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Recent Activities in Research of Analysis and Material Science

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This article reviews the research trends during the last decade in chemical analysis, process control analysis, surface analysis and microscopic characterization in Kawasaki Steel. The analytical methods, such as the highly accurate ultratrace analysis for steels and silicon materials and the spark discharge optical emission spectroscopy for gaseous constituents in steels, have been developed in order to meet the requirements from the material developments and manufacturing process. It is demonstrated that field emission gun Auger electron spectroscopy (FE-AES) and field emission gun transmission electron microscope (FE-TEM) have become novel powerful tools for the surface and structure characterization. The application of X-ray diffraction and Raman spectroscopy to in situ analysis at high temperature are also described.

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Recent Activities in Research of Analysis and Material Science*



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1 Introduction

Continuing efforts to lower the impurities in iron and steels, as well as to control the inclusions and precipitates, have produced a number of iron-based materials of improved material properties, including IF (interstitial atom free) steel, and a variety of higher purity steels for better characteristics are under development. At the same time, on the production line, quick and accurate analyses are being demanded for higher productivity and product quality.

For devising novel materials and improving the material properties, and for improving the production line, physical and chemical evaluation techniques must collaborate with one another where more advanced analytical techniques have been developed and, in some cases, analytical instruments of our own design have been made. The present paper examines the progress in physical and chemical analyses, and in the process control analyses, during the last decade at the Analysis and Materials Science Laboratory of Kawasaki Steel.

2 Recent Technical Progress

2.1 Trace Elemental Analyses

2.1.1 Analysis of the trace elements in iron and steels

Inductively coupled plasma mass spectrometry (ICP-MS) has been coming into use for trace elemental analyses in various applications during the last decade.¹⁾ This is because the ICP-MS is able to analyze multiple elements simultaneously and has much better sensitivity than the inductively coupled atomic emission spectrometry (ICP-AES) for most elements.

In order to fully utilize the high sensitivity of the ICP-MS for the analyses of iron and steel samples, it is essential to isolate the analyte elements from the matrix elements, and minimize the contamination arising from the reagents and labware used in the chemical treatment processes. The chemical pretreatment methods we have developed for the isolation of trace elements from the matrix elements are as follows.²⁻⁵⁾

(1) For the analyses of Al, Cr, Ni, and other metallic impurity elements, a sample was dissolved in an HCl-HNO₃ mixture, and the matrix Fe was removed using 4-methyl-2-pentanone.²⁾ If the sample contained Cr as

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a matrix element, Cr was removed as $\text{Cr}_2\text{Cl}_2\text{O}_2$ vapor.³⁾ This procedure isolated the elements Be, Al, Ca, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ba, Pb, Bi, as well as rare earth elements.

- (2) For the analyses of the elements (Mo, Sn, etc.) which were removed by the 4-methyl-2-pentanone extraction with matrix Fe, and of the elements (W, Zr, etc.) which were sparingly soluble in the HCl-HNO_3 mixture, a sample was decomposed by HF. The elements which formed the fluoro complexes or the oxo anions in the HF solution were adsorbed on a strongly basic anion exchanger resin, where the cationic matrix elements, Fe and Cr, were not adsorbed. This procedure isolated such elements as As, Zr, Nb, Mo, Sn, Te, Hf, Ta, and W.³⁾
- (3) For the analysis of B, a sample was treated with hot $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ to decompose the BN in the sample, and B was collected on a borate specific anion exchanger resin (Amberlite IRA-743).⁶⁾
- (4) For the analyses of Si and P, these elements were converted into molybdosilicate and molybdophosphate, respectively, and were separated from the matrix elements on a dextran gel column. The Si and P were determined by monitoring the Mo in the molybdosilicate and the molybdophosphate by ICP-MS.^{4,5)}

After the isolation of the analyte elements from the matrix, each of the elements was determined by using ICP-MS. The determination limit was 0.01~0.1 ppm for most of the elements studied.

For the analyses of the lighter elements, including C, O, and N, the combustion/fusion method has been employed, because both ICP-AES and ICP-MS are less sensitive for these elements. However, for the analysis of lower ppm levels, contamination on the sample surface significantly skews the analytical values. A means to remove the surface contamination, as well as the standardization method, remains for further study.⁷⁻⁹⁾

2.1.2 Analysis of the trace elements in silicon based materials

Analyses of the trace impurity elements (Al, Cu, Fe, P, and B) in the purified silicon materials for LSI and solar batteries have been another target of our research. In order to minimize contamination from the reagents, the silicon sample was decomposed by HF-HNO_3 vapor at elevated temperature under elevated pressure in a closed container where the sample and the acids were placed in separate cups to avoid immersion of impurities from the decomposing acid. The matrix Si was removed as gaseous SiF_4 , leaving the impurity elements in the sample cup. The addition of a small amount of H_2SO_4 or H_3PO_4 to the sample prevented from losing the analyte elements. The residue in the sample cup was dissolved in water, and the impurity elements were analyzed by ICP-MS.¹⁰⁾

Analysis of the analyte element P by ICP-MS was not

sufficiently sensitive. Therefore, P was converted to molybdophosphate, which was isolated as an ion-pair with cationic surfactant, and Mo in the molybdophosphate was measured by ICP-MS for determination of P.¹¹⁾

Our method enabled the determination of the concentrations of impurity elements down to a few ppb.

2.2 Process Control Analysis

2.2.1 Analysis of ultra-low C and N in steels by optical emission spectroscopy

Optical emission spectroscopy is widely used as an analytical method for quality control in steelmaking process because of its excellent accuracy and rapidness. However, ultra-low C and N have been separately analyzed by combustion/fusion method due to the poor precision of conventional optical emission spectrometers. However, the demand for the rapid analysis of ultra-low C and N increases with the progress of steelmaking technology. In order to meet this demand, a new optical emission spectrometer was developed.¹²⁾

For the analysis of ultra-low C and N, it is quite important to reduce the background intensity. To this end, a horizontal emission stand was developed which could successfully screen the background light generating just above the specimen surface. Moreover, a newly designed ultra-violet spectrometer, whose grating center was adjusted to the vicinity of emission lines of C and N, was developed. In this spectrometer, C and N spectra were measured directly without reflection by mirror. With these developments, ultra-low C and N could be analyzed by optical emission spectroscopy with a repeatability of 0.5 ppm and 0.8 ppm for C and N, respectively.

2.2.2 Analysis of oxygen concentration, particle size distribution and chemical composition of inclusions by optical emission spectroscopy

O in steels influences such properties as formability, weldability and surface condition. The analysis of O concentration, particle size distribution and chemical composition of inclusions has required much time and labor. Therefore, a new rapid analytical technique in optical emission spectroscopy was developed to facilitate the analysis of O concentration, particle size and chemical composition of inclusions.¹³⁾

In optical emission spectroscopy, anomalous emission is observed when discharge occurs to the inclusions. Therefore, discharges showing anomalous emission of O and inclusion-forming elements such as Al, Ti and so on were selected as the discharges to the inclusions. On the other hand, discharges showing normal emission were selected as the discharge to the matrix without containing inclusions. The net O emission intensity was determined as the difference in O emission intensities

between anomalous and normal emissions. The background intensity of O emissions could be significantly reduced with this method and analytical accuracy of 4 ppm was obtained.

Rapid analysis methods for particle size distribution¹⁴⁾ and chemical composition of inclusions were also developed using similar principles. It was found that there was a strong correlation between the anomalous emission intensity and the particle size; therefore, particle size could be calculated by measuring the anomalous emission intensity. The maximum particle size in a certain amount could be determined by using extreme values statistics after measuring at 10 points in a specimen. The developed method was applied to low carbon steels and the result was in good agreement with that obtained by the laser diffraction scattering method.

2.2.3 Other developments

A new X-ray fluorescent spectrometer was developed for the rapid analysis of slag.¹⁵⁾ The chemical composition of slag used to be analyzed by X-ray fluorescent analysis after preparing the glass bead samples, but this procedure took much time. The developed spectrometer can analyze the sampled slag piece directly without pretreatment, therefore, analysis time is significantly shortened and the results can be fed back to the production line.

An on-line analyzer for the pickling solution of HAP and CAP was developed and put into practical use.

2.3 Surface and Interface Analysis

Due to the growing importance of elemental and chemical state analysis at the surface and interface in the development of materials and processes, various surface analytical methods have been applied to steel products. Recently, the performance of spatial resolution, sensitivity and so on has been greatly improved, expanding the breadth and complexity of analyses.

Auger electron spectroscopy (AES), whose incident beam diameter could be focused to 15 nm by using a field emission electron gun (FE), was applied to the analysis of the granular precipitates formed on the surface of Si and Mn-added high tensile steel sheets during annealing. These precipitates, whose diameters were less than a micron, influenced the molten zinc-wettability and alloying behavior. FE-AES revealed that the precipitates were complex oxides consisting of Si, Mn and O, and changed the stoichiometry with the Si and Mn content.¹⁶⁾

The elemental depth profile of insulating films such as thick oxide layer and organic film could be analyzed by glow discharge optical emission spectroscopy (GDS) by using high frequency as a discharge power source.

A charge neutralization method in secondary ion mass spectrometry (SIMS) was successfully applied to the determination of small amounts of Fe, Cr and La in thick oxide film formed on Fe-20Cr-5Al alloy developed

for the catalytic gas converters of automobiles. The developed method consists of the pre-evaporation of Al or Au on the surface of the specimen (except for the analyzing area) and simultaneous irradiation of electrons. The results suggest that the diffusion of O during high temperature oxidation was retarded by the surface oxide film formed by annealing, and consequently resistance to high temperature oxidation was improved.¹⁷⁾

2.4 In Situ Analysis

An *in situ* X-ray diffraction instrument was developed for the dynamic analysis of reactions at high temperature. A Seeman-Bohlin camera using an imaging plate was employed in order to enable rapid and sensitive measurement. The developed instrument was applied to the analysis of the phase change of galvanized coating during annealing¹⁸⁾ and the oxidation/reduction process of steel sheets at high temperature.¹⁹⁾

An *in situ* laser Raman spectrometer was developed in order to analyze the chemical state of initial surface oxides on various steel sheets and its variation with temperature. A single monochromator equipped with a CCD detector enabled rapid and sensitive measurement.

2.5 Elemental and Crystal Structure Analysis by Electron Microscope

With advances in materials research, it has become indispensable to evaluate the effects of microscopic properties, such as crystal structure, crystal orientation and chemical composition near grain boundaries or fine precipitates.

Transmission electron microscopes (TEM) have been playing an important role in such materials research because of their high spatial resolution and capability of microanalysis. Of the recent advances in TEM performance, the most notable is the development of TEM with a field emission gun (FE-TEM). FE-TEM, which produces a very fine electron beam more than 100 times brighter than usual electron emitters. This has made it possible to analyze the structure and chemical composition at the atomic scale.

The FE-TEM being used in our laboratory is equipped with an energy-dispersive X-ray spectrometer and electron energy loss spectrometer. Combining these spectroscopic techniques with the electron beam scanning unit, elemental mapping images can be obtained with high spatial resolution. Applications of FE-TEM to the steels include (1) the observation of the Cr-depleted layer at the grain boundaries in the high-purity 18% Cr steels,²⁰⁾ and (2) the study of the grain boundary segregation in the oxide scales on the Fe-20Cr-5Al alloys containing small amounts of La and Zr.²¹⁾

The focused ion beam (FIB) technique is now widely used as a thin film preparation method for TEM, and has greatly expanded the application limits of TEM. The FIB technique is a micro-fabrication by Ga ion beam sputtering, which has been used to analyze and correct

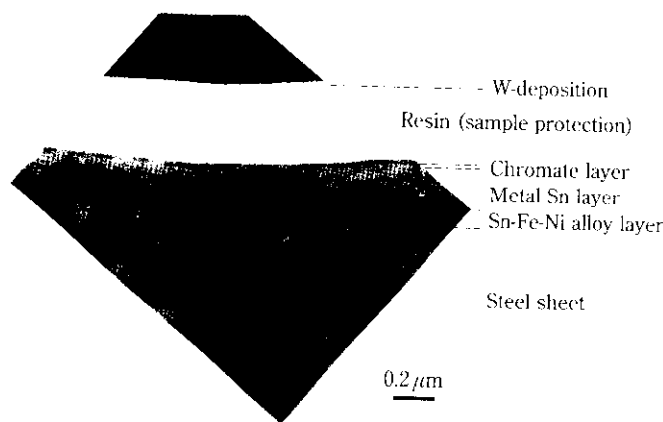


Photo 1 Cross-sectional micrograph of the low tin plated steel with FIB-TEM technique

defects in semiconductor devices. With recent improvement of the ion beam performance, such as large current density and fine beam diameter, FIB has started to be applied to the thin film preparation for TEM. One of the advantages of FIB is the *in situ* observation of the fabrication area on the specimen surface by scanning ion microscopy (SIM). In addition, FIB allows the homogeneous thinning of specimens consisting of different materials, which was not possible by the usual specimen preparation methods, such as electropolishing or ion milling.

In our laboratory, FIB has been applied to the cross-sectional specimen preparation of zinc-plated steels,²²⁾ tin-plated steels²³⁾ and oxide scales formed on stainless steels.^{21,24)} An example is shown in **Photo 1**, which indicates the layered structure of the tin-plated steel. It has been shown that FIB is also applicable to the thin film preparation of materials having several phases with different sputtering rates.

A scanning electron microscope (SEM) equipped with four backscattering electron detectors aligned annularly with respect to the incident beam is being applied at our laboratory to high resolution observations of surface morphology or chemical compositions of steel sheets.

3 Conclusions

Research trends at the Analysis and Materials Science Laboratory in Kawasaki Steel during last decade was reviewed. Great progress has been made in lowering the detection limit of trace element analysis, and in the rapid and accurate process control analysis. Progress was also

made in the research for microscopic material characterization using FE-TEM, FE-AES and so on, and also for dynamic analysis through *in situ* analysis.

These analytical techniques will continue to be the major tools for materials characterization, where further sensitivity and precision will be expected. We should work for the timely development of suitable analytical techniques through close cooperation with the researchers in the area of materials and process developments.

References

- 1) T. Shimamura: *Bunseki*, (1997), 644
- 2) T. Okano and Y. Matsumura: *Tetsu-to-Hagané*, **77**(1991), 1951
- 3) K. Hanada, K. Fujimoto, and M. Shimura: *CAMP-ISIJ*, **10**(1997), 685
- 4) K. Hanada, K. Fujimoto, M. Shimura, and K. Yoshioka: *Bunseki Kagaku*, **46**(1997), 749
- 5) K. Hanada, K. Fujimoto, M. Shimura, and K. Yoshioka: *Phys. Stat. Sol. (A)*, **167**(1998), 383
- 6) K. Fujimoto and M. Shimura: *Tetsu-to-Hagané*, **85**(1999), 114
- 7) H. Yasuhara, Y. Funahashi, T. Mega, and A. Yamamoto: *CAMP-ISIJ*, **7**(1994), 382
- 8) H. Yasuhara, M. Shimura, and K. Yoshioka: *Phys. Stat. Sol. (A)*, **160**(1997), 575
- 9) H. Yasuhara, M. Shimura, and K. Yoshioka: *Tetsu-to-Hagané*, **85**(1999), 138
- 10) K. Fujimoto and T. Okano: *Bunseki Kagaku*, **42**(1993), T135
- 11) K. Fujimoto, M. Ito, M. Shimura, and K. Yoshioka: *Bunseki Kagaku*, **47**(1998), 187
- 12) T. Sugihara, Y. Funahashi, I. Fukui, and T. Miyama: Proc. of the 4th Int. Conf. on Progress in Analytical Chemistry in the Steel and Metals Industry, (1996), 229
- 13) W. Tanimoto, A. Yamamoto, and H. Manda: *CAMP-ISIJ*, **11**(1998), 1352
- 14) T. Matsumura and A. Yamamoto: *CAMP-ISIJ*, **11**(1996), 784
- 15) N. Makiishi, A. Yamamoto, and H. Manda: *CAMP-ISIJ*, **11**(1998), 1348
- 16) A. Yamamoto, T. Yamashita, and J. Shimomura: Proc. of the 1st China-Japan Joint Sym. on Microbeam Analysis, (1994), 245
- 17) Y. Usui, A. Yamamoto, J. Shimomura, M. Kouno, K. Ishii, and K. Yoshioka: *Bunseki Kagaku*, **45**(1996), 625
- 18) T. Fujimura, J. Shimomura, S. Gomi, M. Katayama, and Y. Kobayashi: *Materia*, **34**(1995), 783
- 19) Y. Usui, W. Tanimoto, and A. Yamamoto: *CAMP-ISIJ*, **10**(1997), 698
- 20) S. Ishikawa, M. Fujisawa, and J. Shimomura: *CAMP-ISIJ*, **8**(1995), 1403
- 21) S. Ishikawa, M. Kouno, K. Ishii, J. Shimomura, and K. Yoshioka: *J. Jpn. Inst. Metals*, **60**(1996), 463
- 22) C. Maeda, T. Hoshi, T. Matsushima, J. Shimomura, M. Isobe, and S. Satou: *CAMP-ISIJ*, **8**(1995), 992
- 23) H. Ohta, A. Inenaga, and K. Yoshioka: *CAMP-ISIJ*, **10**(1997), 701
- 24) K. Fukuda, T. Ujiro, S. Satou, and H. Ohata: *Tetsu-to-Hagané*, **84**(1998), 345