Microstructure of Si-Enriched Hard Drawn Steel Wire during Heat Treatment

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An increase in silicon (Si) additive amount to hard-drawn steel wire has successfully improved material characteristics such as tensile strength, fatigue limit and heat resistance. Enriched Si has also realized thinner spring wire and applications for engine valve springs. We have already reported on heat-resistance mechanism in the wire, which was improved by promoting solid solution strengthening of Si and strain relaxation by high-temperature annealing. This report describes a minute analysis on the reaction of cementite in heat-treated hard-drawn steel wire, which wasn't covered in our previous report. The reaction was examined by microstructure observation using a transmission electron microscope and crystallinity quantitatively evaluated by synchrotron radiation X-ray diffraction measurement. This study has revealed that, as for conventional wire equivalent to hard-drawn wire B (JIS SWP-B), strain created in wiredrawing process is relaxed under heat treatment and the cementite starts spheroidizing at 350 to 400 degrees C. Regarding our Si-enriched wire, however, cementite doesn't start spheroidizing below approximately 450 degrees C, maintaining lamellar structures compromised of 10-nm-order microcrystal. Thus, along with our previous report, this paper demonstrates the advantages of the Si-enriched hard-drawn wire from microstructural perspectives.

Keywords: transmission electron microscopy, X-ray diffraction, synchrotron radiation, hard drawn wire and cementite

1. Introduction

A wide range of springs come in various shapes and sizes for use in a variety of equipment such as mobile phones and automotives. Compact and lightweight components are increasingly demanded as expectations grow for the reduction of environmental impacts by such equipment. As for the development of springs, one of those components, high-strength steel wires are required. For engine applications such as valve springs, wires also need to have appropriate heat resistance. We have successfully developed steel wire satisfying the requirements above by adding excess Si up to 1.0% on the conventional hard drawn steel wire (SWP-B, Japan Industrial Standard) [(1)]. The developed Si-enriched wire demonstrates improvements in tensile strength by 10%, fatigue limit by 20% and heat resistance by 50% in comparison to the original wire. Our previous report [(2)] described the improvements, which are achieved by i) strengthening the solid solution of the Si in lamellar ferrite, and ii) reducing strains by high-temperature annealing. In this report, we discuss the reactions of cementite in pearlite lamellas.

2. Experimental procedure

2-1 Subject Material

The Chemical compositions of test wires are shown in **Table 1**. Our developed wire was enriched Si by 1.0% compared with Type B piano wire (SWP-B). Both wires were drawn to 3.6 mm in diameter, heat-treated to obtain pearlite lamella structures, and then drawn again to 1.2 mm in diameter. Drawn wires were heat-treated for 20 minutes at every 50 degrees C. from 300 to 600 degrees C. These heat-treated wires, As Drawn (before heat-treated) wires and patented (before drawing) wires were examined by microstructure observation and X-ray diffraction.

Table 1. Chemical composition of test materials (% m/m)

	C	Si	Mn	P	S
Developed	0.82	0.88	0.51	0.011	0.005
SWP-B	0.82	0.21	0.50	0.013	0.008

2-2 Microstructures observed by TEM

The thickness of cementite and ferrite in the pearlite lamellar structures of the test piano wires was several nanometers and tens of nanometers, respectively. In addition to the shapes of structures, we needed to consider the crystallographic characteristic of cementite. Therefore, transmission electron microscopy (hereinafter, TEM), which visualizes crystallographic information of atomic-level spatial resolution, was employed to observe microstructures in this study. We also used X-ray diffraction technique to cover the shortcomings of TEM that visualizes only local structures.

To observe microstructures using TEM, specimens should be thinned below 100 nm for electron transparency. In this study, electrolytic polishing was employed to minimize artifacts and damages during the specimen preparation process. More specifically, wires were thinned about 0.1 mm thick using emery papers with SiC abrading agent. These thinned specimens were then electropolished with CH_3COOH - 5% $HClO_4$ at 12 degree C. We conducted the electrolytic polishing until luster and very small holes were seen, and then those areas around the small holes were closely observed. With a microscopy of accelerating voltage of 300 kV, bright-field, dark-field and high resolution images were used to characterize the wire microstructures.

2-3 Crystallographic characterization by synchrotron radiation X-ray diffraction

X-ray diffraction (hereinafter, XD) technique can cover the shortcomings of TEM, such as i) possible artifacts and damages during sample preparation, ii) limited observation area of only a few nanometers, and iii) less quantitative capability. On the other hand, XD doesn't allow any intuitive and microscopic understanding. As seen above, TEM and XD make up for each other.

To avoid changes in microstructures, we did not carry out any other process to the test wires but cut them into 20 mm length with a clipper to mount on a diffractometer. **Figure 1** shows the diffraction peaks of cementite in the developed wire under heat treatment at 600 degree C. using three different diffractometers. **Figure 1 (a)** is the result of Bragg-Brentano method, which is widely used in powder diffraction. This method is suitable for powder or tabular block samples because strong diffraction peaks with high angular resolution can be obtained. However, as for the samples with curved surfaces, peak positions move depending on their height, resulting in widened diffraction peaks. In **Fig. 1 (a)**, the peaks of cementite in the wire cannot be recognized for the reasons mentioned above. **Figure 1 (b)** is the result of parallel X-ray beam method, by which the peak positions do not change even with the samples with curved surfaces. In **Fig. 1 (b)**, the diffraction peaks of cementite can be observed. However, the intensity and the angular resolution of the peaks were not good enough. In the parallel X-ray beam optics, the quality of incident X-ray dominates the performance of data including intensities and angular resolution. Therefore, a high quality X-ray source is needed for improved measurement. As shown in **Fig. 1 (c)**, using synchrotron radiation (hereinafter, SR) as an X-ray source distinguished diffraction peaks in various aspects, such as signal-to-noise-ratio, background, intensities and angular resolution, in comparison with **Fig. 1 (a) and (b)**. By using SR-XD mentioned above, the macroscopic characterization of cementite in the wire with curved surfaces was observed. In **Table 2**, the details of terms are described.

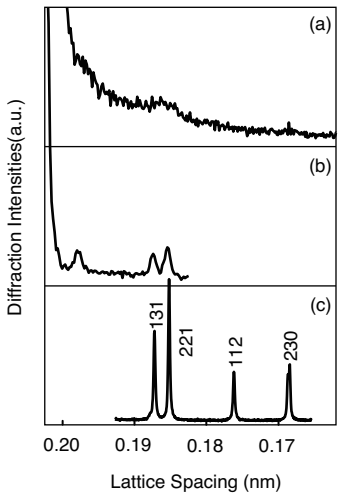

Fig. 1. X-ray diffraction from piano wires with 1.2 mmø
(a) Bragg-Brentano optics
(b) Parallel beam optics, (c) Synchrotron radiation

Table 2. Conditions of synchrotron radiation X-ray diffraction

Beamline	SPring-8 BL16XU (SUNBEAM ID)
Energy of X-ray	20keV、λ = 0.062nm
Beam Size	0.5mm × 0.5mm
Incident Angle	10 arcdegree
Detector Optics	Si 111 monochro + NaI scintillator
Measured diffraction angle (2θ)	18.5 ～ 21.5 arcdegree

3. Results and discussion

3-1 Microstructure

Figure 2 shows the results of TEM observations. In As Drawn samples of the developed and SWP-B wires, pearlite lamellar structures can be observed clearly. Here, the thicker layer was ferrite (α-Fe), while the thinner layer was cementite (Fe_3C). These figures illustrate the microstructure changes as cementite becomes sphere-like shape and lamellar structures are disrupted according to the heat treatment.

It seems that the temperature of microstructure changes is 50 degree C. higher in the developed wire than in SWP-B. To see that precisely, magnified micrographs are shown in **Fig. 3 and 4**.

Figure 3 is the microstructure of SWP-B wire heat-treated at 350 degree C and 400 degree C. As shown in these figures, SWP-B lamellas kept their structures, in other words cementite was plate-like, at about 350 degree C. At 400 degree C, however, plate-like cementite was broken into lines of sphere-like cementite as if the debris of lamella structures. On the other hand, as shown in **Fig. 4**, plate-like cementite in the developed wire was kept even at 400 degree C. At the 450 degree C. a part of the cementite started to form spheres of tens of nanometers, with the rest remaining plate-like structures As shown above, the temperature at which plate-like cementite changes its structures into sphere-like is risen by Si content.

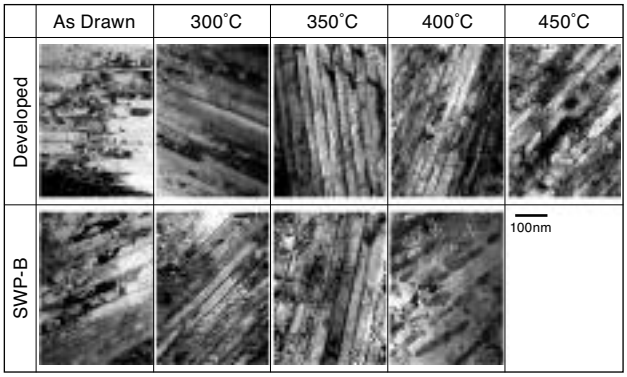

Fig. 2. Results of TEM observations

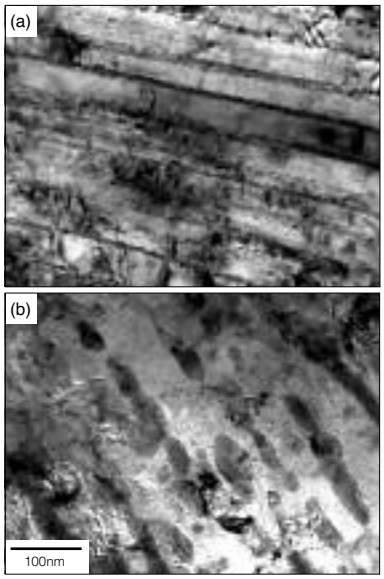

Fig. 3. Microstructures of SWP-B wire
(a) 350 ˚C × 20 min (b) 400 ˚C × 20 min

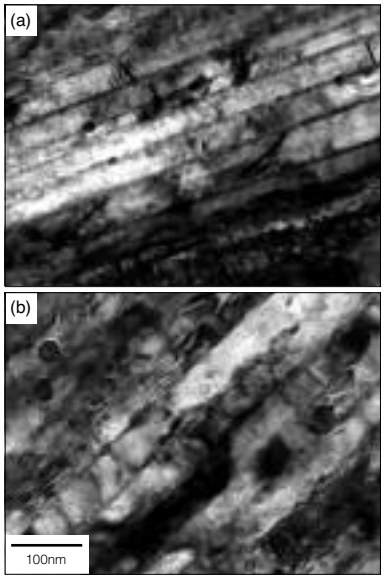

Fig. 4. Microstructures of the developed wire
(a) 400 ˚C × 20 min, (b) 450 ˚C × 20 min

plate-like shape to keep the pearlite structures.

To perform high resolution observations, there were a lot of constraints such as specimen thickness and crystallographic orientation, and therefore, it was difficult to observe a wide area or to compare many samples. Therefore, cementite in the wires was examined using dark-field images, which reflect the crystallographic information. **Figure 6 (a)** shows the dark-field image of As Drawn developed wire, and the cementite shows continua and approximately the same intensity, which implies the cementite is almost the same crystallographic orientation. As for the SWP-B wire with heat treatment at 300 degree C. as shown in **Fig. 6 (b)**, cementite shows almost the same as that of As Drawn shown in **Fig. 6 (a)**. On the other hand, as shown in **Fig. 6 (c)**, cementite of the developed wire under heat treatment at 300 degree C. shows discrete domain-like structure, which illustrates microcrystalline grains observed in high resolution images as in **fig. 5 (b)**.

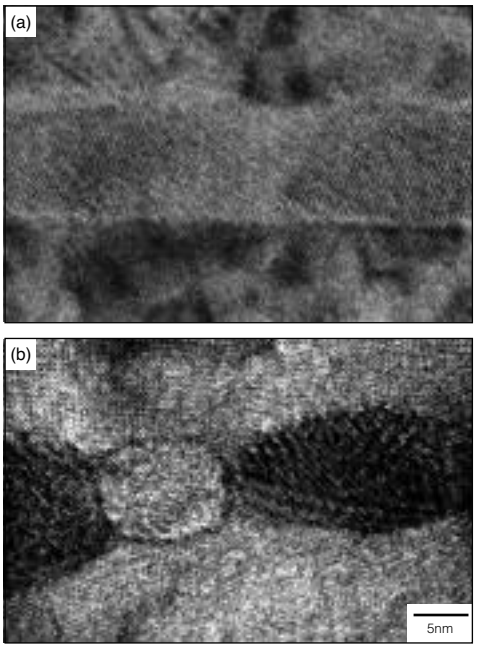

Fig. 5. HRTEM images of cementite
(a) As Drawn, (b) 350 ˚C × 20 min

To detect such structural changes inside of the cementite grain, the high resolution observation of cementite shown in **Fig. 5** was performed. Cementite is thought to grow in a plate-like form while pearlite structures are formed, and to be a single crystal or the like. **Figure 5 (a)** shows cementite in As Drawn sample of the developed wire, and the crystal lattice fringes of cementite were uniform in the field of view, which indicates the cementite is one crystalline grain. **Figure 5 (b)** is a micrograph of cementite in the developed wire heat-treated at 350 degree C. Although the cementite is in a plate-like form macroscopically, cementite was atomized into microcrystals of tens of nanometers, and such microcrystals formed the

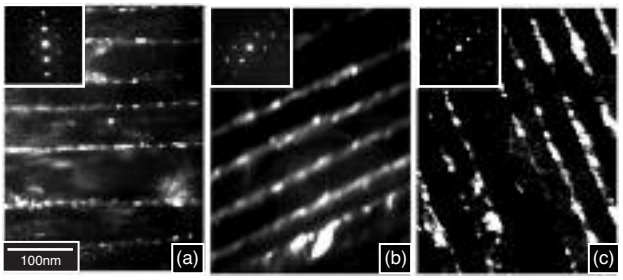

Fig. 6. Dark field images of the wire
(a) Developed As Drawn, (b) SWP-B 300 ˚C × 20 min
(c) Developed 300 ˚C × 20 min

As shown above, enriching Si contents makes difference in the reactions of microstructures. More specifically, in SWP-B wire, plate-like cementite formed a sphere-like shape at about 350 degree C. and lamella structures were disrupted simultaneously. On the other hand, in the developed wire, plate-like cementite kept its profile while it was atomized inside. Furthermore, the starting temperature for coarsening of cementite structures was higher by about 50 degree C, and as a result, lamella disruption started at a higher temperature.

3-2 Crystallinity of cementite

SR-XD measurements were performed to evaluate the reactions of cementite macroscopically and quantitatively as shown in **Fig. 7**. In this angular range, four peaks of cementite, 131, 221, 112 and 230, are observed. In undrawn wires, although peaks are broad and some peaks are overlapped each other, four peaks are recognized in both the developed and SWP-B wires. Drawing makes the peaks broader and heat treatment makes them sharp. Full widths at half maxima (hereinafter, FWHMs) become larger with the increase in the crystallographic strain by drawing. It also increases with the decrease in the crystallite diameter [5]. In **Fig. 7**, FWHMs of diffraction peaks seems to decrease with the increase in the heat treatment temperature, which is thought to be arose from the relaxation of strain and/or coarsening of cementite grains. To see the quantitative changes, FWHMs of 112 diffraction peaks were estimated using peak fitting by the pseudo-Voigt function. The results are shown in **Fig. 8**.

Before drawing, FWHM was about 0.2 arcdegree, and it increased to 0.4 arcdegree by drawing, which arose from the decrease in the size (thickness) of the cementite and strain accumulation by drawing. In the heat treatment process, the reactions of FWHMs in SWP-B wire and the developed wire were not the same. In SWP-B wire, FWHM monotonically decreased with the increase in the heat treatment temperature. It decreased to 0.2 arcdegree at 400 degree C, where the most part of cementite was confirmed to become sphere-like according to TEM observations. Therefore, the decrease in FWHM at this range of temperature is thought to be arisen from strain relaxation. Then it decreases to 0.07 arcdegree with the increase in the heat treatment temperature because of coarsening of cementite grain.

In the developed wire, on the other hand, FWHM increased with the increase in the heat treatment temperature up to 400 degree C, where the lamellar structures kept nano-crystalline cementite. Therefore, in this range of temperature, it is thought that FWHM was increased by the effect of crystalline atomization, and the fact confirms TEM observations. Over 450 degree C, FWHM decreased with the increase in the heat treatment temperature, which was arisen from the coarsening of cementite grains.

As described above, SR-XD measurement shows sharp contrast between the two wires, SWP-B and newly-developed Si-enriched wires. It also confirmed the result of TEM observations, meaning that the atomization of cementite grains is an intrinsic property of the developed wire, and it is not cause by the artifacts in sample preparation process or local singular phenomena.

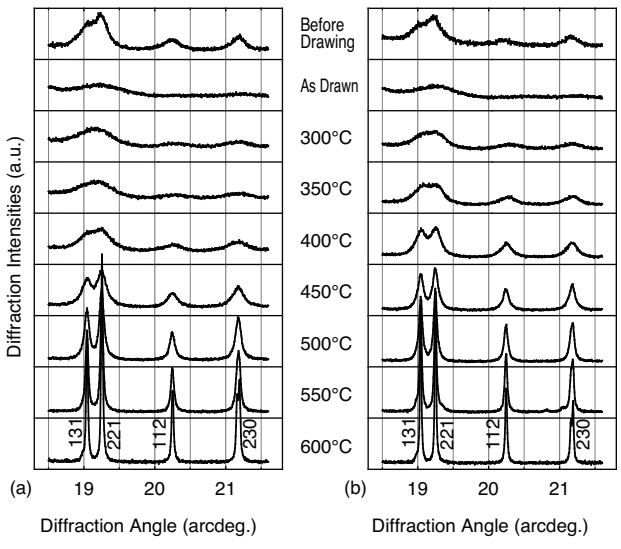

Fig. 7. Results of SR-XD (a) Developed (b) SWP-B

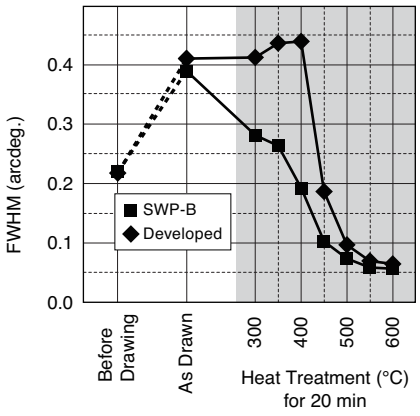

Fig. 8. FWHMs of 112 diffraction peaks of cementite (Fe_3C)

6. Conclusion

The reactions of cementite in Si-enriched piano wire were examined by using TEM and SR-XD techniques. As a result, in SWP-B wire, a conventional material, the strain accumulated by drawing was relaxed by heat treatment and subsequent coarsening of the cementite grains and disruption of lamellar structures. On the other hand, in our developed Si-enriched wire, cementite grains were atomized to tens of nanometer microcrystals and the temperature of forming sphere-like cementite shifts higher by 50 degree C. Combined with our previous report, in which we discussed macroscopic structures and the strain in ferrite, this study revealed the reactions of microstructures in the Si-enriched piano wire during heat treatment.

7. Acknowledgments

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References

(1) Kawabe, N., Murai, T. and Yamaguchi, K. Transaction of Japan Society for Spring Research (Japanese) 44 (1999), 1.
(2) Kawabe, N., Izumida, H., Murai, T., Yamao, N., Matsumoto, S., Yamaguchi, K. and Matsumoto, J. SEI Technical Review 51 (2001), 126
(3) Hirsch, P.B. et al. "Electron Microscopy of Thin Crystals" Butterworths London (1965)
(4) Yamaguchi, K., Yamaguchi, A., Kawabe, N. and Murai, T. CAMP-ISIJ 11 (1998), 348
(5) Cullity, B.D. "Elements of X-ray Diffraction" Addison-Wesley

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