Recovery of Lattice Defects in Cementite in Cold-Rolled Carbon Steels*

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Transmission electron microscopic observations were made on the recovery process of lattice defects in cementite in high carbon steels annealed after 92% cold rolling. Thermomagnetic and X-ray analyses were also performed as additional examinations.

No observable change in the defect structure of cementite occurs at temperatures below about 400°C. Annealing at higher temperatures results in the disappearance of the moiré pattern, a considerable decrease of dislocation density and the formation of well-developed subboundaries. Above about 600°C, these defects disappear gradually with the progress of spheroidization. These results suggest that the recovery of lattice defects in cementite is caused by polygonization accompanied by climbing or cross slipping of dislocations.

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I. Introduction

The present authors have investigated the deformation and fracture behaviors of cementite in steels by cold rolling^{(1)~(4)} and by tension^{(4)~(6)}, mainly by transmission electron microscopy. It has been shown that a large number of lattice defects such as dislocations and stacking faults are introduced into cementite by deformation. For instance, the dislocation density in cementite increases to the order of $10^{10}/\text{cm}^2$ by 92% cold rolling. This fact suggests that the deformation of cementite occurs in a tolerable degree prior to its fracture. It is therefore very interesting to examine the recovery process of these lattice defects in connection with the spheroidization of cementite. Up to date, the change in the shape of cementite in cold-worked steels by annealing has been observed only by optical and replica electron microscopy, and detailed information has not been obtained on the recovery of cementite. The purpose of the present investigation is to examine by transmission electron microscopy the recovery of lattice defects in cementite in steels annealed after cold rolling.

II. Experimental

Two kinds of plain carbon steels containing 1.23 %C and 1.25 %C were used. Their chemical compositions are shown in Table 1. The steels were prepared from electrolytic iron and white pig iron by induction melting in argon atmosphere. The ingots were hot-rolled and then cold-rolled to produce strips with 2 mm and 5 mm in thickness. They were austenitized at 1000°C for 30 min in argon atmosphere, followed by furnace cooling to obtain a large size of lamellar pearlitic cementite. The plates of 5 mm thick were cold-rolled to 1 mm and those of 2 mm thick to 0.16 mm. The respective reductions correspond to 80% and 92%.

Some of the plates were heated for 5 h at various temperatures in a temperature range from 200 to 700°C and the others for various periods up to 15 h at 700°C, followed by water cooling. The annealed plates were thinned to about 50 μm by chemical polishing in a solution containing hydrogen peroxide (100 ml) and hydrofluoric acid (5 ml), and finally electropolished by a modified Bollmann-method in an electrolyte containing 100 g of chromic acid and 200 ml of phosphoric acid. An HU-11 type of electron microscope was used at 100 kV with a tilting device of 10°.

Optical microscopic observations, X-ray

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Table 1 Chemical composition of specimens (wt %).

Specimen	C	Si	Mn	Ni	Cr	Al	P	S	Fe
No. 1	1.23	0.018	0.002	0.004	0.001	—	0.002	0.001	Bal.
No. 2	1.25	0.024	0.001	0.001	0.003	0.098	0.004	0.004	Bal.

diffraction, thermomagnetic analysis and Vickers hardness tests were also made. In X-ray diffraction, Co-K α radiation was used. The intensities of diffraction lines from 112, 021, 113 and 122 planes of cementite were measured by the point-counting method. In the magnetic analysis a magnetic balance with high sensitivity was used under a magnetic field of 3300 Oe. The specimen used was about 1 mg prepared by chemical polishing.

III. Results and Discussion

1. Optical microscopy

Optical microscopic observations were made to examine a structural change in the 92% cold-rolled 1.25%C steel by annealing for 5 h at various temperatures. At temperatures below 400°C no appreciable change in the morphology of cementite was observed. The coalescence and spheroidization of cementite began above about 400°C and became remarkable above 600°C. Such a spheroidization process is quite similar to those reported in previous papers⁽⁷⁾⁽⁸⁾.

2. Ultimate tensile strength and Vickers hardness

In Fig. 1, changes in the ultimate tensile strength σ and the Vickers hardness Hv are shown for 1.25%C steel cold-rolled to 80% reduction as a function of the annealing temperature in the case of annealing for 5 h. The annealing at 300°C results in an increase in hardness and strength, which decrease sharply in the temperature range from 300 to 500°C and gradually above 500°C. The observed sharp drops are undoubtedly due to the recrystallization of ferrite matrix, while the increases in strength and hardness around 300°C are caused by a static strain-aging effect in the ferrite matrix⁽⁹⁾⁽¹⁰⁾.

Fig. 1 Changes in ultimate tensile strength σ and Vickers hardness Hv of 1.25%C steel by annealing for 5 h at various temperatures after 80% cold rolling. C.W.: Cold Working.

3. Transmission electron microscopy

The above results show that the recrystallization of ferrite takes place above about 400°C, and the coalescence and spheroidization of cementite take place above about 600°C. In this section is described the results of transmission electron microscopic observation of the recovery process of lattice defects in cementite during annealing.

Photograph 1 shows the internal defects in cementite for 1.25%C steel cold-rolled to 92% reduction. A large number of dislocations and diffraction contrasts such as the moiré pattern and strain markings are seen in cementite plates. The corresponding selected area electron diffraction pattern indicates that the cementite lattice is heavily deformed.

Such a defect structure of cementite is not appreciably influenced by annealing below 400°C. In contrast, the structure of the fer-

Photo. 1 (a) Transmission electron micrograph showing the internal defects of cementite in 1.25%C steel cold-rolled to 92% reduction after furnace cooling. (b) Selected area electron diffraction pattern.

Photo. 2 (a) Transmission electron micrograph showing the recrystallization of ferrite in 1.25%C steel annealed for 5 h at 400°C after 92% cold rolling. (b) and (c). Selected area electron diffraction patterns taken from the regions A and B, respectively.

rite matrix changes remarkably by annealing below 400°C. Well-defined subgrains are observed in the ferrite matrix in 1.25%C steel annealed for 5 h at 300°C. In the specimen annealed for 5 h at 400°C, partially recrystallized grains are observed as shown in Photo. 2(a). These grains seem to have been formed either by the migration of subboundaries⁽¹¹⁾⁽¹²⁾ or by the coalescence of subgrains^{(13)~(15)}.

Photo. 3 Transmission electron micrograph showing the coarsening of cementite in 1.25%C steel annealed for 5 h at 500°C after 92% cold rolling.

The diffraction pattern (b) taken from the region A gives splitted diffraction spots, indicating remarkable polygonization of ferrite, whereas the diffraction pattern (c) taken from the region B gives distinct Kikuchi lines⁽¹⁶⁾, suggesting the formation of defect-free ferrite. Thus, the recrystallization of the ferrite matrix can be said to take place inhomogeneously at the initial stage of annealing. This is similar to the case of heavily rolled α -iron⁽¹⁷⁾⁽¹⁸⁾.

Photograph 3 shows a microstructure of 1.25%C steel annealed for 5 h at 500°C. This photograph indicates that cementite particles smaller than several thousands Å in diameter might be absorbed into larger cementite particles present on the grain boundaries of ferrite. Such a growth process of cementite is similar to that suggested by Sato *et al.*⁽⁷⁾ In large cementite particles with diameters more than several μm, no appreciable change in the defect structure is observed even after

annealing for 5 h at 500°C. This fact suggests that the recovery temperature of cementite is considerably higher than that of ferrite (about 300°C).

Another microstructure after annealing for 5 h at 500°C is shown in Photo. 4. A recovery region and an unrecovery region are coexistent in the same cementite particle as marked by A and B respectively in photograph (a): in the region A few dislocations are present, but in the region B dislocations are still densely populated. The photographs (b) and (c) are diffraction patterns taken from the respective regions A and B. Both regions have the surfaces nearly perpendicular to the $[001]_c$ direction and the orientation difference is small. Photograph 5 shows a defect structure of cementite annealed for 5 h at 600°C. Dense dislocations and strain markings are no longer observed, but dislocation networks formed by polygonization are observed. Spacings between the dislocations constituting the networks are still very small (about 350 Å), indicating that the lattice is inclined in a large degree at the

Photo. 4 (a) Transmission electron micrograph showing the recovery of cementite in 1.25%C steel annealed for 5 h at 500°C after 92% cold rolling. (b) and (c). Selected area diffraction patterns taken from the regions A and B, respectively.

Photo. 5 Transmission electron micrograph showing the formation of subboundaries in cementite in 1.25%C steel annealed for 5 h at 600°C after 92% cold rolling.

subboundary. This spacing increases to several thousand Å by annealing at 700°C.

Further detailed observations were made on the defect structure of cementite annealed for various periods up to 15 h at 700°C. In the case of annealing for 0.5 h, both the recovery and the unrecovery regions coexist in the same cementite particle, similar to the case of cementite annealed for 5 h at 500°C (Photo. 4). Photograph 6 shows a microstructure of cementite annealed for 1 h at 700°C. As seen in the photograph (a), the density of lattice defects differs in the three regions indicated by the marks of A, B and C. Photographs (b), (c) and (d) show three electron diffraction patterns taken from the regions of A, B and C, respectively. The incident direction of electron beam is nearly parallel to $[1\bar{2}2]_c$ and there is no appreciable difference in the crystal orientations among these regions. However, a difference is observed in the reflection spots: in the region A, where a relatively high density of dislocation are still left, the diffraction spots are splitted, while in the region C, where few dislocations exist, the Kikuchi lines appear distinctly. These results show that the annihilation of dislocations occurs inhomogeneously in the cementite particle.

Photograph 7(a) and (b) show examples of extensive dislocation networks formed by annealing at 700°C for 1 h and 15 h respectively. These networks lie nearly on $(001)_c$ which is one of the slip planes of cementite^{(1)~(4)(19)}. The average spacing between the dislocations is estimated to be 1000-

Photo. 6 (a) Transmission electron micrograph showing the recovery of cementite in 1.25%C steel annealed for 1 h at 700°C after 92% cold rolling. (b), (c) and (d). Selected area deffraction patterns taken from the region A, B and C, respectively.

Photo. 7 Transmission electron micrographs showing the formation of subboundaries in cementites in 1.25%C steel annealed at 700°C for 1 h (a) and 15 h (b) after 92% cold rolling.

4000 Å after annealing for 1 h and 1600-8000 Å after annealing for 15 h. In the present observations, all of the extensive dislocation networks are observed only on the (001)_c plane.

As described above, the annihilation behavior of lattice defects in the cementite particles with diameters of more than several μm is inhomogeneous, and this is different from the case in metals such as α-iron⁽¹⁷⁾⁽¹⁸⁾ and silicon-iron^{(13)(14)(20)~(22)}. In the case of metals, the recrystallization proceeds mainly from the migration of subboundaries or coalescence of subgrains. In the case of cementite, on the other hand, a number of dislocations introduced by deformation decrease gradually by their climbing or cross slipping as the annealing temperature and time increase. This annihilation temperature depends on the size of cementite particles, that is, it decreases with decreasing particle size. This seems to be associated with a local difference of internal strains introduced in the cementite particles by cold rolling.

From many electron micrographs, the dislocation density in cementite was measured as a function of annealing temperature. Figure 2 shows the result. The annealing time is 5 h and the average thickness of foils is about 1000 Å. The measurements were carried out by the aid of both Ham's method⁽²³⁾ and Ham and Sharpe's method⁽²⁴⁾. There is no considerable change in the density at annealing temperatures lower than 400°C. Above 500°C

Fig. 2 Change in the average dislocation density of cementite in 1.25%C steel by annealing for 5 h at various temperatures after 92% cold rolling. C.W.: Cold Working.

the density begins to decrease. It can be said therefore that the recovery of cementite occurs at the temperatures higher by about 200°C than that of the ferrite matrix.

4. X-ray and thermomagnetic analyses

Although transmission electron microscopy is powerful for studying the structural changes in cementite, the information obtained is obtained from the limited areas. Therefore, we performed X-ray and thermomagnetic analyses to obtain further information on the recovery of cementite in steels. The change in the integrated breadth of each diffraction peak of 113, 122, 112 and 021 from cementite is shown in Fig. 3 as a function of annealing temperature. Since the separations of the peaks 113 and 122 and of the 112 and 021 were difficult, the breadths were determined from the integrated breadths of overlapped peaks. All the integrated breadths begin to decrease rapidly near 300°C. A similar behavior is also observed in the diffraction peak positions as shown in Fig. 4, where the peak positions of 122, 112 and 113 are plotted as a function of annealing temperature. All the peak positions shift toward the high reflection angle side by cold rolling. This is probably due to a compressive strain introduced into cementite by cold rolling⁽²⁵⁾. The release of this strain begins to occur markedly at about 300°C. This temperature is lower than the temperature

Fig. 3 Change in the integrated breadth of diffraction lines of cementite in 1.25%C steel by annealing for 5 h at various temperatures after 92% cold rolling. C.W.: Cold Working.

Fig. 4 Change in the peak positions of diffraction lines of cementite by annealing for 5 h at various temperatures after 92% cold rolling. C.W.: Cold Working.

at which a remarkable decrease of the dislocation density begins. This may be due to the fact that the X-ray analysis gives mainly the information on the elastic strain. Therefore, it seems that the elastic strain is released prior to the rearrangement or annihilation of dislocations.

The Curie point of cementite in 1.25%C steel after 92% cold rolling was also measured

as a function of annealing temperature. The result is shown in Fig. 5. The Curie point rises from 210 to about 250°C by cold rolling as reported in previous work on carbon steels⁽²⁶⁾⁽²⁷⁾. The most remarkable decrease of Curie point by annealing occurs in the temperature range between 300 and 500°C, similar to the result by X-ray analysis.

As is evident from Figs. 4 and 5, the strain recovery of cementite is incomplete even after the annealing for 5 h at 700°C. This is compatible with the fact that small numbers of

Fig. 5 Curie point of cementite in 1.25%C steel annealed for 5 h at various temperatures after 92% cold rolling. C.W.: Cold Working.

dislocations still remain in the cementite annealed for 15 h at 700°C as seen in Photo. 7.

Based on the above results obtained from various experimental methods such as optical and transmission electron microscopy, X-ray and thermomagnetic analyses, the recovery processes of lattice defects in cementite and in ferrite in cold-rolled 1.25%C steel are summarized in Table 2. The recovery and recrystallization of ferrite take place in the range between about 300 and 400°C. Accompanied by the recrystallization of ferrite, the Vickers hardness and the ultimate tensile strength of steel are rapidly decreased as seen in Fig. 1. In cementite, on the other hand, the elastic strain introduced by deformation is released in the range of about 300 to 500°C, as suggested from data on the Curie point and the X-ray diffraction lines of cementite as well as from the disappearance of strain markings in cementite by transmission electron microscopy. At about 600°C at which the coalescence and spheroidization of cementite become remarkable, a marked decrease in the dislocation density and the formation of well-developed subboundaries take place in cementite. This temperature is in fair agreement with the temperature where the deformability of cementite

Table 2 The structural change in ferrite and cementite in 1.25%C steel by annealing for 5 h at various temperatures after 92% cold rolling.

Annealing temperature (°C)	300	400	500	600	700
Phase					
Ferrite	Recovery				
		Recrystallization			
			Grain growth		
Cementite	Elastic strain				
		Moire pattern			
			Disappearance of dislocation		
			Formation of dislocation network		
			Spheroidization		

increases remarkably, as reported by the present authors⁽²⁾⁽⁴⁾⁽⁶⁾. This information seems to be very important in understanding the warm-workability of high carbon steels containing cementite.

IV. Summary

Transmission electron microscopic observations were made on lattice defects in cementite in 1.25% C steel annealed after 92% cold rolling. Thermomagnetic and X-ray analyses were also performed as additional examinations. The results obtained are summarized as follows:

(1) In the case of isochronal annealing for 5 h in the temperature range from 200 to 700°C, no obvious changes in the defect structures of cementite take place at temperatures below 400°C. Annealing at higher temperatures results in the disappearance of the moiré pattern, a remarkable decrease of dislocation density and the formation of well-developed subboundaries. These defects disappear as the spheroidization takes place at temperatures above 600°C. The results suggest that the recovery of lattice defects is caused by polygonization accompanied by climbing or cross slipping of dislocations.

The recovery of lattice defects in the ferrite matrix proceeds by annealing below about 400°C, and its recrystallization starts from about 400°C and is completed at about 500°C. The growth of ferrite grains takes place at temperatures higher than 500°C.

(2) Isothermal annealing was carried out for various periods up to 15 h at 700°C. A remarkable decrease of dislocation density and the formation of subboundaries in cementite take place after annealing for 0.5 or 1 h. With increasing the annealing time from 5 to 15 h, the spacing between the dislocations constituting subboundaries increases slightly. On the other hand, the recrystallization of the ferrite matrix is completed within the annealing time of 0.5 h.

(3) X-ray and thermomagnetic analyses

indicate that a considerable decrease in the integrated breadth, slight shifts in the diffraction peak positions and a decrease in Curie point occur at the annealing temperatures of 300 to 500°C. These facts suggest that the elastic strain in cementite is released in this temperature range.

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