

Recent Technical Progress in Analysis and Material Evaluation at Kawasaki Steel*



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Synopsis:

This article reviews the recent technical progress 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 and inclusions in steels, have been developed in order to meet the requirements from the material developments and manufacturing process. It is demonstrated that FE-AES and FE-TEM have become novel powerful tools for the surface and structure characterization. The applications of X-ray diffraction and Raman spectroscopy to in-situ analysis at high temperature are also described.

1 Introduction

Kawasaki Steel has advanced and developed analysis and material evaluation techniques responding to the requirements from process and product development.

Recently, types of steel having various special features enhanced by their high purity, such as IF steel, have been developed, and researches are being made on the development of more advanced high purity steel. Along with this, a sub ppm level determination is being demanded in some elements. Also, in process control analysis, faster and at the same time more precise analytical methods are being demanded to enhance productivity. Our laboratories have, in response to these demands, developed ultratrace analytical techniques and rapid process control analysis methods and so on.

Concerning material evaluation technology, more sophisticated characterization techniques are required both for controlling the material quality and for product development. To meet such demands we have endeavored to enhance material characterization techniques by use of the most advanced analytical instruments for measuring elements and crystal structure. Furthermore, as the analytical instruments which are commercially available are limited in their ability to respond to the recent requirements, analytical instruments of our own design have been built in certain cases, and are used for

evaluating new materials.

Here, the recent technical progress at our company in the field of analytical methods such as chemical analysis, process control analysis, as well as in material evaluation techniques will be reviewed, and some of the developed analytical methods and instruments which have been introduced or developed recently will be presented together with examples of their application in material evaluation.

2 Recent Technical Trends and New Analytical Methods

2.1 Trace Element Analysis

2.1.1 Development of analytical methods for trace elements in steel

As one of the largest progresses in trace element analysis during the last decade, the performance of instruments for mass spectrometry using inductively coupled plasma as an ion source (ICP-MS) have advanced remarkably, and the ICP has been applied in the various field of trace element analysis¹⁾. ICP-MS is capable of determining a number of elements simultaneously, and furthermore, has greater detection sensitivity for many elements than inductively coupled plasma atomic emission spectrometry (ICP-AES), therefore, it

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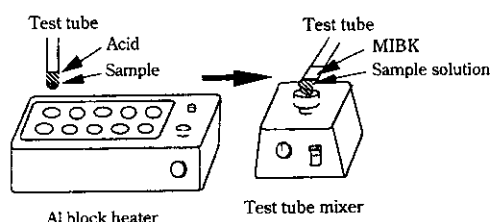


Fig. 1 Method of decomposition in a single test tube

is a very effective tool in the analysis of trace elements in iron and steel.

In the development of high purity iron and high purity stainless steel which are recently attracting a high level of attention, the establishment of the analytical methods for ultratrace elements in steel is indispensable, therefore our laboratories have initiated studies on the application of ICP-AES and ICP-MS to the analysis of iron and steel material since the early days. For determining the ultratrace elements in a material with a high level of sensitivity and accuracy, it is important to convert the analyte elements into a state of solution, under conditions that minimize contamination, and to isolate them from the matrix. Furthermore, from the standpoint of simplification of the chemical pretreatment and reducing the blank values, it is important to develop a chemical pretreatment method which can be applied to as many kinds of elements as possible.

(1) Decomposition

The contamination derived from the reagent or labware used in chemical pretreatment, such as decomposing the steel samples or isolation of the matrix, etc. often hinders the analysis of ultratrace elements. Therefore, for the purpose of reducing the contamination in preparing sample solutions, the decomposition method as shown in Fig. 1 (which the authors here call the test tube decomposition method) has been worked out²⁾. This method uses as small an amount of sample (0.1~0.5 g) as possible to such extent as not to allow the effect of segregation, and carries out the treatment from decomposition of a sample to isolation of the matrix in one test tube made of quartz or Teflon. The use of the test tube decomposition method has allowed a reduction of the amount of sample, reagent, and the number of utensils used, facilitating the cleaning of utensils, and simplifying the handling involved, thus significantly contributing to a reduction of blank values which decisively affects the determination limit.

(2) Isolation of the Matrix

In ultratrace analysis, a process to isolate the analyte elements from the matrix is needed to avoid the interference derived from the matrix which would impede the ICP-MS measurement, and to allow the preparation of a calibration curve using a standard solution

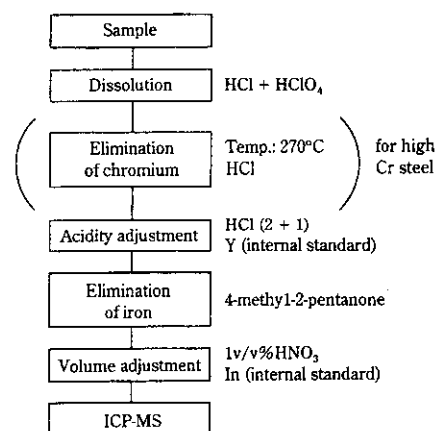


Fig. 2 Analytical procedure of high purity steel

which does not contain any of the matrix. The matrix isolation methods as shown below have been established according to the chemical nature of the analyte elements.

In the analysis of the metallic impurities such as Al, Cr, Ni, etc., the matrix (Fe) was separated by a solvent extraction method which uses 4-methyl-2-pentanone after decomposing the sample with a small amount of hydrochloric acid and nitric acid²⁾. In samples containing a high ratio of Cr, the Cr was removed in vapor as chromyl chloride ($\text{Cr}_2\text{Cl}_2\text{O}_2$)³⁾. An outline of this method is shown in Fig. 2. In this process, the Be, Al (acid soluble portion only), Ca, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ba, Pb, Bi and the rare earth elements can be determined.

To determine the Mo, Sn contents, an isolation of which from Fe is difficult in the above mentioned extraction, and W, Zr which is difficult to dissolve in the hydrochloric acid and nitric acid mixture, the hydrofluoric acid was used for decomposing the sample, and the analyte elements were collected in a strongly basic anion-exchange resin as fluoro complexes or oxo anions, thus isolating them from the matrix³⁾ (Fig. 3). This process can simultaneously determine the As, Zr, Nb, Mo, Sn, Te, Hf, Ta, W contents.

For Si and P, heteropolyacid was formed with molybdic acid, and was selectively adsorbed on a dextran gel such as Sephadex G-25 and separated from the iron, then the Mo in the eluate was measured, thus an indirect determination was made^{4,5)} (Fig. 4).

For B, after a complete decomposition by fuming with sulfuric acid-phosphoric acid, the element was isolated from Fe using a weakly basic anion-exchange resin (Amberlite IRA-743) containing a polyol group⁶⁾ (Fig. 5).

The determination limits of the impurity elements in the high purity iron by the above mentioned methods (10 times the standard deviation (σ) of the blank value) are

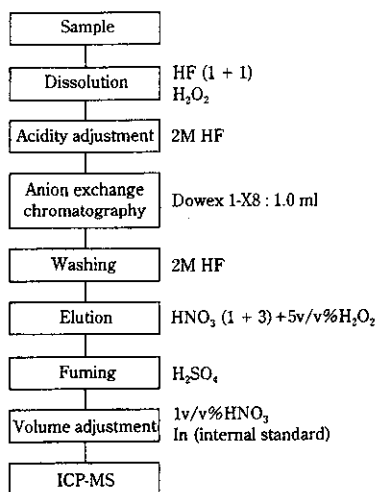


Fig. 3 Analytical procedure for high purity steel

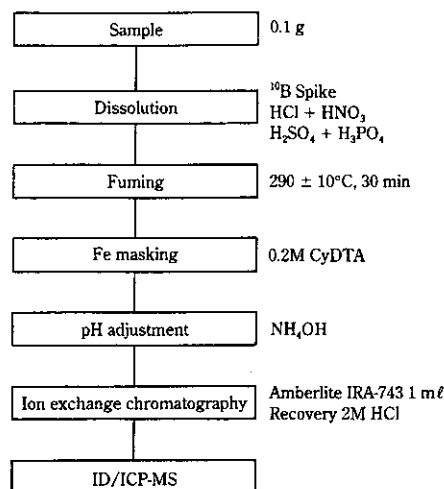


Fig. 5 Analytical procedure for B in high purity steel

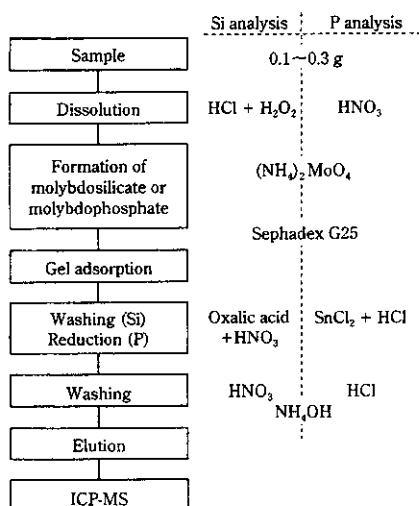


Fig. 4 Analytical procedure of Si and P in high purity steel

Table 1 Determination limits (10σ of blank values) of trace elements in iron and steel

Element	Determination limit (ppm)	Method	Element	Determination limit (ppm)	Method
Be	0.05	1	Zr	0.01	2
B	0.05	4	Nb	0.01	2
Mg	0.3	1	Mo	0.01	2
Al	0.3	1	Cd	0.01	2
Si	0.05	3	Sn	0.1	2
P	0.5	3	Sb	0.05	2
Ca	0.3	1	Ba	0.01	1
Ti	0.1	1 or 2	La	0.01	1
V	0.1	1	Ce	0.01	1
Cr	0.3	1	Ta	0.01	2
Mn	0.01	1	Te	0.01	2
Co	0.01	1	Hf	0.01	2
Ni	0.1	1	W	0.01	2
Cu	0.02	1	Pb	0.01	1
Zn	0.07	1	Bi	0.01	1

Method 1: 4-Methyl-2-pentanone extraction/ICP-MS

Method 2: Anion-exchange chromatography/ICP-MS

Method 3: Gel adsorption/ICP-MS

Method 4: Borate specific ion exchange chromatography/ICP-MS

shown in Table 1. About 30 elements except B, Si, and P could be determined to sub ppm levels with only two types of chemical pretreatment.

2.1.2 Analysis of small amounts of light elements in steel

Both ICP-AES and ICP-MS are less sensitive to such light elements as C, N, O, etc. While a combustion, or fusion method are widely used for analysis of these elements, the effects of surface contamination can not be ignored for the analysis of single digit ppm levels, and the standardization remains as a problem⁷⁻⁹. There are a number of technical problems which need to be solved in this field, thus further studies are required.

2.1.3 Development of analytical methods for trace elements in high purity silicon based materials

Studies have been made to develop an analytical method for trace impurity elements in silicon materials, along with the advancement of our company into the field of high purity silicon based materials. For an evaluation of the ultratrace impurities at a ppb level or below in high purity silicon material used in LSI chips and solar batteries, it was necessary to combine a sample

preparation method, with as little contamination as possible, with a high sensitivity detection method. Therefore, a pretreatment process¹⁰⁾ to decompose the elements with pressurized acid vapor was developed, in which the decomposing acid was placed in a pressurized decomposition vessel, then a mini-cup containing a sample was submerged therein. As samples are not soaked in the acid in this process, the effect of the impurities in the acid can be restricted to the minimum. The matrix Si was vaporized as SiF₄ and was collected in the outside decomposing acid, thus only impurities in the sample remain in a condensed form. To prevent the evaporation of the analyte elements, the addition of a very small amount of sulfuric acid or phosphoric acid was effective. The impurities remaining in the mini-cup were diluted with a small amount of water and then determined by ICP-MS. For an analysis of P, for which sufficient sensitivity could not be obtained by ICP-MS, P was converted to molybdophosphate, which was isolated as an ion-pair with a cationic surfactant, and was collected on a filter, then after dissolving the filtrate, the Mo in the solution was measured for an indirect determination of the P¹¹⁾.

These methods enabled the determination of the Al, Cu, Fe, P, B, etc. concentrations at a ppb ~ 10 ppb level in the silicon material under an ordinary laboratory environment in a simple manner.

2.2 Analysis of Inclusions, Precipitates, Plating Layers

It is important for improving the properties of iron and steel material to understand and control the chemical composition of inclusions and precipitates, thus studies have been made on methods to analyze the chemical compositions and to quantitatively analyze such materials in different types of steel¹²⁻¹⁴⁾. The need for the determination of trace amount of oxide in steel is increasing, and a method to determine in a single digit ppm level has been established¹⁵⁾. Also, a process to measure the particle size distribution of the oxides in steel by the laser diffraction scattering method has been established, so that the material properties can be evaluated from a new view point¹⁶⁾.

Concerning the analysis of plating layers, processes to analyze plating layers were studied along with the development of new plating systems. The behavior of the chemical and electrochemical dissolution of various types of plating layers was investigated to obtain the alloy composition of zinc plating, and the plating weight per unit area. Also, a method for the determination of the dross in a zinc plating bath by extraction has been established^{17,18)}.

2.3 Process Control Analysis in Steelmaking

Along with recent progress in steelmaking technology especially on second refining treatment, the production ratio of ultra-low carbon steel sheets has increased for

the purpose of high formability. In order to reduce the cost and to improve the production yield, rapid analysis of ultra-low C and N with high precision is becoming important. Optical emission spectroscopy, which is simple to handle and can analyze the major constituents in steel simultaneously within a short period of time, has become widely used as a process control analysis method in the steelmaking process. However, for ultra-low C and N, both the analytical accuracy and the determination limits in conventional optical emission spectrometer are inadequate, therefore C is analyzed by the combustion-infrared absorption method, and N by the inert gas fusion-thermoconductivity method. Under the circumstances, our company has developed a new optical emission spectrometer, which can make quantitative analysis of ultra-low C and N simultaneously with all elements whose concentrations are needed to be known for process control¹⁹⁾. The special features of the developed apparatus will be described below.

To determine ultra-low C and N levels with high accuracy, it is quite important to reduce the background intensities which are contained in respective emission intensities. As the sources of such background light, the light emitted from a sample which is heated by discharge, white light from Ar plasma and the light scattered by sample vapor could be thought. Conventional inclining emission stands allow such a background light generated directly above the sample to enter into a monochromator in order to increase the quantity of light. Therefore a horizontal emission stand was developed for the purpose of screening such background light from the field of view of the monochromator. In such a horizontal emission stand, a spacer can be positioned between the light emission stand and the sample, thus the background light can be substantially reduced and at the same time the optimum measuring position can be selected.

Also, an ultra-violet spectrometer whose grating center is in the vicinity of the emission lines of C and N (150 nm in periphery), was newly installed, thus the spectrum resolution of the ultra-violet region was enhanced. This ultra-violet spectrometer is designed with a structure so that spectral lines of 170 nm or shorter can be directly received by its detector instead of having the lines reflected once at a mirror and then directing them to the detector like in a conventional system, thus the measuring intensity was substantially increased.

The repeatability (σ) of C and N when standard samples, JSS 1006 (C: 12 ppm), STN-1 (N: 18 ppm) were analyzed with the new spectrometer was 0.5, 0.8 ppm, respectively, indicating a remarkable improvement over the conventional apparatus. Also, the determination limits (10σ) of C, N are 5 ppm and 8 ppm, respectively. Thus ultra-low C and N concentrations, which had been previously determined by the conventional combustion or the fusion method, can now be analyzed with optical

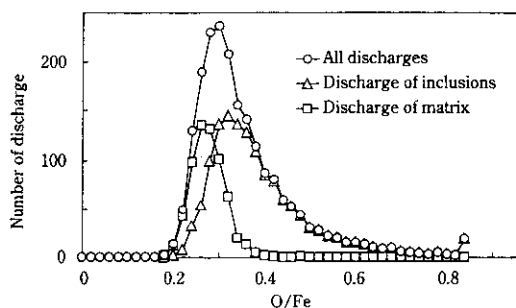


Fig. 6 Frequency distribution curves of O/Fe

emission spectroscopy, and this new method has been partially put into practical use.

On the other hand, concerning the analysis of the concentration of O, chemical composition and particle size distribution of inclusions, which substantially affect the quality of steel such as formability, weldability, resistance to fatigue, surface conditions. Conventionally O has been determined by the inert gas fusion infrared ray absorption method, and the particle size distribution or chemical composition of inclusions has been determined by the chemical extraction method, the optical microscopic method, the electron beam melting method, and the laser diffraction scattering method. However, as these methods required much time before the results of measurements were known, the development of more rapid analytical methods had been required. In response to such requirements, we have developed a quick and highly accurate analytical method for O and particle size distribution and chemical composition of inclusions by optical emission spectroscopy. An outline of the thus developed method will be described below.

In optical emission spectroscopy, it has been known that when a discharge occurs to the oxides of Al and Ti, etc. in steel, very intense emissions (anomalous emissions) of inclusion-forming elements and O take place. The anomalous emissions could be identified by using the thresholds which were respectively prescribed after taking the ratio of the emission intensity of inclusion-forming elements and O to Fe over 2 000 discharges (one measurement). Furthermore, when a discharge occurs to oxides in steels, anomalous emissions are observed simultaneously in at least one of the inclusion-forming elements and O, thus such discharges were determined to be the discharges to the oxides. The frequency distribution of the ratio of emission intensity of O to Fe (O/Fe) when such an extraction method was applied to low alloy steels is shown in Fig. 6 for the total discharges, the discharges selected as the discharges to the oxides and the unselected discharges to the matrix. It was revealed from the results that the O/Fe could be clearly distinguished between the discharges to the oxides and the discharges to the matrix. Therefore, the O/Fe in the selected discharge is regarded as the O/Fe in

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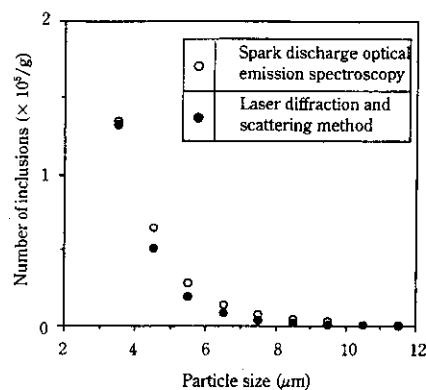


Fig. 7 Particle size distribution of Al_2O_3 inclusions in a low carbon steel

the discharges to the oxides. On the other hand, the O/Fe in the discharges showing no anomalous emission is regarded as the O/Fe in the discharges to the matrix. The background intensity could be remarkably reduced by using the difference in these two kinds of emission intensity ratios²⁰⁾ and a rapid and highly accurate analysis of O was made possible. The analytical accuracy (σ_a) of the developed method was 4 ppm, and we are planning to apply this method to process controlling analysis.

Furthermore, it was revealed that such anomalous emission intensities have a close mutual relationship with the particle size of the inclusions, and a rapid analytical method of the particle size distribution for inclusions with an optical emission spectroscopy has been developed.²¹⁾ The particle size of the inclusions can be obtained by converting the amount of vaporized Al when an anomalous discharge occurs to the amount of Al_2O_3 , and computing the sphere equivalent diameter. Figure 7 shows the particle size distribution of low carbon steel measured by the developed method comparing with that measured by the laser diffraction scattering method. The particle size distribution in both methods showed a fair agreement. The maximum particle size of the inclusions of a certain amount of sample can be assumed by making the measurements a number of times, and applying extreme values statistics to the maximum particle size in each measurement.

The maximum particle sizes obtained in low carbon steel by the developed method and those obtained by the laser diffraction scattering method (corresponding to 1 g of sample) were compared, and the results of both methods showed a good agreement.

The inclusion-forming elements such as Ca and Mg can be also determined with satisfactory accuracy by extracting the discharge at which the inclusion forming elements and oxygen show anomalous emissions.

By this development of the discharge separation extraction method, the particle size distribution of inclusions and analysis of their chemical composition, which would take a long time by chemical analysis, can be

made rapidly by the optical emission spectroscopy analysis.

Besides the development of an analysis method for gas elements in steel, an analytical method was established for Ni, and Cr in stainless steel by optical emission spectroscopy, which had been analyzed in the past by the X-ray fluorescent analysis method, and shortened the analysis time.

As far as the expediting of the process control analysis is concerned, on-site X-ray fluorescent spectrometer for steelmaking slag was also developed realizing a substantial shortening of the analysis time. The chemical composition of the steelmaking slag is an important indicator for process control, and had been analyzed heretofore by the glass bead method or the briquet X-ray fluorescent analysis method. However, as these methods took a long time for preparation of the glass bead, the analytic results could not be used in process control. In the spectrometer developed, slag pieces collected can be directly analyzed without converting them into glass beads, and shortens the time for slag analysis from 50 min in the conventional method to 1 min²²⁾. The accuracy of the analysis was $\pm 1\%$ or better for CaO, SiO₂, Al₂O₃ and MgO respectively, and was $\pm 0.1\%$ or better for T.Cr.

2.4 Surface and Interface Analysis

The analysis of composition, chemical state of films and scale on steel sheets, or of impurities of small amounts at film/steel sheet interfaces is becoming increasingly important recently for the development of products and processes. Therefore, our company is effectively using various surface and interface analysis methods with electron, ion, X-ray, and light beams and so on serving as probes. These surface analysis methods have been used mainly in the analysis of surface treated steel sheets since the 1970's, and their spatial resolution and sensitivity improved substantially in the 1990's, which has widened the area of analysis where they are used. It is now also becoming important to analyze the information obtained by these methods in a comprehensive manner.

In Auger electron spectroscopy (AES), the adoption of the field emission electron gun (FE) has enabled the analysis with an incident beam diameter of 15 nm. It is widely used for the analysis such as light elements in precipitates²³⁾ and oxides precipitated on the surface of annealed high tensile steel sheets.²⁴⁾

In secondary ion mass spectrometry (SIMS), the use of the field emission Cs⁺ ion gun and the low energy ion beam have allowed the analysis with a beam diameter of 0.1 μm and with a high depth resolution, respectively. Furthermore, the development of charge neutralizing method consisting of simultaneous irradiation of electron beam has enabled the quantitative analysis of trace elements in insulating film²⁵⁾.

In X-ray photoelectron spectroscopy (XPS), by the

refinement of the analyzing area, a resolution of 10 μm was obtained in chemical state mapping. It is widely used in the analysis of surface film, adhesion on the steel sheets and so on.

As the glow discharge optical emission spectroscopy (GDS) can rapidly analyze the elemental depth profile, it has been widely used for the analysis of plated steel sheets and surface oxides. However, as a direct current source was used as the discharge source in the conventional apparatus, the glow discharge cannot be maintained for a thick oxide film or organic film. On the other hand, when radio frequency is used as the discharge source, glow discharge can be maintained by the self bias voltage generated on the surface of such samples. GDS with radio frequency source is now widely used for the element depth profiling of scale, insulating film on silicon steels and so on.

2.5 Elemental and Crystal Structure Analysis Using the Electron Microscope

With advances in material research, it has become indispensable to evaluate the effects of the 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 the research and development of iron and steel materials because of its high resolution of about 0.2 nm and its capability of analyzing the chemical composition of microscopic regions.

The performance of the microscope has remarkably advanced recently. The development of TEM equipped with a field emission electron gun as a highly bright electron emitter (FE-TEM) has enhanced the structural analysis and defect evaluation on the atomic scale. The advantages of FE-TEM, which include ultra-fine probe with the brightness more than 100 times higher than that of a conventional thermal electron emitter (LaB₆), have realized the analysis in the region of 1 nm or smaller.

Our company has introduced an FE-TEM unit and is effectively using it for structural analysis and composition analysis in small regions of steel materials. As the FE-TEM introduced in our laboratory is equipped with an energy-dispersive X-ray spectrometer (EDX) and an electron energy loss spectrometer (EELS), it functions as an analytical electron microscope. Elemental mapping images can be obtained by using a scanning transmission electron microscope system in combination with the EDX. By analyzing electron energy loss with the energy filter attached at the post column position, the analysis and imaging of light elements such as B, N, which is hardly detected by EDX analysis, is available.

Also, focused ion beam fabrication (FIB) system is now widely used as a thin film preparation instrument for TEM. The FIB can prepare a TEM specimen from the samples for which a thin film preparation had been difficult, and has expanded the application fields of TEM in our company. Application examples include the

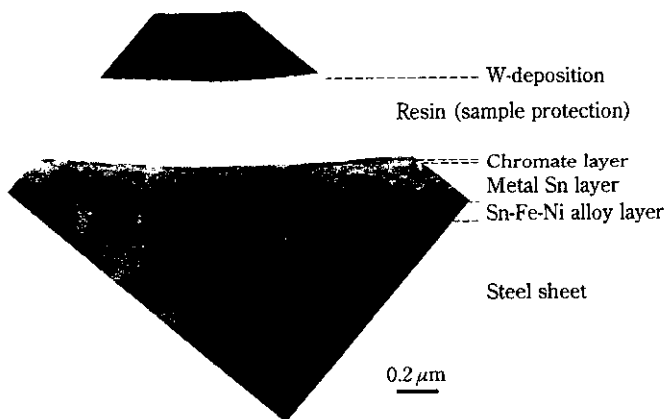


Photo 1 Cross-sectional micrograph of the low tin plated steel sheet with FIB-TEM technique

cross-sectional observation of Zn plated steel sheets²⁶, Sn plated steel sheets²⁷, oxide scale on stainless steel sheets^{28,29}.

In the observation of Sn plated steel sheets shown in Photo 1, a layered structure comprising a chromate layer, a metal Sn layer, an alloy layer and a steel sheet were clearly observed²⁷.

One of the examples of FE-TEM application to iron or steel is the analysis of the grain boundaries in high purity 18% Cr steel³⁰. The difference of the precipitation along the grain boundaries accompanied with the amount of added C, N and sensitizing treatment is analyzed in detail and the presence of a Cr depleted layer formed near the boundary has been revealed with the nano meter scale. Another example, which is combined with the FIB method, is the analysis of the oxide scale of Fe-20Cr-5Al alloy²⁸. The structural change of the scales by the addition of La, Zr and the segregation of the added elements within the film were analyzed, in order to clarify the mechanism of the improvement of high temperature oxidation resistance.

In a scanning electron microscope (SEM), an SEM, which has the quadrant detector for the backscattered electrons, has been introduced and applied to the three dimensional measurement of the surface roughness and elemental composition measurement with high spatial resolution at the surface of various types of steel sheets.

2.6 In-situ Analysis

A high temperature X-ray diffraction instrument has been developed for the *in-situ* analysis of the reaction process at high temperatures such as the alloying process of Zn plated steel sheets and scale-forming behavior of steel sheet³¹. A Seemann-Bohlin camera with an imaging plate (IP), enabled the rapid and sensitive measurement. The sample is heated by a direct electrical heating furnace under the atmosphere of inert gas,

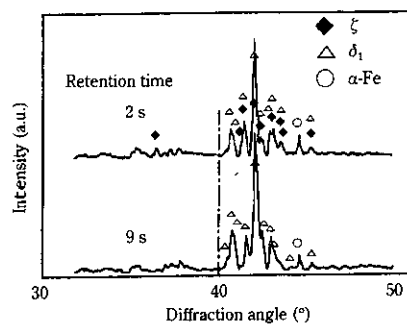


Fig. 8 X-ray diffraction patterns of galvanized steel sheets retained at 470°C for 2 s and 9 s

oxidizing and reducing gas and low vacuum with dew point controlled. With this instrument, research is being made on an alloying process of galvanized steel sheets and on high temperature oxidation/reduction processes of various kinds of steel sheets. The results are shown in Fig. 8 for the measurements on galvanized steel sheets, when the sheets were heated from room temperature to 470°C in 1 s, and then retained at the temperature for 2 s or 9 s. It was revealed that the ζ phase (FeZn_{13}) and δ_1 phase (FeZn_7) coexist in the 2 s retention and the coexisting state changes to δ_1 single phase in the 9 s retention³¹.

An *in-situ* analyzer employing laser Raman spectroscopy, which has high sensitivity for thin films and can analyze amorphous materials, has been also developed for dynamic chemical state analysis of initial surface oxides and their variation with temperature.

This *in-situ* analyzing apparatus was consisted of a single monochromator using a notch filter for removal of Rayleigh scattering light and a CCD detector. These two apparatus have made the rapid and sensitive measurement possible. Samples are heated by an infrared heating furnace to 1 000°C in about 60 s. The sample chamber is capable of evacuation and introduction of atmospheric gas with dew point controlled.

The developed apparatus was applied to the analysis of scale forming phenomena of stainless steels. The variation was analyzed in chemical states of initial surface oxides and in scale-forming temperature derived from the differences in types of stainless steel and the differences in surface finishing³².

3 Conclusions

Research trends in analysis and material evaluation in our company were reviewed. Great progress has been made in lowering the detection limits of trace element analysis along with the advance of products and processes development. An expediting of process control analysis in steelmaking has been an important theme, where remarkable progress has been made such as the development of an optical emission spectroscopy

and a rapid slag analyzer.

On the other hand, concerning the material evaluation technology, the microscopic characterization technique has made progress by the use of FE-AES, FE-TEM and so on. These instruments are now widely applied in product development. Furthermore, an *in-situ* analysis apparatus has been developed and enabled the dynamic analysis under high temperatures.

While these technical themes will continue to have important significance in the days to come, the research and development in the forthcoming century need further enhancement in quality and higher speed. We will endeavor to fortify our fundamental technique in analysis and material evaluation, and will proceed with the research for the timely development through swift grasp of the trends of R & D in various fields.

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