Progress and Future Prospects of Microbeam Analysis in JFE Group†

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Abstract:

This paper presents a brief history of microstructural analysis in the JFE Group. Emerging technologies have always played a key role in modern steel production. The JFE Group has consistently introduced state-of-the-art microbeam analysis tools and employed those techniques in R&D. Electron microscopy, surface analysis tools and particle beams are now capable of leading the design and development of high performance steel products and other JFE products. Further strengthening of microbeam analysis as an indispensable core technology is crucial for continuing to meet new challenges.

1. Introduction

We have entered an era in which observational science leads control science. Phenomena which cannot be seen and measured cannot be controlled. Research and development and stable production of Japan's high performance steel products were not realized without advanced analysis and measurement technologies. Microbeam analysis technologies revealed the microstructure and surface structure of steel materials, which was beyond the realm of imagination before that time, and the analytical results provided by those technologies enabled precise, detailed design of steel products.

"Physical analysis" is generally called microanalysis or microbeam analysis in English. As these terms suggest, this field of analysis, unlike chemical analysis, focuses on the analysis of microscopic regions. In actuality, this field also includes high resolution microscopy and diffraction methods. These techniques have played a crucial role in the design and development of steel products and in the design and optimization of processes.

This report reviews the history of microbeam analysis technologies in the JFE Group and describes directions for the future. Recent research results achieved by utilizing the technologies outlined herein are introduced in separate articles in this Special Issue.

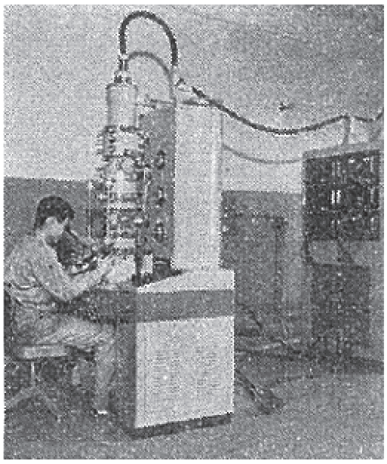

Photo 1 Hitachi, Ltd. HU-11 transmission electron microscope (TEM) 150 kV special model in 1962 installed at Keihin, NKK (now JFE Steel) (Reproduced from reference 1) with permission)

2. Early Period: From the 1960s

Photo 1 shows a photograph which was used in an article introducing a transmission electron microscope (TEM) in the Laboratory News of NKK (now JFE Steel) in June 1962. This TEM is a special model of the Hitachi, Ltd. HU11. Although the standard accelerating voltage at the time was 100 kV, this was increased to 150 kV in this TEM in order to increase its electron transmission capacity. It was introduced at NKK, a predecessor of JFE Steel Corp., following introduction at Daido Steel Co., Ltd. The late Dr. Kazuo Horikawa, former Director of the NKK Technical Research Center, recalled that "Researchers entreated me to buy a TEM for microstructural observation. Thinking that it isn't possible to develop new steel products without a technique for

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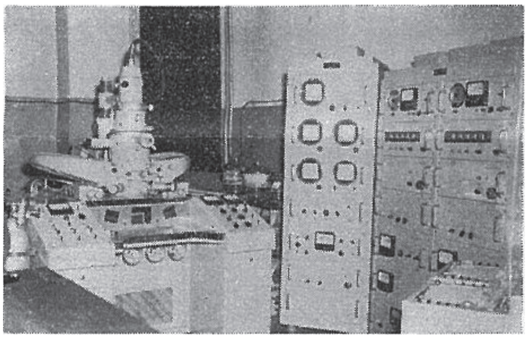

Photo 2 JEOL Ltd. JXA-3 electron micro probe analyzer (Photo taken in 1964) installed at Keihin, NKK (now JFE Steel) (Reproduced from reference 1) with permission)

highly accurate microstructural observation, I obtained the understanding of top management. "

Photo 2 shows the appearance of an electron probe microanalyzer (EPMA; at the time, called X-ray microanalyzer, XMA), which was introduced at NKK's Keihin District in March 1964. EPMA was commercialized in France and subsequently gained acceptance. The JXA-3 introduced at Keihin was developed by JEOL Ltd., and one of the first five units manufactured by that company was installed at Keihin District. EPMA was used by researchers in steelmaking area for X-ray analysis of micro regions, and led to a deeper understanding of nonmetallic inclusions, etc. in steel. The fact that the researchers in steelmaking area Miyashita et al. wrote their own quantitative analysis program to enhance analytical accuracy is worthy of admiration[2)].

Today's JFE researchers and engineers have inherited the DNA of this enterprising spirit. Since the year 2000, the JFE Group has led the industry in introducing ultra-low voltage scanning electron microscope and the aberration-corrected TEM, and has cultivated these technologies as strategic assets. At JFE, this stance of closely following global trends in emerging technologies and applying those technologies to steel research as quickly as possible has continued in an unbroken line from the past.

3. Period of Development: From the 1980s

From around 1980, analytical electron microscopes (AEM), in which the TEM was given analytical functions, entered the stage of practical application. This increased the usefulness of TEM, as elemental analysis of precipitates and individual phases could be realized in microstructural analysis. The AEM was utilized in microstructural analysis of various types of steel products, beginning with analysis of precipitates in IF (interstitial free) steel[3)]. In the first half of the 1980s, Chiba District of the Steel Research Laboratory of Kawasaki Steel (a predecessor of JFE Steel) introduced a JEM-100C manufactured by JEOL Ltd., which was equipped with a cold FEG (field emission gun), taking the lead in analysis of light elements in fine precipitates in steel[4)]. The use of FEG in TEM, beginning with maintaining a high vacuum in the electron microscope, represented the introduction of a challenging device in a period when this was not a general technology. Amid the trend toward higher voltages, new model 300 kV AEMs manufactured by Philips (now FEI Company) were introduced at Technical Research Center Keihin and Fukuyama Districts. A 400 kV TEM manufactured by JEOL was introduced at Chiba. During this period, all major steel makers were expanding into research on various types of materials other than steel, and this instrument was also used in analysis of semiconductors and new materials[5)]. In 1990, an iterative averaging method was developed, solving the problem of channel-to-channel gain variation, which had been an issue in analyses using PEELS (parallel detection electron energy loss spectroscopy). This dramatically enhanced the sensitivity of light element analysis using EELS[6)]. The experiment was performed with a device manufactured by Philips (now FEI Co.), which was the world's leader in AEM technology.

Accompanying the heightened usefulness of AEM technology, there was increased demand for FEG-equipped microscopes that could be used in everyday research. In 1991, an AEM equipped with a Schottky emitter was installed at Keihin. This instrument was a model CM20-FEG manufactured by Philips (now FEI Co.). It was a new type, being the 1st unit installed in Japan and only the 4th in the entire world. With its introduction, analysis of nanometer-sized regions became constantly available[7)].

Until the mid-1990s, focused ion beam (FIB) instruments had been used in failure analysis of semiconductor devices, but from the second half of the decade, FIB was widely adopted in the steel industry as well. Previously, TEM specimens of coated steel sheets had been prepared by ion milling or mechanical polishing of sample materials which were bonded together, but FIB enabled easy cross-sectional observation of the coated steel sheets. Moreover, thanks to the development of a technology for taking microsamples, FIB was firmly established as a technology that makes it possible to observe only a specific region of interest[8,9)]. Up to this point, we have reviewed the progress of electron microscope related technologies.

Strengthening of surface analysis accelerated from the 1980s. Use of X-ray photoelectron spectroscopy, Auger electron spectroscopy, secondary ion mass spectroscopy and other techniques based on ultra-high vacuum conditions in research on steel began. Many of instruments introduced at the time were manufactured in Europe or the United States, which were superior in vacuum technology. In this period, the number of researchers working in surface analysis and electron spectroscopy also increased. The use of surface analysis instruments strengthened the foundations for the development of new steel products such as advanced surface-treated (coated) steel sheets, and also deepened the understanding of the basic phenomena that occur in steel materials, for example, by direct analysis of grain boundary segregation[10–12].

Analysis of steel products by analytical technologies utilizing synchrotron orbital radiation began in the first half of the 1990s. This was also supported against the background of promotion of industrial use of synchrotron orbital radiation. JFE Steel devoted great effort to chemical state analysis of elements of interest in steel products by using XAFS (X-ray absorption fine structure) technology[13]. XAFS was also applied to chemical state analysis of trace elements in investigations of environmental issues and contributed to the development of treatment methods for fly ash[14] and sewage sludge[15].

In addition to the above, the JFE Group also grappled with improvement and modification of commercial instruments. As one example, JFE and the instrument manufacturer jointly developed an EPMA with enhanced automatic analysis functions by improving the electron optics and specimen stage[16]. This strengthened JFE's steel product and process analysis capabilities.

4. Microbeam Analysis-Led Material Design: From the Year 2000

Around 2000, the era of target-driven microbeam analysis finally began, thanks to the development of more advanced microbeam analysis instruments and improvement of their operability.

Field emission SEM (FE-SEM) was widely adopted in the field of scanning electron microscopy (SEM) prior to TEM, and high magnification surface observation became possible. In the National Project "Super Metal Technology: Creation Technology for Mesocopic Structured Ferrous Materials," a technology for utilizing in-lens SEM, which had not been considered suitable for ferromagnetic materials, was developed, enabling high-order microstructural observation of ultra-fine grained steels[17]. In observation of the surface and structure of practical materials, control of the secondary electrons and backscattered electrons which are to be measured is critical. JFE Steel was among the first to focus on ultra-low voltage SEM, which realizes surface sensitive observation. JFE introduced a Leo Ltd. (currently Carl Zeiss Microscopy GmbH) SEM with an electron beam deceleration lens in March 2001 and then pioneered extreme surface layer observation by SEM. This technique clarified the surface structure of steel products,

Photo 3 Ultra fine carbides in steel observed using aberration-corrected electron microscope (Cover of JFE Steel R & D brochure, 2009)

which had been overlooked until then. This understanding of the surface of steel materials provided decisive information for the development of Only 1, No. 1 JFE Steel products such as the high lubricity galvannealed (GA) steel sheet JAZ™[18], among others. For recent examples of research utilizing ultra-low accelerating voltage SEM, see the article entitled "Selective Visualization Techniques for Surface and Microstructure of Steel Products by Scanning Electron Microscopy"[19] in this Special Issue.

JFE Steel was also the first to introduce EBSD (electron backscatter diffraction), which is now established as a technology for crystal orientation analysis, and developed this technology to analysis and control of the texture of steel[20,21].

The largest remaining issue for TEM was overcoming spherical aberration. A spherical aberration correction technique for the objective lens of electron microscopes finally reached practical application as a result of long years of research by Rose, Haider et al[22]. In 2006, JFE Steel introduced the Titan™ aberration-corrected electron microscope (FEI Co.) and installed the instrument at the Keihin District of the JFE Steel Research Laboratory. JFE Steel was the first company in the global steel industry to adopt this technology. The aberration correction of the electron probe realized sub-Å (sub-angstrom) level observation and sub-nm (sub-nanometer) analysis. A number of important results have been achieved, including highly accurate analysis of precipitates (**Photo 3**) and grain boundaries in steel and direct observation of the passive film of the new stainless steel JFE443CT[23]. The citation for the Okochi Memorial Prize for "Development of high formability new high strength steel sheet[24] for automotive applications by nano carbide control" in 2010 highly evaluated the results of TEM analysis[25], which elucidated the mechanism responsible for the properties of JFE Steel's NANOHITEN^{TM}. For details, please refer to the article "Sub Nano World in Steels Clarified by Cs-Corrected STEM"[26] in this Special Issue.

JFE Steel, which has organically utilized the aberration-corrected STEM (Cs-STEM) and ultra-low accelerating voltage SEM in the development of leading-edge steel products, was introduced as the "leader in metal nanotechnology" at the nanotechnology platform "17th nano tech Japan"[27].

In addition to instruments owned by the company itself, JFE Steel also actively utilizes large-scale facilities outside the company. Analysis utilizing synchrotron orbital radiation, which was introduced in Chapter 3, is already used on a regular basis. In collaboration with Kyushu University, JFE Steel developed a use technology for a high voltage TEM equipped with an Ω-filter and realized microstructural observation of steel materials exceeding 2 μm[28]. This technology is expected to provide a deeper understanding of strengthening, deformation, and other behaviors of steel as a structural material. JFE is also promoting the use of neutron technology as a microstructural analysis technology for large volume specimens which have greater representativeness. JFE Steel received the 2011 Tawara Award of the Iron and Steel Institute of Japan (ISIJ) in quantitative analysis of precipitates by utilizing small angle scattering[29]. At present, JFE is promoting analysis of residual stress, retained austenite, texture, etc. by neutron diffraction in ISIJ activities and collaborations[30]. The company is also working to expand neutron analysis technology to analytical techniques which use not only large-scale facilities such as J-PARC (Japan Proton Accelerator Research Complex) and nuclear reactors, but also compact neutron sources. The approach adopted by JFE Steel is introduced in "Micro Structural Evaluation Technique of Steel Using Neutron Beam"[31] in this Special Issue. Industry is also placing increasingly high expectations on neutron technology; for more information on that topic, see the RIKEN Channel Youtube presentation, "Science Frontier 17: Neutrons Transforming Japanese Manufacturing-A Record of RANS R&D" (RANS: RIKEN Accelerator-driven compact Neutron Source; in English, https://www.youtube.com/watch?v=FXLtM6Lqct0)[32].

As examples of the application of microbeam analysis to material analysis in the JFE Group companies, this Special Issue introduces the results analysis of positive electrode materials for nickel based lithium ion cells from JFE Mineral Co., Ltd[33]. and the development of a PVD film from JFE Precision Co[34]. Also in the JFE Group, JFE Techno-Research Corporation, which provides analytical services, is promoting introduction of the ultra-low accelerating voltage SEM, FE-EPMA and aberration-corrected electron microscopy and the development of use technologies. JFE Techno-Research is engaged in a wide range of problem-solving activities with a solution-type organization, not from the viewpoint of techniques, but based on the field of application[35,36].

5. Future Prospects

Up to this point, this paper has presented an overview of the history of microstructural analysis (microbeam analysis) in the JFE Group. The introduction and development of new technologies with a wide global perspective has contributed to the businesses of the group. In the JFE Group, problem-solving and proposal-type research have always been carried out based not only on specialized knowledge of analytical technologies, but also a thorough knowledge of the object materials and processes.

The JFE Group is continuing to take on the challenges of improving spatial resolution and analytical sensitivity. It is also necessary to perform analyses of wider regions with higher speed. At present, the JFE Group is also strengthening multiscale analysis, which links the macro and nano scales, and techniques which are capable of following temporal changes in composition, defects and 3-dimensional structures, such as 3D/4D analysis. Moreover, development to*in-situ*or operando observation under various environments is also essential.

The challenge of steel is also continuing. In particular, analysis of the light elements B, C, N, O and also H in steel is still far from adequate. As part of research in this direction, this Special Issue reports "Analysis Technology of Microstructure Formation in Dual Phase Steel with High Performance"[37] and "Analysis of Micro-Alloy Elements as Solute and Nanometer-Sized Precipitation in Hot Rolled Steel Sheet"[38]. Knowledge of the partition of elements between phases in multiphase steels and the condition of existence of added elements, including light elements, is indispensable for achieving dramatic progress in steel products. In order to understand the behaviors of light elements, in addition to strengthening analysis methods, a fusion of new characterization techniques and computational materials science is demanded. Improvement of techniques for maximizing the information extracted from analytical data is also required.

As mentioned in Chapter 1, "phenomena which cannot be seen and measured cannot be controlled. " Because our predecessors coveted "seeing" and were filled with the desire to "know, " they always actively introduced emerging analytical technologies. As we carry on that legacy, we must strengthen microstructural analysis aiming at new horizons with an even wider vision than our predecessors.

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