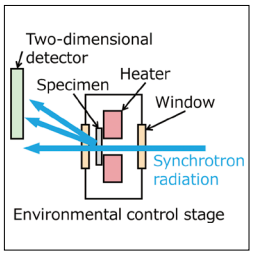

In-situ Analysis of Heat-Treatment Process of Metallic Materials by Synchrotron-Radiation

Kazuya TOKUDA*, Kazuhiro GOTO, and Koji YAMAGUCHI

The properties of electric wires made of copper and aluminum are largely affected by the temperature and time of heat treatment. In order to optimize heat-treatment conditions, we have developed an in-situ measurement technique that uses synchrotron X-rays, which have high transparency and intensity. While this technique is expected to reduce measurement and analysis time, its application to actual operation has been limited due to the opportunities for measurement and the time required for data analysis. In this paper, we report new environmental control systems at our synchrotron beamline in SAGA-LS and a newly developed program for the automatic analysis of large amounts of data. We have confirmed that the in-situ measurement of copper and copper alloys is possible and the difference in softening behavior can be analyzed in a short time.

Keywords: synchrotron radiation, in-situ measurement, X-ray diffraction

1. Introduction

Customer requirements for copper wires and aluminum wires, used for electric wires, and steel wires, primarily used as structural materials, have become increasingly sophisticated and diversified in terms of such properties as electrical conductivity, strength, and workability. To meet these requirements, Sumitomo Electric Industries, Ltd. has been working continuously to develop materials and optimize the processes. For example, metallic wires for electric wires are manufactured through multiple processes, from large-diameter wires after casting to small-diameter wires, which are shipped as products, as shown in Fig. 1. In these processes, heat treatment is performed multiple times to adjust the strength and electrical conductivity. To optimize the heat treatment conditions and meet the desired product properties, it is necessary to conduct in-depth analysis of specimens with different treatment (heat treatment and processing) histories from the viewpoint of metallographic structure and crystal structure in order to ascertain the conditions that should be improved. However, such analysis can basically only clarify the status of the materials after the processes. The status during the processes can only be inferred through multiple systematic analyses. For this reason, such prototype production and evaluation cycle were often repeated multiple times, and this involved a lot of time and cost.

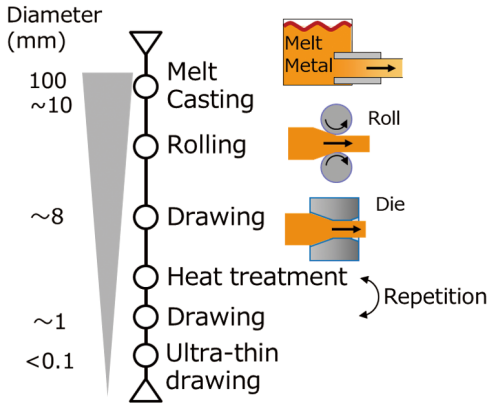

Fig. 1. Example of the metallic wire manufacturing process

Against this backdrop, we have worked on the development of in-situ measurement technology to conduct measurement in simulated processes while heating specimens and applying external force loads to them. This aimed to optimize highly efficient manufacturing conditions in a shorter period than usual by directly analyzing the behavior of materials during treatment processes. Although this may be achieved by an electron microscope or an X-ray diffraction system in a laboratory, this paper reports an example of using synchrotron radiation,*1 which is X-rays using an accelerator as a light source. Compared to laboratory systems, synchrotron radiation can use X-rays of high strength and high transparency. This makes it possible to conduct continuous measurement in short time steps through an environmental control stage. Sumitomo Electric has for some time applied synchrotron radiation in-situ measurement technology to superconducting wires[1] and catalysts for fuel cells[2] to optimize the manufacturing conditions.

Measurement has been conducted at public beamlines of SPring-8*2 and the Kyushu Synchrotron Light Research Center*3. Since these beamlines are public apparatus, it has taken several months or more, for example, from the time when needs for analysis arise to the time when actual measurement, including in-situ measurement, is conducted. For this reason, Sumitomo Electric constructed two contract beamlines*4 to use synchrotron radiation analysis in daily operations. The beamlines have been operated since November 2016. Environmental control stages, which can model a metallic material heat treatment process, have been introduced to these beamlines, enabling in-situ measurement to be carried out the day after the safety review of specimens is completed, at the earliest. However, in-situ measurement conducted with short time steps often

involves an enormous amount of data. It was not unusual to take several weeks for analysis after the end of measurement.

This report introduces our new analysis program to process a large amount of in-situ measurement data concurrently with the measurement at Sumitomo Electric beamlines. The program has made it possible to conduct analysis in a much shorter period.

2. Sumitomo Electric Beamlines and Environmental Control Stages

The detailed specifications of Sumitomo Electric Beamline are omitted because they were reported in a previous paper.[3] It consist of the hard X-ray beamline (BL16), which covers 2 keV or more, and the soft X-ray beamline (BL17), which covers 2 keV or less. This enables various analysis techniques. In the in-situ measurement, it is effective to use hard X-rays, whose transparency is high. Thus, we installed environmental control stages that can support three techniques (i.e., X-ray diffraction, X-ray absorption spectroscopy, and small angle X-ray scattering) available on the hard X-ray beamline.

Figure 2 shows the supported range of the newly installed specimen environmental control stage. Manufactured by Linkam Scientific, the environmental control stages can cover a wide temperature range. One model covers the range from −190°C to 600°C, and the other model covers the range from room temperature to 1,500°C to enable high-accuracy temperature control and output of measurement value. These environmental control stages cover the melting points of Al and Cu and the phase transformation point of Fe. Measurement can be conducted in the range lower than these temperatures. It is possible to simulate various heat treatment processes. In-situ measurement can be used not only in the manufacturing processes but also in the degradation analysis in the actual usage environment. It is also applicable to the cooling side. This paper focuses on the heating process using X-ray diffraction.

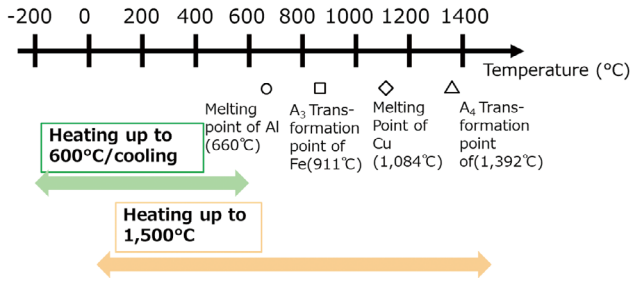

Fig. 2. Supported range of the environment control stage

3. Speedup of Analysis of In-situ X-ray Diffraction Data

X-ray diffraction techniques enable quantitative evaluation of atomic-scale information related to the strength properties of products, such as crystal defects and orientation, by using the diffraction phenomena on the atomic planes.[4],[5] They are indispensable tools for the analysis of metallic materials, including for the optimization of heat treatment processes. Specifically, quantitative analysis of peaks, which are derived from X-ray diffraction by fitting, enables analysis of information, including the lattice constant based on the peak position, volume fraction and crystalline orientation of multiple substances based on the peak area, and heterogeneous strain and crystallite size based on the peak width (FWHM: Full Width at Half Maximum or integral width). X-ray diffraction techniques can be used in a laboratory system, but the measurement takes up to about an hour in a laboratory. Synchrotron radiation at the Kyushu Synchrotron Light Research Center enables measurement with high angular resolution in a very short period (e.g., a few seconds). When it is necessary to conduct measurement in shorter time steps (e.g., one second or less), such measurement can be conducted by bringing an environmental control stage to SPring-8 where X-rays of higher intensity can be used.

3-1 Experiment setup

A typical setup is shown in Fig. 3. A specimen is installed by pressing it onto a heater with a hole in it. The specimen is exposed to a synchrotron radiation X-ray through the hole, and the scattered X-rays are detected by a two-dimensional detector. The two-dimensional detector is an X-ray detector that consists of many pixels. Sufficient signals can be obtained even in a short measurement time by detecting multiple diffraction lines at the same time. If in-situ measurement is conducted (one point/second) for one hour, for example, the two-dimensional detector generates as many as 3,600 images, which poses an issue.

3-2 Data analysis procedure

The data analysis procedure consists of four steps:

I. Convert the image data of the two-dimensional detector into one-dimensional data (intensity vs. diffraction angle)
II. Perform peak fitting of one-dimensional data
III. Calculate the physical quantity based on the fitting parameters obtained

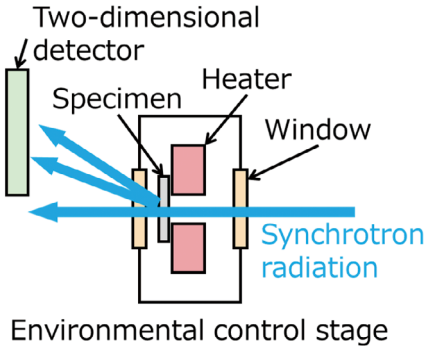

Fig. 3. Setup of the in-situ X-ray diffraction experiment

IV. Compare the result with the temperature data

Conventionally, this was time-consuming work. Different software products were required for each step and it took about one hour for each measurement. As shown in Fig. 4 (a), when in-situ measurement is conducted six times a day, for example, it is difficult to process the more than 20,000 images obtained from six experiments (one hour each) on the same day. In most cases, analysis had to be conducted on a different day from measurement. When not enough time was available at the time, it sometimes took several weeks until all the analysis was completed.

3-3 Automatic data analysis program

Against this backdrop, we developed a program to conduct analysis easily. The key point was to process data concurrently with measurement (see Fig. 4 (b)). First, we made it possible to conduct the operations from I to IV using a single program. The analysis program was created using the Igor Pro 8 analysis software available from WaveMetrics Inc. Here, a divided histogram method[6] was used for the one-dimensional conversion (I). For the peak fitting (II), we made a Gaussian function, Lorentz function, pseudo-Voigt function (combination of Gaussian and Lorentz functions), and Toraya's split pseudo-Voigt function,[7] which is applicable to asymmetric shapes, selectable.

In the newly developed program, as shown in Fig. 5 (a), parameters required for one-dimensional conversion (e.g., distance between the detector and a specimen), type of peak function, and fitting range (an arbitrary number can be set) are entered, and the first two-dimensional detector data file is selected. (Data files are output with serial numbers.) The software constantly monitors the status of generation of subsequent files. When a new file is generated, I and II are performed automatically. The time required for processing is 0.5 seconds or less per data file. Even measurement with exposure time of one second can be followed to conduct analysis. The measurement data and corresponding fitting curves, as well as the trend of the changes in parameters, such as the peak top, peak area, FWHM, and integral width, which are derived from fitting, are displayed on the GUI in real time, as shown in Fig. 5 (b). This makes it possible to interpret the phenomena while monitoring the trend of changes and reflect the interpretation in the heating conditions on the same day. Thus, I and II are completed almost concurrently with the end of measurement. Subsequently, III and IV can be continuously implemented manually with several clicks. Analysis can be completed in a short period (within about five minutes) after the end of measurement.

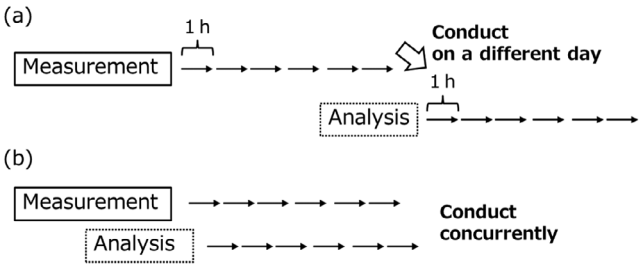

Fig. 4. Schematic diagram of data analysis by using (a) conventional program and (b) newly developed program

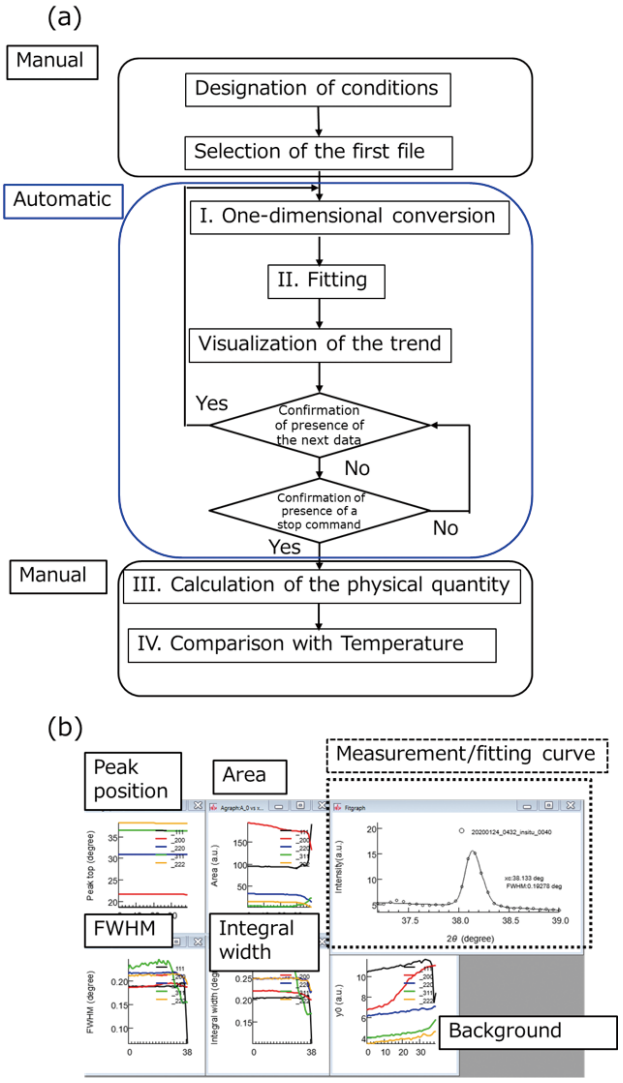

Fig. 5. Example of (a) flow and (b) operation screen of the newly developed program

In some systems, the peak may appear at an unexpected location in automatic fitting, or the peak may be too close to isolate in automatic fitting. In such cases, fitting (II) is required by manual operation, but it can be conducted by a relatively easy operation.

4. Simulation of the Heat Treatment Process for Copper

This section introduces an example of simulation of a copper heat treatment process based on actual experiment data. Here, standard copper and a copper alloy were used as specimens to confirm the operation of an environmental control stage and automatic data analysis program. Specifically, pure copper (purity: 4 N) with a thickness of 0.05 mm was compared with a Cu-Fe alloy (Fe content: 9 wt%) with a thickness of 0.07 mm.

4-1 Experiment conditions

The photon energy of X-rays was set to 18.0 keV

(wavelength: 0.0689 nm). PILATUS 100K manufactured by Dectris AG was used as the detector. The longitudinal direction of a specimen was set to the perpendicular direction. A specimen was arranged vertically against the beam axis. The distance between the detector and a specimen was calibrated using a standard specimen of CeO_2 (NIST SRM 674a). It was 148.1 mm. The measurement interval was set to 10 seconds. An environmental control stage whose highest temperature was 600°C was used for the experiment. The temperature was increased from room temperature to 600°C while feeding the nitrogen gas at the rate of 30°C/min.

4-2 Comparison of X-ray diffraction profile trends

Figure 6 shows the contour map of the X-ray diffraction profile at each point in time of the two specimens. Diffraction angle 2θ is plotted on the horizontal axis, while time is plotted on the vertical axis. The diffraction intensity at each point is indicated in gradation. In Fig. 6 (a), which shows the result of pure copper, the diffraction lines of 111, 200, 220, 311, and 222 of the fcc structure were observed at the same time. At around 400 seconds, the diffraction intensity ratio indicated by the gradation of each exponent changed significantly. This indicates changes in the crystalline orientation, which strongly influences the strength properties. Figure 6 (b) shows the result of the Cu-Fe alloy. Both Cu of the fcc structure and Fe of the bcc structure were detected as precipitates. The changes in the intensity ratio were difficult to determine in appearance. They were significantly milder than those of pure copper.

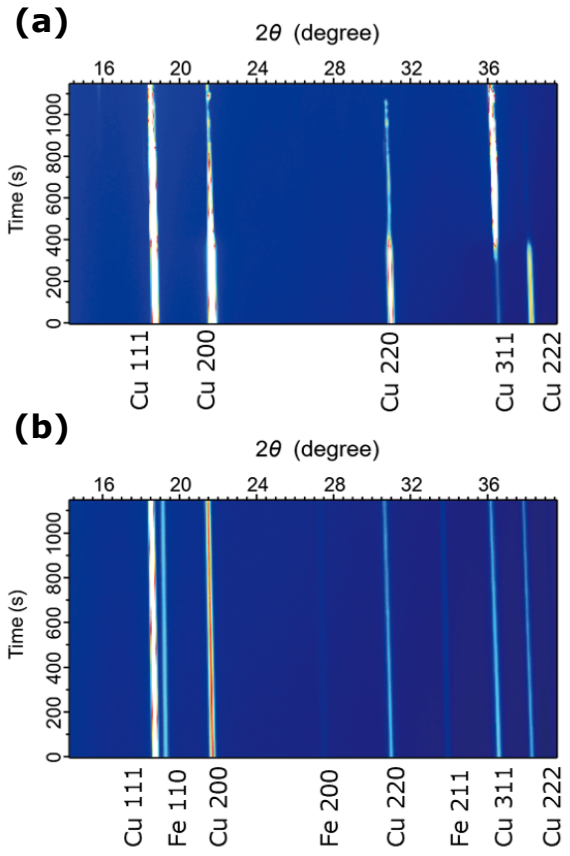

Fig. 6. Change over time of the diffraction position and intensity of (a) pure copper and (b) Cu-Fe alloy

The 220 diffraction line extracted every 200 seconds is shown in Fig. 7. As time progressed, each diffraction line shifted to a low angle. This is because each spacing increased due to thermal expansion, causing the diffraction angle to decrease based on Bragg's Law $2d\sin\theta = \lambda$ (λ: X-ray wavelength).

4-3 Quantitative analysis using automatic data analysis

To perform quantitative analysis of the peak shape changes, whose typical example is shown in Fig. 7, the analysis parameters and temperature profiles were compared by using the automatic fitting discussed above, as shown in Fig. 8. These graphs were obtained within 10 minutes after the end of measurement of each specimen. We confirmed the time reduction effect by automatic data analysis. Figure 8 (a) shows the peak position. Regarding the Cu-Fe alloy, the graph shows a shift to a low angle at constant variation in line with the temperature rise at a constant rate. Regarding pure copper, the changes were constant up to around 400 seconds (200°C). Subsequently, the changes were mostly at a low angle but exhibited irregular behavior. The integral width of the 220 peak is shown

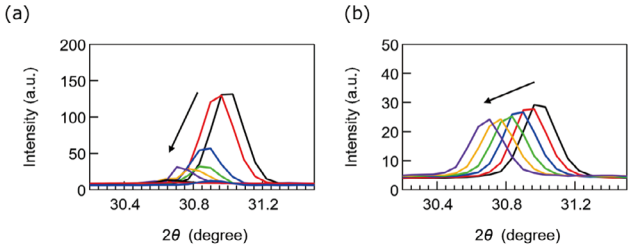

Fig. 7. Change over time of the 220 diffraction line of (a) pure copper and (b) a Cu-Fe alloy

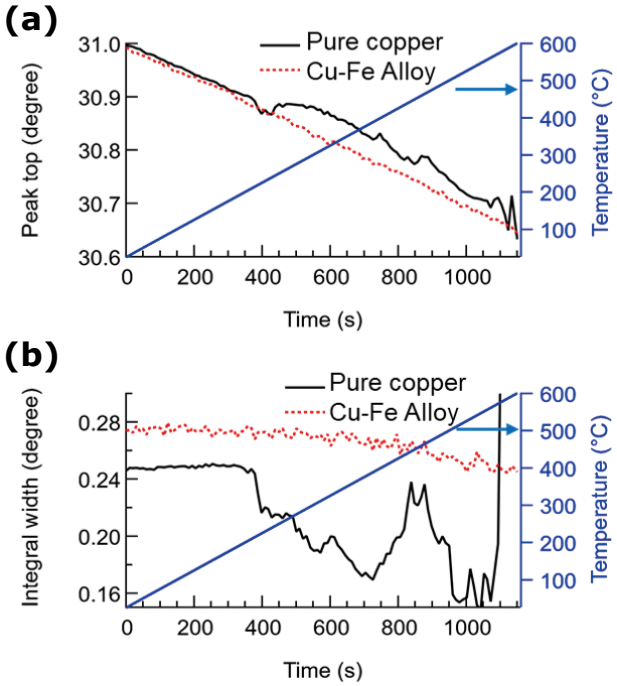

Fig. 8 Change over time of (a) peak top and (b) integral width of the 220 diffraction line of pure copper and a Cu-Fe alloy

in Fig. 8 (b). Regarding the Cu-Fe alloy, it gradually changed from around 600 seconds (350°C), demonstrating reduction in heterogeneous strain and an increase in the crystallite size. Regarding pure copper, a decrease trend was observed from 400 seconds, but irregular changes occurred. Such irregular changes observed in pure copper are attributable to the decrease in the number of crystals contained in the X-ray beam exposure area due to the increased size of crystals (so-called "worsening of the particle statistics").

4-4 Discussion

As shown in Fig. 6, the intensity ratio changed significantly after 400 seconds (200°C). In pure copper, recrystallization (growth of low-defect grains whose orientation is different from the original grains) is considered to have occurred at these temperatures. The Cu-Fe alloy did not show any irregular changes accompanied by such intensity ratio. Thus, gradual recovery (defect reduction) is considered to have occurred after 600 seconds (350°C). They are considered to be the result of the precipitate Fe in the Cu-Fe alloy that stabilized the grain boundary.

Only synchrotron radiation in-situ measurement makes it possible to determine the behavioral differences as a function of time and temperature during heat treatment. It can be used as an important source of information in determining the softening temperature and time, which vary depending on the composition and processing history.

5. Conclusion

By introducing a new system and developing a new analysis program, we have made it possible to conduct synchrotron radiation in-situ measurement in a short period after the needs arise. This report focused on heating, but we are working on the development of in-situ measurement of tension[8] and others to promote diversification and advancement. The reduction in measurement and analysis time that we have achieved, including the results above, is important in optimizing manufacturing conditions within a short period and with high efficiency. We will utilize the accomplishments in the future.

6. Acknowledgements

This experiment was conducted on the Sumitomo Electric Beamline BL16 (project number: SEI2019C-012), which was installed at the Kyushu Synchrotron Light Research Center. We would like to express our thanks to the staff members of the facility.

Technical Terms

∗1 Synchrotron radiation: Synchrotron radiation represents extremely intense white electromagnetic waves that are generated in the tangential direction by bending the electron orbitals, which are in motion at velocities close to the speed of light due to an accelerator, using electromagnets.

∗2 SPring-8: SPring-8 is the abbreviation of Super Photon ring-8 GeV. It is one of the largest synchrotron radiation facilities in the world (stored electron energy: 8 GeV) in Sayo-gun, Hyogo Prefecture. It came into service in October 1997.

∗3 Kyushu Synchrotron Light Research Center: This is a synchrotron radiation facility with the stored electron energy of 1.4 GeV. It was installed in Tosu City by the Saga Prefectural Government and is operated by the Saga Products Promotion Public Corporation. It came into service in February 2006.

∗4 Sumitomo Electric Beamline: The beamlines (experimental stations) were installed in the Kyushu Synchrotron Light Research Center by Sumitomo Electric. They started operation in November 2016. Synchrotron radiation analysis is conducted for about 3,000 hours a year using two beamlines.

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