Atomic-scale Physical Analysis for Material Development

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Abstract

In the pursuit of realizing a safe and secure society and advancing toward a green society through the development of metallic materials, it is essential to achieve higher strength and corrosion resistance by controlling the microstructure. This control has been miniaturized to the atomic scale. Observing microstructure is key to expressing desired properties, and observing and measuring at the atomic level is required. As part of Kobe Steel's efforts to enable these capabilities, the company has been utilizing techniques such as synchrotron radiation X-ray, three-dimensional atom probes, soft X-ray emission spectroscopy, and energy-dispersive X-ray spectroscopy using scanning transmission electron microscopes. Furthermore, Kobe Steel is also engaged in microstructure prediction using first-principle calculations. Amidst the significant changes toward achieving carbon neutrality enabled by these technologies, Kobe Steel will strive to support the development of next- generation materials through atomic-level analysis and evaluation technology.

Introduction

Kobe Steel's materialities include contributing to a green society and ensuring safety and security in community development and manufacturing. Accordingly, the company develops and provides a wide variety of materials including steel, aluminum, and other metal materials to sectors including transportation, civil engineering, architecture, societal and industrial infrastructure, and high-function materials. Material properties must be enhanced to solve societal challenges by reducing the weight of vehicles and other transportation equipment and by extending the service life of bridges and other structures. As a materials manufacturer that provides metal structural materials, Kobe Steel has focused on developing new materials and manufacturing processes to satisfy the aforementioned demands. To reduce the weight of transportation equipment and extend the service life of structures, materials must exhibit high strength and high corrosion resistance alongside other favorable properties associated with these characteristics. Kobe Steel meets these needs by developing multi-material solutions that capitalize on the diversity of materials we offer. The company furthermore applies advanced core technologies such as metallographic structure control technology, metal surface control technology, and metal working process technology.

To develop materials and processes, it is necessary to determine the mechanisms behind and parameters for expressing a desired property such as high strength or high corrosion resistance. Proposing new materials in conjunction with the mechanisms behind the desired properties instills confidence in the customer. Physical analysis and evaluation techniques are indispensable for revealing these mechanisms. **Fig. 1** shows how physical analysis and evaluation techniques support Kobe Steel's products and, by extension, the company's materialities. Physical analysis and evaluation techniques underpin materials development by providing, evaluating, and interpreting measurement data and by revealing and modeling mechanisms. Increased demand for high strength and high corrosion resistance is driving continuous improvement among the requisite physical analysis and evaluation techniques. The core technologies for materials and process development as well as physical analysis and evaluation techniques are inextricably linked to the resolution of societal challenges.

This paper provides an overview of the atomic-level analysis and evaluation technologies Kobe Steel has developed, used, and applied to materials development.

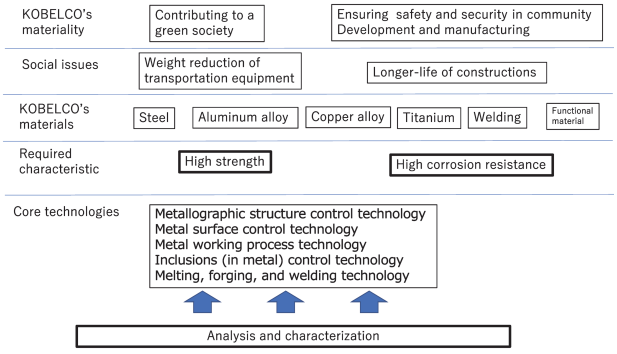

Fig. 1 Physical analysis and evaluation techniques supporting the KOBELCO Group's core technologies for research and development of materials and processes

1. The KOBELCO Group's physical analysis and evaluation techniques

Fig. 2 depicts the role of Kobe Steel's physical analysis and evaluation techniques in materials development, with functions on the horizontal axis and the order of magnitude controlled on the vertical axis. Physical analysis and evaluation techniques for observation and measurement use charged particles such as electron beams or ions, or radiation such as in the form of X-rays, as a probe to excite the material to be measured (sample). The energy of the reflected or secondarily generated waves or particles is then measured, thus providing data regarding the state of the sample. Data analysis has traditionally been used to evaluate the results of physical analysis, with machine learning and similar techniques being introduced as further validation methods in recent years. Going one step further, computational science can verify phenomena and hypotheses deduced from data analysis at the atomic level.

Physical analysis techniques involve various probes, charged particles and electromagnetic waves to be detected, and energy ranges. These techniques clarify the mechanisms behind the degradation and expression of properties by revealing information about microstructure, composition, surface morphology, and chemical state. Examples of such techniques include scanning electron microscopy (SEM), which observes surface morphology on a submicron scale, and X-ray photoelectron spectroscopy (XPS), which evaluates the chemical bonding state of the sample surface.

Microstructure control technology is important in the development of high-strength steel and aluminum alloys because of its roles in managing deformation and fracture. However, the structures to be controlled are becoming finer, from the microstructure of the base metal to grain boundaries and atomic-level structures. Furthermore, the degree to which additives and segregation must be controlled is becoming infinitesimally small. Kobe Steel has been developing physical analysis techniques to overcome the challenges associated with these parameters. In particular, we were among the first to introduce and develop the microstructure analysis techniques around which much of our research centers, namely synchrotron radiation and three-dimensional atom probing (3DAP).

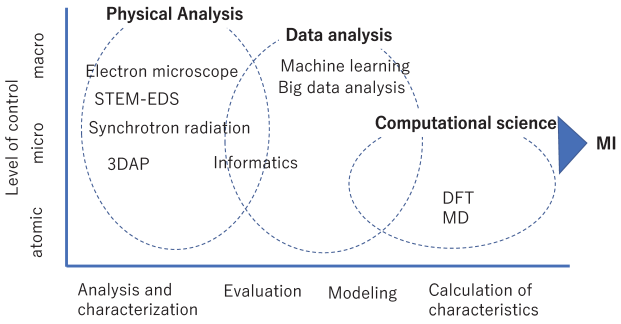

Fig. 2 Elements of physical analysis and evaluation technology

Also playing a role are our developments in SEM-SXES (soft X-ray emission spectroscopy) to evaluate carbon distribution in microscopic areas and STEM-EDS (scanning transmission electron microscopy, energy dispersive X-ray spectrometry) to quantify trace elements.

Synchrotron radiation is the light produced when a magnetic field redirects the travel path of accelerated electrons. SPring-8 in Hyogo Prefecture boasts the world's highest synchrotron radiation energy and brightness (one billion times higher than standard laboratory X-rays). Synchrotron radiation provides information that is normally impossible to obtain regarding the inside of a sample and its trace elements, and in a short time and at remarkably high resolution. As a member of the SPring-8 SUNBEAM Consortium since 1998,[1] Kobe Steel maintains a beamline to develop various materials and processes.

One such development is related to delayed fracture caused by hydrogen embrittlement, which is particularly problematic in high-strength steels such as high-tensile-strength steel plates. Assessing delayed fracture susceptibility necessitates evaluation of transition metal carbides, which serve as hydrogen traps. Since carbides can be nanometer-sized precipitates, it is necessary to evaluate the phase in which they are dispersed in the steel. In developing martensitic steels, Kobe Steel focuses on trace carbides, using synchrotron X-ray diffraction to determine the carbon concentration and process conditions that reduce susceptibility to delayed fracture.[2] We used synchrotron X-ray diffraction to analyze the solute carbon concentration in austenite at different heat treatment temperatures in TRIP (transformation-induced plasticity) steels. The data collected were used to formulate microstructure control guidelines for the expression of desired properties.[3]

3DAP is a microanalysis tool that provides multi-dimensional imaging of the atomic structure inside materials. 3DAP has both high spatial resolution, on the order of nm, and excellent mass resolution. It is highly effective for detecting and analyzing clusters (nm-scale aggregates of added elements) and precipitates within materials.[4] One example application of 3DAP is in the development of 6000-series aluminum alloys for automotive panels.

Here, 3DAP can quantify the number density and composition of Mg-Si clusters that affect bake-hardness. This information is then used to determine the heat treatment conditions that support favorable cluster formation.[5)]

Data analysis technology for evaluation and interpretation plays a particularly important role in 3DAP evaluation, as it clarifies the mechanisms behind the data collected via physical analysis techniques. 3DAP entails an inevitable degree of uncertainty in data regarding elements and atomic structure. However, the incorporation of information about a sample's crystallography[6)] and statistical analysis of the data ensure the validity of 3DAP results. Our developments in statistical analysis of the number density and composition of clusters based on the interatomic spacing of added elements further improve accuracy.

We have also combined recent developments in machine learning and mass data processing techniques with physical analysis methodologies. As one application example, these techniques are used in controlling the progression of rust in steel to yield high corrosion resistance. This is because rust exists in many forms, which took a great deal of time to analyze and quantify. As such, we used machine learning to evaluate structural analysis data from synchrotron radiation X-rays to determine the state of rust and visualize its distribution. The results are helping to reveal the mechanism behind rust formation. For more information, see Metal Surface Control Technology Contributing to Safe and Secure Society through the Creation of Highly Functional Surfaces on pages 45-46 of this issue.

Recent years have seen remarkable developments in computational science and technology, including in processing power. First-principles calculations and molecular dynamics can compute atomic structures and physical properties. Data evaluated and interpreted by physical analysis and data analysis are increasingly being integrated with calculated estimations to understand phenomena and the mechanisms behind them. As such, computational science and technology are now indispensable in materials development.

As described above, Kobe Steel's physical analysis and evaluation techniques have progressed in tandem with the development of materials and processes to achieve target properties such as high strength and high corrosion resistance. Kobe Steel is also part of the recent trend of combining physical analysis techniques with data analysis technologies such as machine learning and computational science and technology to reveal atomic-level phenomena.

2. Applications of atomic-level analysis and evaluation technologies

This section introduces two example applications of physical analysis and evaluation techniques. One is microscopic carbon distribution evaluation technology using SEM-SXES for the development of high-strength TRIP steels. The second is grain boundary segregation analysis technology using STEM-EDS and computational science for joint determination of the mechanisms behind high strength.

2.1 Microscopic carbon concentration evaluation in TRIP steels via SXES

Reducing vehicle weight requires steel plates with high strength and high workability - properties that can be improved via the TRIP effect. Murakami et al. reported that strength-elongation balance can be improved by controlling the concentration of solute carbon in retained austenite (retained γ) and redistributing the retained γ grains with heterogeneous solute carbon in each crystalline grain.[7)] However, conventional methods for evaluating the heterogeneity of carbon in retained γ have insufficient spatial and mass resolutions, necessitating a new method of analysis. We developed an SXES analysis technique that enables carbon analysis at a spatial resolution of 200 nm or less to analyze carbon concentration in fine retained γ grains.[8)]

When inner-shell electrons are excited by an electron beam, outer-shell electrons transition into core holes and characteristic X-rays are emitted. SXES specifically analyzes low-energy X-rays to assess the abundance and bonding state of light elements.[9), 10)] We used an SEM (JEOL JSM-7100F) with an SXES spectrometer (JEOL SS-94000) for SXES analysis. Carbon-containing contamination must be absent from the sample surface while analyzing carbon in steel.[11)] To meet this need, samples were excited via a GCIB (gas cluster ion beam) during SXES measurement to reduce the influence of contamination.

SXES was used to evaluate the amount of solute carbon in each grain of retained γ in the microstructure of 1.5 GPa-grade TRIP steel with a carbon concentration of 0.4 mass%. The ferrite (α) grains and retained γ grains were discriminated via EBSD (electron backscatter diffraction) before the solute carbon concentration in the retained γ was measured. **Fig. 3**(a) shows the EBSD map and Fig. 3(b) shows the frequency distribution of the solute carbon concentration in the retained γ. Carbon

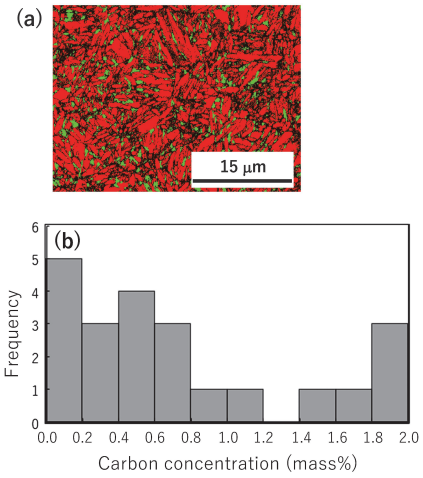

Fig. 3 Analysis of C concentration in retained γ phase
(a) EBSD phase map (red: body-centered cubic; green: face-centered cubic)
(b) Histogram of C concentration in retained γ phase, measured by SXES

concentrations were found to be separated into grains with greater than 1.2 mass% and grains with less than or equal to 1.2 mass%.

SXES can determine carbon concentration at a microscopic level, which governs the properties of steel. A spatial resolution of 200 nm or less and a mass resolution of 0.1 mass%, which are on par with SEM, enable more detailed research into the effects of microstructure on strength. SXES can also analyze light elements and metals in addition to carbon and can be applied to the observation of precipitates and corrosion morphology. We will use this technology to develop safer and more reliable materials with reduced environmental burden.

2.2 Analysis and computational science to inhibit embrittlement via grain boundary segregation

It is well known that grain boundaries in steel are prone to brittle fracture, especially when impurities such as P and S segregate at the grain boundaries.[12), 13)] Two methods in particular can suppress grain boundary embrittlement. One is to reduce P and S impurities to the extent possible. Another is to account for the effects of other added elements in the steel on the grain boundary segregation of impurities. For example, Mn promotes cosegregation and has a high affinity for P. This is notable because the type and amount of alloying elements affect the grain boundary segregation of P. As such, analyzing and predicting the degree of segregation are essential for developing materials with reduced embrittlement. Grain boundaries account for a relatively small proportion of an entire sample. Trace elements must therefore be analyzed within microscopic areas, necessitating a very high resolution. As for prediction, using empirical data to quantitatively evaluate the effects of atomic interactions on grain boundary segregation is challenging. This is because added elements such as P and S form carbides and alloying compounds in steel. The following sections detail technologies that suppress grain boundary embrittlement caused by segregation. These technologies involve evaluating microscopic amounts of grain boundary segregation using STEM-EDS and applying first-principles calculations to determine the effects of added elements on grain boundary segregation and grain boundary strength.

2.2.1 STEM-EDS evaluation of P segregation at grain boundaries in steel

AES (auger electron spectroscopy), 3DAP, and STEM-EDS can evaluate microscopic amounts of grain boundary segregation. The advantage of AES is the ability to measure a large number of grain boundaries in a relatively short time. However, a disadvantage lies in that AES measures intergranular cracks from the surface and cannot easily distinguish between intergranular and transgranular fractures. Transgranular fracture surface measurements might be duplicated in materials exhibiting both types of fracture and a low proportion of intergranular fracture, making the two fracture types difficult to distinguish. As such, the amount of grain boundary segregation may be underestimated depending on the proportion of intergranular cracking.[14)] Although 3DAP and STEM-EDS do not present the same challenges as AES, STEM-EDS entail a degree of inherent measurement error and 3DAP entails statistical errors in the signal count. For example, STEM-EDS determines concentration by measuring the intensity of characteristic X-rays emitted by each atom upon electron excitation. However, because the sample absorbs characteristic X-rays, results depend on sample thickness, yielding errors. Differing mass attenuation coefficients of each element is a further source of error. We are collaborating with the National Institute for Materials Science to improve the accuracy of these techniques by using a large-solid-angle EDS detector and the ζ-factor method.

To correct for absorption error, the sample thickness must be known. Historically, sample thickness had to be measured separately by methods such as EELS (electron energy loss spectroscopy). Kobe Steel, however, uses the ζ-factor method[15)] to measure sample thickness via EDS measurement alone. This method begins with a standard sample

that has the element to be measured as well as a known composition, density, and thickness. EDS quantifies the element to be measured and reveals the ζ-factor, relating the X-ray intensity to the electron dose.[16), 17)] The ζ-factors for each element are then used to calculate the thickness of the sample at each measurement point, thus correcting for absorption errors that depend on sample thickness. **Fig. 4** shows a map of P around the grain boundary of a sample of Fe-1.44wt%Mn-0.01wt%P-2.23wt%Cr that was heat treated after solution treatment. P segregation is observed over a width of about 2 nm. **Fig. 5** shows the P concentration profiles across the grain boundary with and without ζ-factor absorption error correction. The P concentration, which is usually underestimated because of sample thickness, is now evaluated more accurately. The grain boundary segregation per unit area of grain boundary Γ (atom/nm^2) is obtained from the P concentration profile. **Table 1** compares the statistical error in the amount of grain boundary segregation Γ measured in this study and by other research institutes. A large-solid-angle EDS detector achieved a standard error in the amount of grain boundary segregation Γ of 0.1 atom/nm^2, which is about one-third of the error reported by other research institutes.

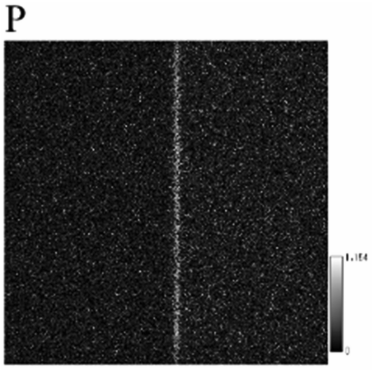

Fig. 4 Map of P concentration around grain boundary (measured area: 100 nm × 100 nm)

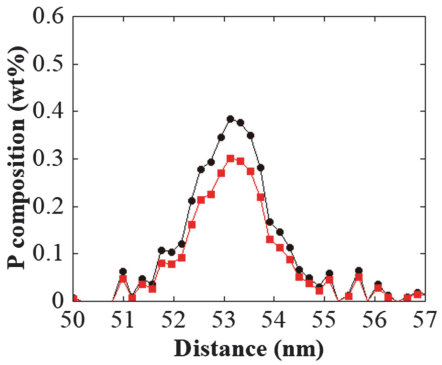

Fig. 5 P concentration profile across grain boundary (black: absorption corrected; red: absorption uncorrected)

Hence, using an EDS detector with a large solid angle and correcting by the ζ-factor enable more accurate evaluation than previously reported methods[18), 19)] and helps reveal the mechanisms behind embrittlement and its suppression.

2.2.2 First-principles calculations regarding the cosegregation of P and transition metals at the Fe grain boundary

Enhancements in computer performance and first-principles calculation methods have propelled materials development in recent years by making it possible to perform highly accurate computations with a standard desktop computer. First-principles calculations related to atomic interactions can reveal the mechanisms behind grain boundary cosegregation in steel and other metal materials. For example, it is possible to predict whether the segregation of an element at a grain boundary will promote or inhibit the segregation of another element, and how the bonding strength will change, which provides guidance for developing better materials. Transition metals are commonly used to strengthen steel. Kobe Steel has been using first-principles calculations[20)] to evaluate the effects of transition metals on P segregation at grain boundaries and on grain boundary strength; the following is an explanation of our computation methodology and results.

Fig. 6 shows the grain boundary model used in the first-principles calculations. We used the bcc-Fe Σ3(111) grain boundary model (76 atoms) in our calculations. The grain boundary interface is set at the center, and the grain boundary energy calculated for this model is 1.23 J/m^2. The grain boundary segregation sites are designated as 0 to 3 in the figure. Cr, Mn, and Mo were arranged here as X atoms together with P. We determined the P-X interaction potential and cosegregation energy at the grain boundary for each atomic arrangement.

Fig. 7 shows the relationship based on these results between the P-X interatomic potential and the interatomic spacing when P is at sites 0 and 2. The repulsive potential is strong around 2.2 Å, where

Table 1 Comparison of amount of grain boundary segregation Γ reported in this study and in previous studies by other research institutions

Reference	Method	Bulk material	Segregated element	Γ (atom/nm2)
This study	STEM-EDS	Fe	P	0.7±0.1(3σ)
[18]	STEM-EDS	boron carbide	Si	0.7±0.3(3σ)
[19]	3DAP	Fe	P	0.6±0.3(1σ)

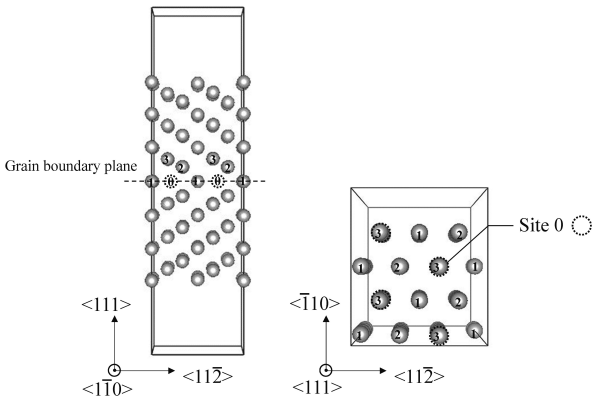

Fig. 6 bcc-Fe Σ 3(111) grain boundary model for density functional theory calculation

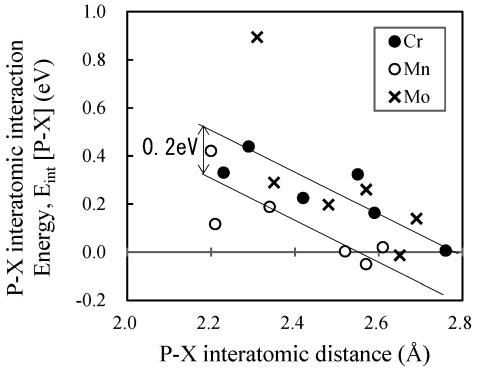

Fig. 7 Relationship between P-X interaction potential and interatomic spacing at grain boundary

the interatomic spacing is low, and the interaction potential is zero around 2.6 Å for Mn and 2.8 Å for Cr and Mo. This suggests that the interaction potential depends on the P-X interatomic spacing, that there is little difference in the dependence on the interatomic distance among added elements, and that Cr and Mo have greater repulsive potential than Mn, which inhibits P segregation. Actual materials have additional factors to account for, such as grain boundary strengthening caused by the grain boundary segregation of added elements as well as the effects of carbides and precipitates on the amount of solute. However, physical analysis of the grain boundaries validates our calculations and the physical phenomena determined to support embrittlement suppression.

Conclusions

This paper demonstrates why atomic-level analysis and evaluation technologies are necessary and how Kobe Steel uses them to develop materials in support of the company's materialities of contributing to a green society and ensuring safety and security in community development and manufacturing. Reducing the weight of transportation equipment and extending the service life of structures call for materials with higher strength, ductility, and corrosion resistance. These objectives require the microstructure and structure of materials to be controlled at the atomic level. Samples and datasets to be analyzed have become extremely large in tandem. This drives Kobe Steel's work in the advancement of high-throughput databases, measurement informatics, and AI for enhanced high-speed analysis. Furthermore, there is a global shift toward carbon neutrality, which is a prerequisite for a safe and secure society. Material performance requirements are also undergoing major changes in support of a hydrogen society, alternative energy, and carbon-neutral processes. Physical analysis and evaluation techniques to evaluate atomic-scale behavior, which governs material performance, will take on increasing importance against this backdrop.

Atomic-level analysis and evaluation technologies are essential for developing safer and more reliable materials. Making the invisible visible provides direction, which we will use to continue refining our techniques to explore the ways in which materials can support carbon neutrality.

Evaluation of P segregation at grain boundaries via STEM-EDS was performed in collaboration with the research team led by Toru Hara at the National Institute for Materials Science. We hereby express our gratitude.

References

1) SUNBEAM Consortium. What is Sunbeam?. https://sunbeam.spring8.or.jp/. Accessed 2023-08-30.
2) K. Shibata et al. Materials Science Forum. 2021, Vol.1016, pp.1331-1336.
3) T. Murakami. Materials Science Forum. 2021, Vol.1016, pp.984-989.
4) Y. Aruga et al. R&D Kobe Steel Engineering Reports. 2017, Vol.66, No.2, pp.42-47.
5) Y. Aruga et al. Materials Science and Engineering: A. 2015, Vol.631, pp.86-96.
6) A. C. Day et al. Microscopy and Microanalysis. 2019, Vol.25, pp.288-300.
7) T. Murakami. R&D Kobe Steel Engineering Reports. 2019, Vol.69, No.1, pp.29-32.
8) A. Hino et al. R&D Kobe Steel Engineering Reports. 2021, Vol.71, No.1, p.53.
9) M. Terauchi et al. Surface Science. 2015, Vol.36, No.4, pp.184-188.
10) K. Tanaka. Bulletin of the Japan Institute of Metals. 1976, Vol.15, No.12, pp.753-761.
11) M. Amman et al. Journal of Vacuum Science & Technology B. 1996, Vol.14, No.1, pp.54-62.
12) Y. Murakami et al. Bulletin of the Japan Institute of Metals. 1981, Vol.20, No.9, pp.784-793.
13) J. Murakami et al. Iron and Steel. 1987, Vol.73, No.1, pp.191-198.

14) A. Partridge et al. Surface and Interface Analysis. 1992, Vol.18, p.713.
15) M. Watanabe et al. Journal of Microscopy. 2006, Vol.221, No.2, pp.89-109.
16) K. Yamada et al. e-Journal of Surface Science and Nanotechnology. 2020, Vol.18, pp.94-99.
17) K. Yamada et al. R&D Kobe Steel Engineering Reports. 2021, Vol.71, No.1, pp.58-63.
18) C. Marvel et al. Ultramicroscopy. 2019, Vol.202, pp.163-172.
19) L. Zhang et al. Journal of Nuclear Material. 2019, Vol.523, pp.434-443.
20) S. Morita. R&D Kobe Steel Engineering Reports. 2021, Vol.71, No.1, pp.3-7.