be a single vector characteristic of carbon-deposited dislocations with the gradient depending on the concentration of trapped carbon.** It was further postulated that any position vector during recrystallization could be resolved into two vectors; one representing the cementite precipitation at 250°C and the other characteristic of the carbon-deposited dislocations with the minimum gradient. The antiparallel vector of the former can be regarded as representing the dissolution of semi-coherent cementite particles into the dislocation-free regions of the iron matrix⁴⁾ and its length would be proportional to the amount of carbon atoms that have occupied the normal interstitial sites of the iron matrix.

The interpretation of the S - σ plots on the above postulates is made by the $(-\Delta\sigma)$ -component diagrams given below the S - σ plots in Fig. 3. The lengths of the filled columns in these diagrams are proportional to the amount of carbon atoms that have occupied the normal interstitial sites*** and the lengths of the open columns are proportional to the density of carbon-deposited dislocations. The value of gradient g in $\mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$ unit is noted in each open column. These diagrams include several physically inexplicable anomalies in the variation of the gradient and the length of each segment, though some of them can be attributed to fluctuation in the annealing and quenching operation. Neglecting such minor anomalies, the following explanation can be given on these diagrams.

The gradients of the carbon-deposited dislocations in state 0, or the cold-rolled state, are 350, 390, and $380 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$ respectively in specimens A, B, and C. All these values are lower than $500 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$ of pure dislocations, which suggests that a certain amount of carbon atoms must have been liberated from cementite and trapped by dislocations during cold rolling. The concentration of trapped carbon must have been largest in specimen A since its gradient is lowest.

By comparing the length of the open column for state 2 or 3 with that for state 2' or 3' in specimens A and B, it is presumed that the electrical resistivity contribution from a unit density of carbon-deposited

dislocations increases slightly with increasing the concentration of trapped carbon, or with a decrease of the gradient g . Taking this into consideration, a comparison of the lengths of $(-\Delta\sigma)$ -component for state 0 in the three specimens leads to a conclusion that the dislocation density after cold rolling was lowest in specimen B, and specimens A and C had nearly the same density.

In every specimen the g -value of carbon-deposited dislocations decreases in the sequence of state 0, 1, 2, and 3. The rates of the decrease in the three specimens do not differ noticeably. This means that there were no noticeable differences in "the rate" of cementite dissolution in these three specimens at least within the early period of annealing. However, this should not be confounded with the fact that "the quantity" of cementite dissolution at a given annealing time was always smaller in specimen C than in the other two specimens.

From the changes in length of the open column during annealing it is evident that the annihilation of dislocations before the commencement of recrystallization proceeded most slowly in specimen A and most rapidly in specimen C. The slow rate of dislocation annihilation in specimen A can be attributed to the strong pinning of dislocations by the segregated carbon atoms as indicated by its low g -values, though it should be taken into consideration that the degree of carbon-segregation must be much smaller at the annealing temperature than in the quenched state.

At the beginning of recrystallization, the gradients of the dislocation-vectors in specimens A, B, and C are 240, 250, and $290 \mu\text{V}\cdot\mu\Omega\cdot\text{cm}\cdot\text{deg}^{-1}$, respectively, indicating that the concentration of trapped carbon at that stage was highest in specimen A and lowest in specimen C, though, as mentioned above, the degree of carbon-segregation must have been much smaller at 695°C than in the quenched state.

The fraction recrystallized *vs.* log time graph is reproduced in Fig. 5 from the previous paper.⁵⁾ The commencement of recrystallization is faster in speci-

Fig. 5. The fraction recrystallized *vs.* log time graph.⁵⁾ Marks $\circ$, Δ , and $\square$ are for specimens A, B, and C, respectively.

* The vector characteristic of the carbon-deposited dislocations must be resolved into two components; one characteristic of pure dislocations and the other representing the adsorption of carbon atoms to dislocations. However, the gradient of the latter is at present unknown.

** The carbon-concentration profiles at the initial stages of cementite dissolution are not considered here because the present method gives no information on the inhomogeneity of carbon concentration.

*** They correspond to the "nominal dissolved carbon contents" defined in the previous paper.⁵⁾

men C than in specimen A or B, while the overall recrystallization rate around the stage of half recrystallization is lower in specimen C than in specimen A or B. The earliest commencement of recrystallization in specimen C appears to be explained by the weak pinning of dislocations by carbon atoms as indicated by the high gradients for the carbon-deposited dislocations in states 0, 1, and 2 given in Fig. 3(c), while the lowest recrystallization rate of this specimen can be explained as due to its lowest dislocation density in the unrecrystallized regions as seen from the short lengths of the open columns for states 3 and 4 in the diagram of Fig. 3(c). However, it should be remarked that the commencement of recrystallization is rather late in specimen B despite the low concentration of trapped carbon during the incubation period of recrystallization as indicated by the high values of the gradients in states 0, 1, 2, and 3 given in Fig. 3(b). As reported in the previous paper,⁵⁾ the earliest commencement of recrystallization in specimen C is obviously due to the acceleration of nucleation around large cementite particles, and the lowest recrystallization rate of specimen C is partly attributable to its low nucleation frequency as suggested by the large size of the recrystallized grains.

It is an established fact that the large cementite particles accelerate nucleation. The diagrams shown in Fig. 3 suggest that the rate of dislocation annihilation in the incubation period of recrystallization affected the overall recrystallization rate. The pinning of dislocations by carbon atoms seems to retard dislocation annihilation, resulting in a high recrystallization rate. When the amount of carbon atoms liberated from cementite and trapped by dislocations is large as in the case of specimen A, the rate of dislocation annihilation would be low and the overall recrystallization rate would be high. The reverse may be said of specimen C.

Liberation of carbon atoms from cementite to combine with dislocations during cold working has been expected to occur because the binding energy of a carbon atom with a dislocation ($0.5 \text{ eV}^{7)}$ is higher than that of a carbon atom in the cementite lattice ($0.4 \text{ eV}^{8-10)}$. Such a reaction was observed by Gridnev *et al.*¹⁾ by means of the measurements of the Mössbauer spectra in iron-1 wt.% carbon alloy cold rolled to a reduction of 90% in thickness, whilst the present study has shown that it occurs even in low-carbon steels. A result different from that by Gridnev *et al.* is the less amount of cementite dissociation in specimen B in which most of the cementite phase existed as lamellae in pearlite.

In the first plan for this series of experiments, it was attempted to cold roll the specimens with a very low concentration of carbon in solution. However, the present results have manifested that a certain amount of carbon atoms were liberated from cementite and trapped by dislocations during cold rolling. Such a reaction was found to occur most markedly in specimen A in which the cementite existed as fine spheroidal particles. In the previous paper,⁵⁾ it was emphasized that the size and spacing of cementite

particles affected the fine details of the deformation structure. In addition to the constrained deformation around the cementite particles as referred in that paper, the amount of carbon atoms liberated from cementite and trapped by dislocations should be taken into consideration as an important factor which might probably contribute to the formation of deformation bands during cold rolling.

Contrary to the opinion, proposed by Kubotera *et al.*,¹¹⁾ that emphasized the effect of the rate of cementite dissolution during annealing, the present study has suggested the importance of the amount of carbon atoms liberated from cementite and trapped by dislocations during cold rolling as a decisive factor which controls the kinetics of recovery and recrystallization.

Finally, it seems to be worthy of note that the gradients of the long-time segments for specimens A, B, and C are different as seen in the plots of Fig. 2. The gradients of the straight lines connecting the data-points in the period from 12 to 6 000 sec in specimen A, from 60 to 1 400 sec in specimen B, and from 30 to 1 400 sec in specimen C, are 260, 280, and $320 \mu\text{V} \cdot \mu\Omega \cdot \text{cm} \cdot \text{deg}^{-1}$, respectively. These gradients have been regarded as characteristic of the carbon in solution in the completely recrystallized iron matrices.⁴⁾ The differences of these gradients may be attributed to the differences in manganese content of their respective cementite (or θ) phases. It is likely that the annealing behaviour of the three specimens might be also affected by the manganese content of the cementite phase. This problem should be taken into consideration in the future studies of this series.

IV. Summary

Annealing processes in low-carbon aluminium-killed steel sheets have been studied by means of vector analyses of the thermoelectric power *vs.* electrical conductivity plots on the basis of the postulates, that the gradient of the vector characteristic of dislocations is $500 \mu\text{V} \cdot \mu\Omega \cdot \text{cm} \cdot \text{deg}^{-1}$ in pure iron but decreases by trapping of carbon atoms, and that the gradient of a vector representing the cementite precipitation at 250°C is $310 \mu\text{V} \cdot \mu\Omega \cdot \text{cm} \cdot \text{deg}^{-1}$. Main conclusions are summarized as follows:

- (1) A certain amount of carbon atoms is liberated from cementite and trapped by dislocations during cold rolling. The amount depends on the size and morphology of cementite particles.

- (2) The rate of cementite dissolution in the early period of annealing does not vary noticeably with the size and morphology of cementite particles contained in the hot band.

- (3) Annihilation of dislocations before the commencement of recrystallization is retarded owing to the pinning of dislocations by carbon atoms. The retardation is most marked when the cementite particles are fine.

- (4) The amount of carbon atoms liberated from cementite and trapped by dislocations during cold rolling is deemed to be a decisive factor which con-

trols the kinetics of recovery and recrystallization.

Acknowledgements

One of the authors, JJL, wishes to acknowledge the support of Institut de Recherches de la Sidérurgie Française enabling him to study at The University of Tokyo. He is also grateful to Mr. L. Coche, Directeur Général of IRSID, and to Dr. P. Parnière for their encouragement during the course of this work.

REFERENCES

- 1) V. N. Gridnev, V. V. Nemoshkalenko, Yu. Ya. Meshkov, V. G. Gavriluk, V. G. Prokopenko and O. N. Razumov: *Phys. Stat. Sol.*, (a) **31** (1975), 201.
- 2) P. M. Robinson, K. V. Barratt and P. N. Richards: *J. Aus. Inst. Metals*, **7** (1962), 34.
- 3) M. Sudo, M. Higashi and M. Ishigami: *Tetsu-to-Hagané*, **63** (1977), S866.
- 4) H. Abe and Tak. Suzuki: *Trans. ISIJ*, **19** (1979), 689.
- 5) H. Abe, Tak. Suzuki and Kim. Takagi: *Trans. ISIJ*, **21** (1981), 100.
- 6) H. Abe, Tak. Suzuki and H. Hoshina: *Trans. ISIJ*, **19** (1979), 355.
- 7) J. Friedel: *Dislocations*, Pergamon Press, Oxford, (1964), 407.
- 8) L. S. Darken and R. W. Gurry: *Physical Chemistry of Metals*, McGraw-Hill Book Co., New York, (1953), Chapt. 16.
- 9) R. A. Johnson, G. I. Diens and A. C. Damask: *Acta Met.*, **12** (1964), 125.
- 10) R. A. Johnson: *Acta Met.*, **15** (1967), 513.
- 11) H. Kubotera, K. Nakaoka, K. Araki, K. Watanabe and K. Iwase: *Tetsu-to-Hagané*, **62** (1976), 846.