

Development of Materials Characterization Techniques and Their Future Prospects

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Abstract

The steel industry incorporates various quality items uniformly in its products produced in manufacturing lots of tens of tons by controlling their metallographic structure and surface conditions in the scales of nanometers. Development of high-grade steels over the last years pushed the requirements for quality realization more to finer scales, and the scales of analysis technology is shifting from nanometers to the atomic level. On the other hand, in consideration of the short supply of raw materials, the rise in their prices and other adverse cost-related conditions, analysis technology is expected to serve effectively for the development of new products for generations to come and their manufacturing processes. This article presents typical examples of the latest techniques in the field of materials characterization and the expected future trends of the field.

1. Introduction

What is required in developing new steel products and the manufacturing processes to produce them as designed is becoming more and more complicated, and analysis technology is expected to play an increasingly important role in optimizing development activities and designing production processes for the generations to come. In this situation, analysis technology has recently made remarkable progress.

This special issue on materials characterization science, compiled 14 years after the previous one, presents the technical advances in this field during the period and the development of elementary techniques for materials characterization made by Nippon Steel Corporation.

2. Analysis and Characterization Technology to Support the Development of New Steels

Materials characterization based on analysis techniques on the nanometer scale is playing an increasingly important role in the development of high-grade steels, in which the Japanese steel industry excels. While advanced devices such as transmission electron microscopes (TEM), scanning electron microscopes (SEM), and electron probe micro-analyzers (EPMA) have been effectively employed for characterizing micro-metallographic structures, textures, and non-metallic inclusions that govern the material properties of steel products, the level of analysis required for the process development of high-grade steels is shifting from the nanometer- to the atom-size scale. In this situation, Nippon Steel has introduced a three-dimensional atom probe (3DAP) having atom-scale resolution and scanning transmission electron microscopes with correction of spherical aberration (Cs-STEM), etc., and has made concentrated efforts in the development of new techniques and methods for materials char-

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acterization to effectively support the development of manufacturing processes for high-grade steels. On the other hand, surface treatment of sheet products has come to require higher analysis capacity in relation to structural control on the scale of nanometers at steel surfaces. In this field, too, the use of field emission-type electron guns for SEM, EPMA, and Auger electron spectrometers (AES), and other advanced analysis facilities and methods have proved effective in supplying important information for materials evaluation.

In addition, Nippon Steel has been developing new and original applications of advanced methods and techniques such as nuclear magnetic resonance (NMR), synchrotron radiation (SR), and environmental assessment techniques, and has in fact put many fruits of development into field practice.

2.1 Structural and elementary analysis techniques to accelerate the development of new steels

Clarifying the effects of an additional alloy or an impurity element on steel properties is an effective approach to the development of high-functionality steels. Along with this philosophy, the Materials Characterization Laboratory of the Advanced Technology Research Laboratories of Nippon Steel considered it essential to establish analysis techniques to evaluate the metallographic structure of steel with high precision on the atomic scale, and have bent efforts in this field. The 3DAP that the company introduced ahead of other steelmakers proved instrumental in developing high-tensile steels and other high-functionality products.

In addition to 3DAP, we introduced a Cs-STEM, the most advanced type of electron microscope equipped with correction of spherical aberration, and employed it for clarifying the metallographic structure of steel on the atomic scale, more specifically, for things such as analysis of nanometer-size precipitates responsible for precipitation hardening as well as segregation of component elements at crystal grain boundaries, which determines the quenching properties of a steel material. The Materials Characterization Research Lab. expects 3DAP and Cs-STEM to complement each other to make powerful tools for clarifying the metallographic structure of steel on the atomic scale and for identifying new factors that govern material properties, and thus to drive the development of new high-functionality steels in the future.

2.1.1 Scanning transmission electron microscope with correction of spherical aberration (Cs-STEM)

Cs-STEM is capable of focusing an electron beam more finely on the observation object by decreasing the spherical aberration of the magnetic lens, which controls the trajectory of the electron beam, to zero. This has brought about a drastic improvement in structural analysis by electron microscopes, enhancing the spatial resolution from 1.0 nm or so, conventionally, to less than 0.1 nm, thus making it possible to analyze material structure on the atomic scale. At its installation, thoroughgoing measures were taken against vibrations of the foundation that could possibly affect the observation accuracy, and as a result, a spatial resolution of less than 0.1 nm is maintained in daily use. As an example, it has been used for analyzing the segregation behavior of extremely small quantities of boron at grain boundaries, which is important in clarifying the quench-hardening mechanisms of high-tensile steels for marine structures and other applications, and successfully quantified the concentration profile of boron condensing at original austenite grain boundaries about 1 nm in width. The facility is also being effectively used for the analysis of extra-fine precipitates and grain boundary segregation essential for development of high-grade steels.

2.1.2 Three-dimensional atom probe (3DAP)

Because 3DAP can measure the species and positions of individual atoms composing a steel material, it can determine the positions of all atoms of alloying elements in the space of crystal lattices with high resolution. While the device has very high spatial resolution, its field of measurement is extremely small, about the size of the tip of a needle. For this reason, it is necessary to process a specimen beforehand into a needle shape in such a way that its portion to be examined comes at the tip. To meet this requirement, applying the lift-out method using a focused ion beam, Nippon Steel worked out an original method of fabricating any part of a material into a needle-shaped specimen for 3DAP. With this and tools such as electrostatic field calculation by finite element analysis, the company also established a technique to bring virtually any part of a steel material to the tip of a needle-shaped specimen. These solutions made it possible to observe extremely small parts of various steels whose metallographic structures were unclear on the atomic scale because of the difficulty in the machining of specimens, and in this way, significantly expanded the applicability of 3DAP.

2.2 Materials characterization techniques to support the development of steel production processes

2.2.1 Structural analysis techniques applying X-rays and radiation rays

X-rays scatter or fluoresce as a result of interaction with electrons in the material to which they are irradiated. These phenomena are useful for obtaining information about the details of the structure of an object and the state of its constituent atoms. X-ray diffraction has been widely used in the steel industry for evaluating the arrangement of crystal grains (orientation and texture) and their integrity (defects and dislocations) as well as for identifying reaction products.

To serve for steel materials studies and the development of new processes, Nippon Steel is actively developing advanced analysis methods employing X-rays, and has actually applied the methods developed to practice on the plant floor. Typical examples of applications of X-rays include the following:

- (1) Observation of the structural change of materials under reactions in manufacturing processes or the environment (in-situ observation) taking advantage of the characteristic of X-rays of passing through materials in air or gas;
- (2) Obtaining high-accuracy information on material structure unobtainable by conventional methods (such as information on the state of a particular element in steel, precision measurement of strain fields, and the structure of materials of low crystallinity); and
- (3) Obtaining structural information on materials in regions micrometers to nanometers from a surface or a phase boundary.

For developing advanced analysis techniques in this field, powerful, high-quality sources of X-rays are indispensable, and to this end, Nippon Steel has accelerated the use of X-rays emitted from large particle accelerators, called synchrotron radiation, for research activities (see Subsection 4.3 below).

2.2.2 Stress evaluation

Application of diffraction of X-rays and neutron beams enables non-distractive measurement of stress imposed on steel materials. The penetration depth of X-rays into steel varies significantly depending on their energy. With X-ray sources for laboratory use, the penetration depth is some tens of micrometers at best, and it is suitable for stress measurement in regions near a surface. To measure the stress in regions deeper from a surface, synchrotron radiation is

used because X-rays of higher energy are available; it is used for measuring stress in regions some hundreds of micrometers away from a surface. Neutron beams have far higher penetrability into matter than ordinary X-rays, and taking advantage of this, neutron beams are used for the stress measurement of portions of structures and welded joints of heavy plates up to some tens of millimeters from a surface.

2.2.3 NMR analysis

Nuclear magnetic resonance (NMR) spectroscopy is an analysis method taking advantage of the resonance of the nuclear spin of an object in a magnetic field up to tens of teslas in flux density with electromagnetic waves in the radio-wave region to ultra-shortwave bands. This method is used for obtaining information on the chemical structure of a specimen on the molecular scale; specimens may be solid, liquid, or gas. It is unsuitable for analyzing steel because, according to its principle, it is not applicable to magnetic materials. However, non-metallic oxides having complicated structures such as coal (fuel) and slag (byproduct) play important roles in steel production processes, and NMR, capable of obtaining structural information on individual elements, is expected to be effective in clarifying the chemical structures of these objects. In steel works, there is especially strong demand for analysis of solid materials, but with solid NMR, resolution and sensitivity have seldom been compatible. To solve this problem, efforts have been bent on improving both resolution and sensitivity at the same time as making the method applicable to the analysis of materials consumed in or arising from steel manufacturing processes (see Subsection 4.2).

3. Advanced Analysis Techniques to Support Steel Production Processes and Process Control

In a steel works, huge blast furnaces and converters output molten iron and steel at high temperatures around the clock and all year round, and the people responsible for analyzing specimens from different production processes are requested to render their services accurately and rapidly 24 hours a day, 365 days a year.

The rapid analysis equipment that analytical engineers in a steel works use must satisfy the following requisites:

- (1) Stable continuous operation for long periods;
- (2) Simultaneous analysis of different elements in varieties of steels;
- (3) Rapid analysis
- (4) High accuracy and wide range of analysis for quantification; and
- (5) Compatibility with automation and computerization.

As seen here, the analysis technology supporting steel production processes must supply accurate and reliable information for materials characterization rapidly and at low cost.

On the other hand, the kind of information expected of analytical technologies changes from time to time, and thus, in order to supply relevant information to production personnel, researchers, and customers in a timely manner, it is necessary to continue innovating techniques for materials analysis, evaluation, and characterization. This section focuses on techniques for raw materials evaluation, laser-induced breakdown spectroscopy, precipitate analysis, and non-contact analysis of organic substances.

3.1 Raw materials evaluation (coal evaluation)

Effective utilization of raw materials (iron ore and coal) of lower quality is now one of the most important issues of the steel industry. For example, the composition of the gas generated from coke ovens (COG) changes with different blends of coal brands charged into them, significantly affecting its energy conversion. We developed a

gas monitoring system applying infrared absorption spectroscopy (IR), and used it for clarifying the difference in the COG generation behavior of different coal brands in laboratories. The developed system was also installed in a commercially operating coke oven to evaluate the change in gas composition at different stages of a coking cycle, as well as the change in gas composition with different coal blends.

3.2 Quick analysis of defect causes applying laser-induced breakdown spectroscopy

Defects occur in steel products, and since they directly and adversely affect the quality and yield of the products, it is essential in the manufacturing of steel to quickly identify their causes and specify the process from which they originate. A method for the rapid evaluation of surface defects of sheet products based on laser-induced breakdown spectroscopy (LIBS) was developed to meet this requirement. A laser beam decomposes a specimen portion into atom vapor, which ionizes into plasma, and the light emitted from the plasma is transmitted through an optical fiber to a polychromator. Through evaluation of defective portions, elements peculiar to the defective portion are specified, and nonmetallic inclusions causing the defect and its origin (slag, casting powder, refractory, etc) are then identified, and if no such elements are found, the defect is attributed to residual scale. This method enables rapid and reliable defect analysis since it takes less than 30 minutes from sample preparation to final judgment, making it possible to take countermeasures quickly on the plant floor.

3.3 Precipitate analysis

The contents of carbon and alloying elements in steel are controlled in steelmaking furnaces such as converters, and it is imperative in repetitive mass production of high-quality steel to control the chemical composition and temperature of steel to the respective target ranges within a short time in every operation cycle. Spark-source optical emission spectroscopy (spark-OES, also known widely as QuantVAC (QV)) is capable of rapidly and accurately quantifying the component elements of steel samples taken from refining furnaces, allowing quick feedback of the results to the furnace operation, and for this reason, it is used in most steel works worldwide.

By pulse distribution analysis (PDA) in spark-OES, among others, it is possible to quickly classify the compounds of deoxidizing elements (such as Al) in steel into those soluble in acid (Sol.) and those insoluble (Insol.), so that it is used in metal refining industries all over the world. To solve problems related to conventional quantification methods based on PDA, we recently examined the time-resolved monitoring of the light-emitting process, which is accompanied by the breakdown of nonmetallic inclusions under spark discharge, pointed out the intrinsic limitations of conventional PDA theory, and obtained findings leading to a more advanced method of chemical state analysis.

3.4 Analysis of organic matter on steel surfaces

Oils play an important role in improving the rolling properties of sheet products and protecting their surfaces against corrosion. However, to obtain information on organic substances on steel surfaces, it was necessary to extract them through special treatment and evaluate them employing methods such as IR, gas chromatography, and mass spectrometry. To obviate the necessity for pretreatment and evaluate organic matter directly on steel surfaces, which are not always flat or smooth, using a non-contact method, we established an analysis method for organic matter, whereby sheet specimens undergo infrared emission spectroscopy at temperatures of about 100°C.

4. Original Analysis Techniques of Nippon Steel's Development

Nippon Steel has developed various original analysis methods in response to in-house requirements. This section presents the pinpoint sampling technique for analysis of metallographic structures, solid NMR for analyzing non-metallic materials such as coal and slag, the use of synchrotron radiation, and environmental assessment techniques, the importance of which is increasing lately

4.1 Pinpoint elementary and structural analysis to enable local materials characterization at the atomic level

Regarding micromachining by use of a focused ion beam (FIB), we have, as an eventual user, actively cooperated with the equipment maker from the very beginning of development of the device, and as the front-runner in the steel industry, installed equipment and developed methods of preparing specimens for examining microscopic portions of steel materials. While FIB devices are mainly used for micromachining of specimens for transmission electron microscopes, they can also serve as scanning ion microscopes. An article in this special issue describes the characteristics of scanning ion microscopes excellent in channeling contrast, citing some analysis applications. As this function of a FIB device is generally suitable for observing things such as grain boundaries and bainite lath structures, since the device can process the object portion of a specimen suitably for sectional observation, it is possible to estimate the three-dimensional configuration of an entire structure with it. In addition, a method has been developed whereby a three-dimensional, 10 μm cuboid structure is reconstructed on a computer by employing FIB serial sectioning. Further, we studied the use of FIB devices as scanning ion microscopes for the in-situ observation of structural changes at high temperatures, and this was applied to the observation of structural changes such as bainitic transformation and its reverse transformation.

4.2 Solid NMR analysis

Clarifying the chemical structures of coal and slag is important for enhancing fuel efficiency and recycling slag. Coal ash and slag have complicated three-dimensional structures where Si, Al, and other inorganic elements form networks with oxygen atoms serving as joints; NMR is effective in analyzing such structures. However, while structural analysis with advanced techniques such as NMR is required for nuclear species such as ^{27}Al , ^{17}O , and ^{25}Mg , they are quadrupolar nuclei having nuclear spin other than 1/2, and for this reason, their peaks obtained with NMR often tend to be broad and the resolution is insufficiently high.

Facing this problem, as a first attempt in Japan to obtain high-resolution spectra of quadrupolar nuclei by solid NMR, Nippon Steel directed its efforts towards establishing the multiple-quantum magic-angle spinning (MQMAS) method. In the meantime, stronger magnetic fields have come to be applicable to NMR over the last few years, and through its combination with MQMAS, the method has successfully clarified the microscopic details of the structures of coal ash and slag.

Jointly with the equipment supplier, we also developed a new type of probe for measuring satellite-transmission magic-angle spinning (STMAS) spectra, by which it became possible to achieve at maximum a sensitivity about five times that by MQMAS; the new probe proved effective in clarifying the chemical structure of trace amounts of boron, in several hundreds of ppm, in coal ash. Although solid NMR for quadrupolar nuclei has been practically inapplicable for structural analysis of trace elements owing to its low sensitivity, the developed technique is expected to make it usable more widely

for studying quadrupolar nuclei, which are in low concentration and not very easy to detect by NMR.

Iron- and steelmaking processes proceed at high temperatures, and there is strong need for in-situ observation of slag and other inorganic materials in the liquid state at high temperatures. NMR probes available on the market are unsuitable for directly observing molten slag because their working temperature is roughly 150°C at the highest. To solve this problem, we developed a new type of NMR probe that can be used for the in-situ observation of objects at temperatures up to roughly 1500°C. In fact, using this type of probe, it became clear that the NMR spectra of an object in molten inorganic glass is quite different from that obtained by the melt quench method, that the structure of a specimen after rapid cooling is not necessarily the same as that in the molten state, and that the thermal motion of a specimen at the atomic level obtained by NMR is closely related to its viscosity, a macro property.

4.3 Application of synchrotron radiation

Synchrotron radiation, the kind of X-ray emitted from large particle accelerators, is intense and forward-focused, has a wide range of energy, and shows pulse-shaped emission, and it is useful for clarifying various phenomena in materials. For the research and development of steel and other materials and their production processes, Nippon Steel has used synchrotron radiation in the following four fields (see Fig. 1):

- (1) To observe the change in material structure with time (dynamic observation) during various reactions in conditions similar to those of real production processes and environments (in-situ observation)
Examples of such changes include alloying reactions during hot-dip galvanizing, pitting corrosion of stainless steel, and the precipitation processes of Cu in steel.
- (2) To obtain structural information on materials in regions micrometers to nanometers from a surface or an interface
Examples of such objects include oxide film on titanium surfaces, and phase transformation of the surface structure of intermetallic compounds.
- (3) To obtain information on the state of specific elements in steel or the structure of low-crystallinity materials by an analysis method capable of extracting information selectively on specific elements
Examples of reactions of interest include corrosion reactions of atmospheric anti-corrosion steel and redox reactions of catalysts for treating automobile exhaust gas.
- (4) To measure crystal domains and strain fields through precision measurement of crystallinity
Examples of objects of such measurement include secondary recrystallization processes and strain fields of electrical steel.

4.4 Nippon Steel's original analysis techniques to support environmental assessment

Harmonious relations with local communities are very important for the steel industry, which operates heavy production facilities at large steel works, and in this sense, it is imperative to operate the works from the viewpoint of conserving the global environment. What is essential in this sense is on-site, real-time, ultra-high-accuracy analysis of environmental load gases and individual analysis of airborne particles. Few environment evaluation facilities conventionally available on the market incorporate the concept of on-site analysis, which requires intensive technical development. In consideration of this, Nippon Steel has drawn up a basic plan for a national project on the technical development of environment evaluation technol-

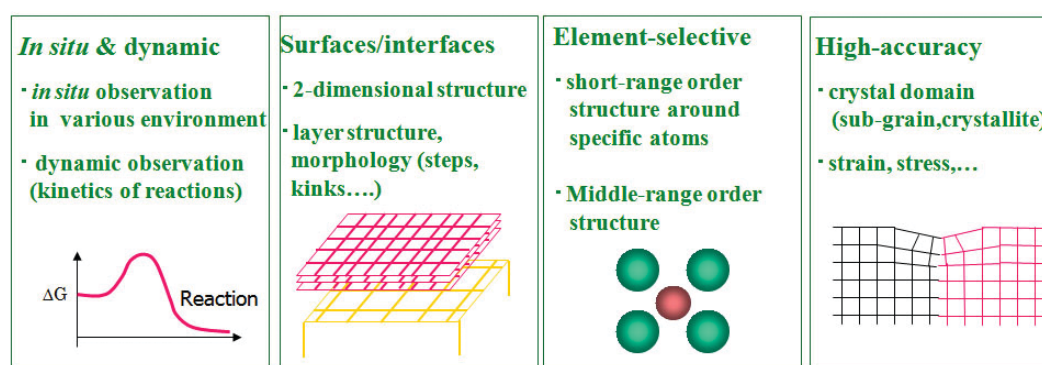


Fig. 1 Information on atomic structures obtained by observation using synchrotron radiation

ogy, and has fostered the project from the very beginning through academic-industrial partnership over the last 10 years.

4.4.1 Development of high-sensitivity, on-line analysis techniques for environmental load organic compounds

It was not long ago that emission of dioxin and other highly environmentally hazardous organic substances attracted public attention. It is imperative for the steel industry, which operates high-temperature facilities such as blast furnaces, coke ovens, and sintering machines, to be always mindful of the emission of environmental load substances. Hence, we have proposed several national projects for developing high-sensitivity, real-time analysis techniques for organic pollutants, and have actually developed facilities and methods useful for this field.

For example, in a project approved in fiscal year 2000 under the Framework for Fostering Innovative Research Products promoted by the Japan Science and Technology Agency (JST), Nippon Steel successfully developed a high-sensitivity detection method for hazardous organic molecules applying supersonic jet resonance-enhanced multi-photon ionization (Jet-REMPE). In addition, under the Subsidy for Creating Industrial Innovations that the Ministry of Education, Culture, Sports, Science and Technology offered in fiscal years 2002 to 2004, we also developed a device capable of analyzing environmentally harmful compounds in high-temperature furnaces in real time and with high sensitivity. This project focused on extensive modification of the measurement device developed under the JST project in 2000 to add a real-time measurement function as well as on verification tests of the modified device in operating waste incinerators. The modified device succeeded in monitoring, in real time, how monochlorobenzene, a precursor of dioxin emitted from waste incinerators, was emitted and disappeared from the furnace within 30 seconds.

4.4.2 Development of methods for historical analysis of individual particles

What is important for overall evaluation of the environment is not only examining organic molecules in the atmosphere with high sensitivity but also detecting organic compounds and harmful elements on the surfaces of airborne particles such as fly ash. Since airborne particles originate from a variety of sources, a method of dealing with particles individually is required for identifying the origins of pollutants.

The effects of airborne particles called PM_{2.5} (particles less than 2.5 μm in diameter) on human health have come to cause public concern over the last few years, and an analysis technique to detect suspicious elements and organic molecules contained in them with

high sensitivity has been sought. Facing this issue, we considered it possible to develop an analyzer capable of responding to this need by combining the high-intensity laser ionization technique, which we assimilated during the project in 2002 to 2004 under the subsidy mentioned earlier, with time-of-flight, secondary ion mass spectrometry using FIB as a probe (FIB-TOF-SIMS) with high lateral resolution. The activities under the Framework of JST in 2004 to 2009 confirmed the possibility of devising an analyzer capable of measuring the elementary distribution on the surface of a PM_{2.5} particle, detecting organic molecules on the surface, measuring the elementary distribution inside the particle, identifying its origin, and clarifying its historical formation during its suspension in the air.

4.4.3 Development of analysis techniques for measuring the fertilizing effects of slag and trace Fe in seawater for ocean cultivation

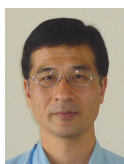
Calcareous algae sometimes cover sea bottoms, causing damage to giant kelp and other varieties of edible algae; the phenomenon, called rock shore denudation, is recently taking place at many spots along the coast of Japan. While its presumed causes include rise in water temperature, water pollution, and feeding damage by sea urchins, some maintain that a decrease in Fe solute in seawater is also responsible. As a countermeasure, Nippon Steel thought of supplying solute Fe to seawater by mixing iron-rich slag from steelmaking processes and humic compounds, forming them into modular units and submersing the units in the sea. Since the concentration of Fe solute in seawater is several tens of ppb at the highest, it was necessary for confirming the effects of the above measure to work out a method of determining an infinitesimal amount of Fe in a high-concentration solution of salt. Eventually, an analysis technique to determine Fe in saltwater to an accuracy below 1 ppb was established, wherein a chelate resin capable of selectively extracting Fe and other heavy metal elements was used for separating salt in high concentration, disturbance due to stray Fe in the analysis environment was minimized, and a low-background measurement method was employed under a plasma condition to prevent the generation of molecular ions composed of Ar and O. The concentration of Fe solute in seawater was actually measured near a site where the units had been submerged.

5. Conclusion

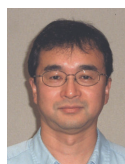
Nippon Steel's development of analysis techniques has been outlined above. These pages have hopefully served to illustrate how deeply analysis techniques are related to the operation of integrated steel production processes covering raw materials and fuels to waste

emission, and that the necessity for the development of analysis technology continuously arises from plant operation needs for new process techniques. On the other hand, some analysis needs are so demanding that few devices available on the market can offer satisfactory solutions. In this situation, analytical researchers in the Materials Characterization Laboratory are expected to develop elementary analysis techniques for the future, turning latent in-house analysis

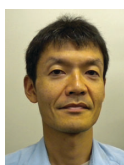
demands into new seed techniques. The roles of analysis technology in the development of new products of higher added value and advanced production processes will certainly increase, and it is thus the responsibility of analytical researchers to respond to these expectations and to hold the company in a leading-edge position of technical competitiveness.



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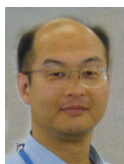
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