

Development and Application of Non-Destructive Evaluation Technology for Chemical Equipment Materials

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In chemical plants an important objective is to ensure safety and stable operation of equipment such as widely-laid pipe lines, aged equipment (used for more than 40 years), and large-sized equipment for overseas expansion. In order to achieve this objective, it is important to understand the condition of exhaustive equipment in a plant, and to invest intensively in cost-effective maintenance based on diagnosis test results. A study on non-destructive evaluation techniques for chemical plant equipment, developed based on the keywords of low cost, high speed and high quality, is described here.

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Introduction

In 1913, Sumitomo Chemical set the goal of manufacturing fertilizer from sulfurous acid gas and achieved innovations in operations along with making the transition to a new era. Sumitomo Chemical maintains and runs various plants across its five current fields of operation such as basic chemical, petrochemical, IT-related chemical, and health and agricultural related operations as well as medicine, and the forms of products, liquids, powders, molded products and other products, are diverse. With this long history, plants for manufacturing basic products and facilities for supplying utilities have aged, and the number of facilities running for more than 40 years since construction and start-up is not small. In addition, combined operations are carried out at large sites; therefore, the pipes for transporting raw materials and bringing in utilities are spread out like human arteries and laid out around plants in a complex manner. It is important to inspect and monitor the performance and quality of these aging facilities and extremely long pipes on a daily basis, discover deterioration or signs of deterioration as early as possible and repair or update facilities before problems occur. Therefore, at Sumitomo Chemical, we are trying to determine risk rankings for equipment by creating an index from the importance of the equipment and the frequency of deterioration and damage, so we can effectively use the time and expenses related to maintenance. Even so, the inspections and

diagnostics are enormous, and in addition to risk management, we need cost reductions for scaffolding equipment and incidental construction for inspections, overall improvements in the speed of inspections, including pre-treatment, and development and practical application of inspection methods that can give as accurate grasp of the presence and degree of deterioration and damage to equipment as possible.

With this background as a basis, our group has developed various non-destructive evaluation techniques for the inspection and diagnosis of materials in chemical equipment with low-cost, high-speed, and high quality as keywords. In this article, we will introduce some of the recent developments including an inspection method for ferromagnetic pipes using magnetic eddy current flaw testing techniques, an inspection method for the detection of material deterioration that uses an electromagnetic acoustic wave technique, corrosion inspection method for contact parts in pipe framing, and carburizing measurements that apply eddy current for testing.

Development of Magnetic Eddy Current Testing Techniques

In chemical plants, many carbon steel vertical multi-tube reactors that handle heat transfer salt (HTS) as a heating medium are used and this equipment has become increasingly large for this application in recent

years. In addition, if air becomes mixed into the HTS in carbon steel reactors and an air layer forms below baffle plates and other parts, a barrier to heat transfer to the HTS is formed and local temperature increases arise. There is a concern that corrosion and thinning of the outside surfaces of the reactor tubes will arise (Fig. 1). Therefore, maintenance inspections of the areas below baffle plates in carbon steel tubes are necessary, but the only inspection method that answer this requirement are internal rotary inspection systems (IRIS).

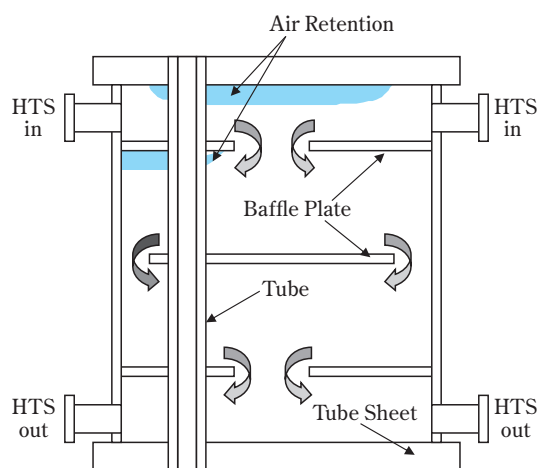


Fig. 1 Schematic of air retention in a Vertical reactor

While IRIS have a high thickness evaluation precision in units of 0.1 mm, water is required as a medium for propagating the ultrasonic waves. The weak points of these measurements include the fact that these measurements cannot be used in chemical plant equipment in which water is prohibited, material adhering to the inside surfaces of tubes must be completely eliminated for propagation of the ultrasonic waves in the direction of tube thickness and the inspection speed is slow with the number of tubes that can be inspected per day being around 50 to 100. Therefore, the development of inspection techniques that do not use water, can be implemented with simple pretreatment and are high-speed is necessary for effectively carrying out maintenance inspections for large reactors.

1. Problem of Eddy Current Testing in Ferromagnetic Materials

With nonmagnetic pipes such as austenite stainless steel typified by SUS 304 steel and SUS 316L steel superior eddy current testing with an inspection rate of 1000–1500 pipes per day has been applied. Eddy cur-

rent testing is not expected to have as high a precision as IRIS, but it has the merits of no contact medium such as water being required, and non-contact, high-speed inspection can be possible. The current situation of also wanting to apply eddy current testing to carbon steel pipes, which are ferromagnetic pipes, has been an important need up to this time, and special eddy current testing techniques such as magnetic saturation eddy current testing and remote field eddy current testing have been developed since the 1970s. However, they have not reached the point of being applicable to inspections of reductions in thickness beneath baffle plates.

2. Probe Development

If any of the current inspection tests are used on ferromagnetic pipes, strong magnetic noise accompanying variations in magnetic permeability becomes an impediment, but it is known that this magnetic noise is reduced by applying a strong magnetic field. However, it is necessary to integrate a permanent magnet into the probe inserted into the pipe during maintenance inspections; the space in the probe is extremely limited, and correspondingly the strength of the magnetic field is small. Thus, along with using rare earth magnets, which have high coercive force, a Halbach array, which generates the strongest form of magnetic field and which is used in maglev trains and medical magnetic resonance imaging systems (MRI), is used for the magnet array (Fig. 2 (a)). However, the area to which a strong magnetic field is applied by the permanent magnet integrated into the probe is limited to only part of the pipe in the axial direction as shown in Fig. 2 (b). With a common two coil type probe, an eddy current flows widely in the axial direction of the pipe as shown in Fig. 3 (a); therefore, induction only needs to be devised in the areas where a magnetic field with a strong eddy current is formed. Thus, as shown in Fig. 3 (b), a four coil probe with eddy current control coils positioned on both sides of the detection coils is used, and a method is used in which the eddy current is generated by the detection coils and an eddy current in the opposite direction is generated by the control coils to negate excessive eddy currents.^{1), 2)} Fig. 4 shows the external appearance of the probe (called magnetic eddy current probe in the following) used in the magnetic eddy current testing. In addition to having a strong magnetizing force, the area in which the eddy current is generated by the detection coils can be controlled by adjusting the proportion of

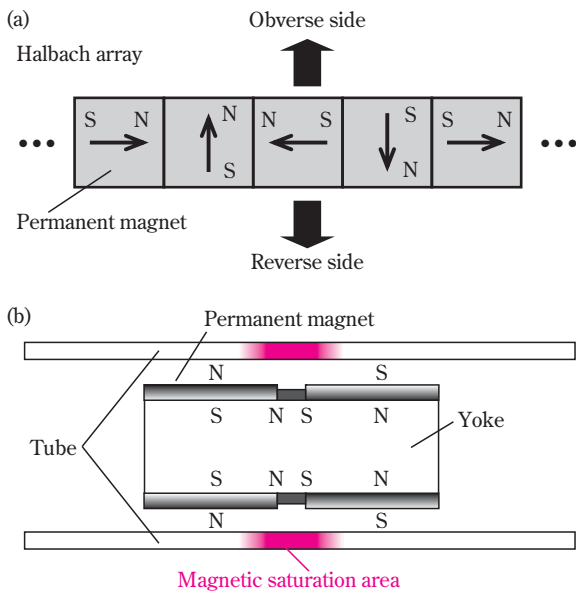


Fig. 2 Magnet array (Halbach array)

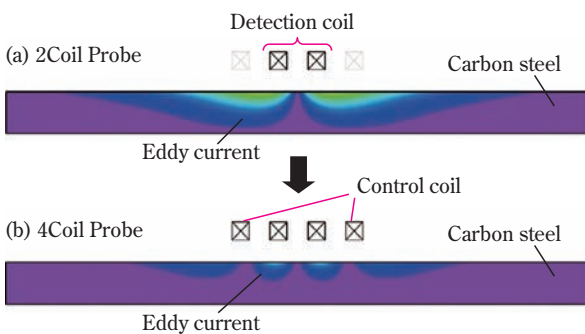


Fig. 3 Eddy current limitation through control coil

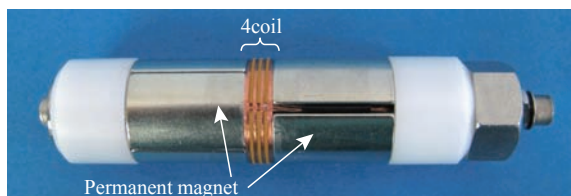


Fig. 4 External appearance of magnetic eddy current probe

current flowing in the detection coils and the eddy current control coils.

The characteristics of the magnetic eddy current probe are such that the defects on the inner surface are detected by disturbance in the eddy current caused by the defects themselves and the defects on the outer surface are detected from the irregularity of permeability which is caused by the surrounding defect by the addition of a magnetic field generated by the magnet.

Therefore, it is important to apply magnetization to

pipes to an extent that does not weaken the irregularity in the magnetic permeability around the defects on the outside surface while sufficiently controlling magnetic noise in the carbon steel pipes. Therefore, we are devising a magnetic eddy current probe for applying the optimal magnetism according to the outside diameter and thickness of pipes.

Specifically, as is shown in Fig. 5, the yoke to which the magnets are attached is given a hollow structure, and a cylindrical yoke for making adjustments is introduced into that space such that the cross-sectional surface area of the yoke for the path in which the magnetic flux flows is changed (controlling the magnetic resistance).³⁾

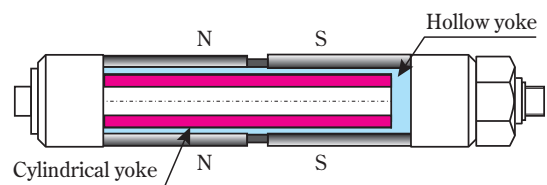
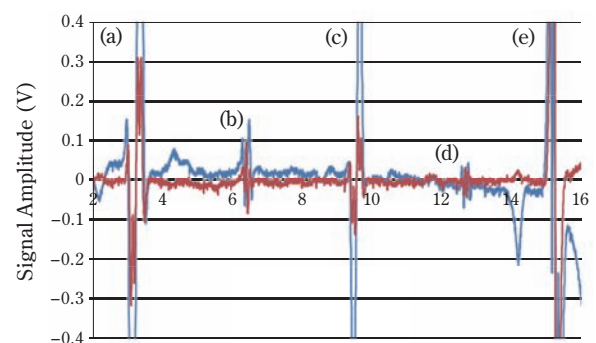


Fig. 5 Magnetizing force adjustment mechanism in a magnetic eddy current probe

3. Performance of Magnetic Eddy Current Probe

Fig. 6 shows the results of evaluations of the defect detection performance of the magnetic eddy current probe. Through holes with a diameter of 0.5 mm (ϕ) could be detected as small defects with a high S/N ratio. In maintenance inspections with normal eddy current testing, the standard defect that is used is commonly a through hole with a diameter of approximately 2 mm (ϕ), so the detection performance here is sufficient. In addition, detection is carried out with excellent



(a) Angular groove 5L × 50%t (b) Drilled hole ϕ 1.0mm (c) Angular groove 5L × 25%t (d) Drilled hole ϕ 0.5mm (e) Inner groove 1.5W × 20%t

Fig. 6 Evaluation of defect detection limit

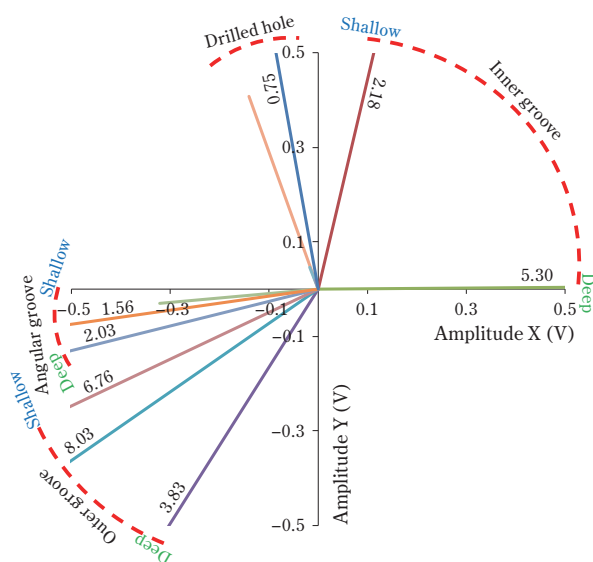


Fig. 7 Phase characterization of the magnetic eddy current probe

S/N ratios even for processed groove-shaped defects by changing the depth of the inside surface of the pipe. **Fig. 7** shows the relationship between classifications of artificial defects in the test pieces and the phase angle of the signal obtained by carrying out magnetic eddy current testing.

We were able to confirm that the phase angle of the signal varied according to differences in the surface (hole, inside surface, outside surface) where the defect occurred and differences in the depth of the defect. The evaluation level for defect depth has not reached that of eddy current testing for nonmagnetic pipes, but determination of the presence of defects and the surface on which a defect occurred as well as qualitative evaluations of defect depth are possible. In addition, the baffle plate signals and defect signals can be separated by the phase angle of the signals; therefore, the effects of the baffle plate signal could be reduced using a multiple frequency method and defects under the baffle plates could be evaluated.

4. Applications of Magnetic Eddy Current Flaw Testing in Actual Equipment

(1) Application in carbon steel multi-tube reactor

We introduced magnetic eddy current flaw testing into the periodic inspection of multi-tube reactors that use HTS as a heating medium at Sumitomo Chemical. As a result, in terms of detection quality, it was possible to carry out inspections for the presence of defects in reactor tubes under baffle plates by reducing the effects of the baffle plate signal using a multiple frequency

method. In addition, we confirmed that recesses and protrusions of approximately 10% of the tube thickness (approximately 0.2 mm), which were detected by IRIS could be detected by the magnetic eddy current flaw testing. Thus, we confirmed that magnetic eddy current flaw testing has the inspection quality for practical use and could be an alternative inspection method to IRIS.

In terms of the inspection speed per reactor tube, approximately five times that of the ultrasonic method has been achieved. In addition, if the time required for the pretreatment process to conduct an IRIS test is included, it can be possible to carry out efficient inspection in a shorter period of time. In principle, the probe strongly adhere to the inside surface of the reactor tubes because of the magnet in it, but the operability of the probe is excellent because of the effect of a sleeve that improved sliding, and there were no problems, such as wear, in terms of the durability of the probe. In addition, if the state of the inside surface of the tube is one of comparatively few recesses and protrusions, the probe can be operated even more easily by blowing out a small amount of compressed air around the probe.⁴⁾

(2) Application in duplex stainless steel / nickel equipment

Other than carbon steel, ferromagnetic pipes such as duplex stainless steel pipes and nickel pipes are used as corrosion resistance materials in chemical plants. The magnetic permeability of these materials is sufficiently smaller than that of carbon steel (μ_r = several hundred to several thousand); therefore, magnetic saturation is possible using the magnetic eddy current probe that has been developed by us.

Fig. 8 shows a measurement chart for comparative reference pieces given through holes and simulated thinning defects on the inside and outside surfaces of heat transfer tubes made out of SUS 329J4L (outside diameter 19.0 (ϕ) $\times$ 1.6 t), which is a representative type of duplex stainless steel, and also shows a phase angle-thinning rate calibration curve based on the same. Each simulated defect could be detected with a good S/N ratio, and a sufficient change in phase angle due to thinning depth was obtained. We confirmed that inspection quality equal to that of typical nonmagnetic materials was obtained for duplex stainless steel and nickel using the magnetic eddy current flaw testing. Thus, we are promoting as well as switching to this method as an alternative to IRIS during periodic shut-down inspections.

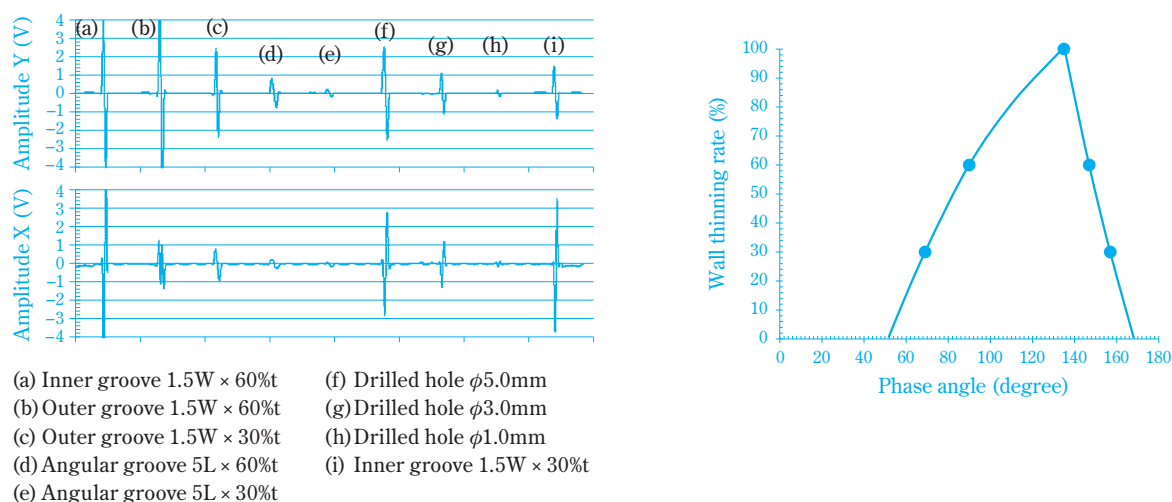


Fig. 8 Flow detection result (left) and evaluation curve (right) of the reference piece

Applications of Electromagnetic Acoustic Wave Technique

The electromagnetic acoustic wave technique can transmit and receive ultrasonic waves to and from targets of inspection using a probe (electromagnetic acoustic transducer (EMAT)).

The merit of this method is being able to excite ultrasonic waves inside materials without any contact. Making use of this merit, the velocity of sound in materials is measured with high precision and deterioration in material quality is evaluated from changes in the modulus of elasticity in the materials. We have been investigating the inspection and diagnostic techniques that improve inspection efficiency by simplification of pre-treatment such as elimination of paint and rust, which are obstacles to irradiation by ultrasonic waves in conventional ultrasonic testing, and promoting applications in actual equipment.

1. Generation Principles of Electromagnetic Acoustic Waves

Generation of oscillation by applying a high-frequency voltage to an oscillator made of a piezoelectric element and converting to ultrasonic waves is the most typical excitation method for ultrasonic waves. In the case of electromagnetic acoustic waves an electromagnetic force is used as the driving force and ultrasonic waves are generated by converting the electromagnetic energy into mechanical oscillation. Conversely, ultrasonic waves are received by converting the mechanical energy into electrical signals. There are cases of the Lorentz force being used and cases of magnetostriction effects being

used for the electromagnetic force that forms the driving force. But for the operating principles, an example of a shear wave EMAT when the Lorentz force is used as a driving force is shown in **Fig. 9**. When the EMAT is placed close to a test piece made of metal and therefore a high-frequency current flows in the coil, following which an eddy current (J) is generated in the sample by the electromagnetic induction principle. A magnetic field (B) from the permanent magnet acts on this and the Lorentz force (F) is generated in a direction parallel to the sample surface according to Fleming's left-hand rule.

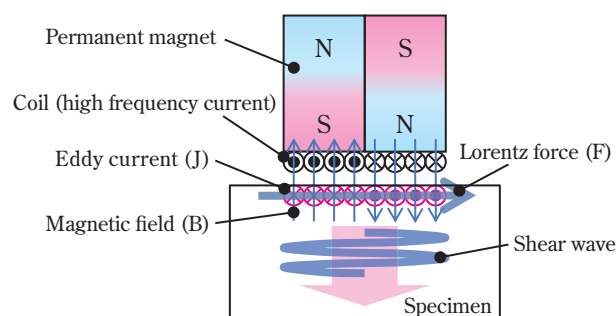


Fig. 9 Mechanism of Lorentz force generation in EMAT

This force oscillates the sample and generates ultrasonic waves. In addition, ultrasonic waves can be received by means of a phenomenon that exactly reverses to that of excitation. Thus, longitudinal waves and transverse waves can be received and transmitted by combining the directions of the eddy current and magnetic field.

2. Applications in Material Degradation Diagnostics

There are cases among the materials used in equipment in chemical plants where material quality degrades if used in a certain environment. Consideration is given to eliminating degradation during the selection of materials for equipment, but there are cases in which degradation arises because of long-term use, changes in usage conditions and formation of local special environments. This degradation of material quality causes phenomena such as reductions in corrosion resistance, reductions in mechanical properties and hardening. For inspecting this degradation, destructive inspection methods have the greatest reliability, but such methods are not applicable in the sense of maintenance inspections for equipment even though the state can be clearly grasped. Here, we will discuss 475°C embrittlement and hydrogen embrittlement that make use of electromagnetic acoustic wave resonance (EMAR) as a non-destructive method for evaluating material quality degradation.

(1) Detection of 475°C embrittlement

Duplex stainless steel, typified by SUS 329J4L, is a material formed from approximately 50% each of an austenite phase and a ferrite phase and has a combination of superior corrosion resistance and high strength. In chemical plants, it is used as a material for various types of equipment because of its superior resistance to stress corrosion cracking in chloride environments in particular. However, duplex stainless steel is known to undergo embrittlement when used for long periods in high temperature environments. The embrittlement mechanism can be breakdown into two phases, α solid solution with a low concentration of Cr and α' solid solution with a high concentration of Cr. Because of the ferrite phase undergoing spinodal decomposition, and the material initially hardens due to precipitation of the α' solid solution, therefore there is a simultaneous dramatic reduction in the impact energy value. In particular, reduction in the impact energy value is more sensitive than hardening, and beginning with the very start of increases in hardening, there is a large reduction in the impact energy value. The temperature at which embrittlement, which is caused by precipitation of the α' solid solution, is generated most remarkably at around 475°C. Therefore, it is called 475°C embrittlement.⁵⁾

With 475°C embrittlement, the degree of embrittlement becomes more remarkable when the time to initial

embrittlement is reduced with increases in Cr concentration in the material. In addition, even if the temperature is at or below 475°C embrittlement progresses because of thermal aging when the retention time is long.

The modulus of elasticity for the ferrite phase in the material increases with 475°C embrittlement. Therefore, the velocity of ultrasonic waves propagated in a sample changes, but the change in the velocity of sound versus in a healthy material is only a several percent difference. Hence, a high precision sound velocity measuring technique is required for the evaluation of this difference. Therefore, EMAR[®] that has been studied by us is used. EMAR compensates for the demerit of the conversion efficiency of the EMAT being low. In EMAR the sample is put into a resonant state and therefore the amplitude of the ultrasonic waves is increased.

As is shown in Fig. 10, the resonant frequency of the sample is measured by making measurements while sweeping with a high output burst wave frequency that causes excitation, and the velocity of ultrasonic waves propagated in the sample is found with high precision from the resonant frequency and the thickness of the sample.

Measurements of the velocity of ultrasonic waves propagated in samples by EMAR and Charpy impact

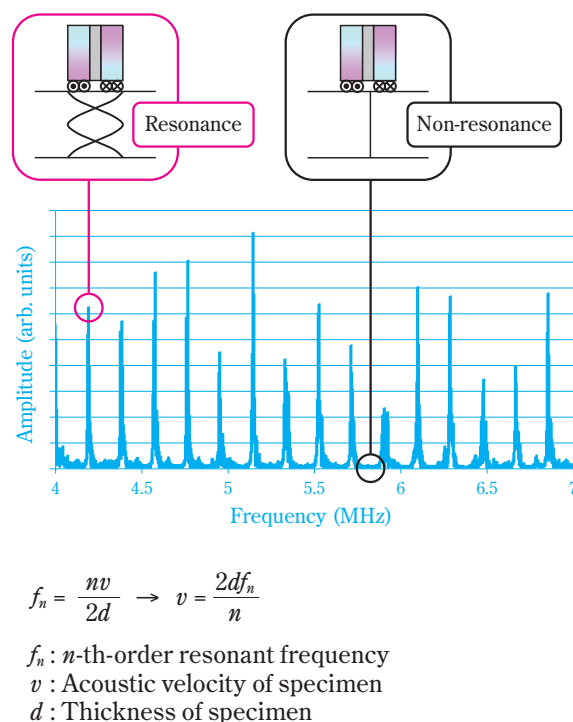


Fig. 10 Resonance spectrum obtained in EMAT

tests were conducted with SUS 329J4L material in which 475°C embrittlement had been generated artificially by adjusting heating temperature and heating time in an electric furnace. Fig. 11 gives results showing the relationship between the average value of the velocity of longitudinal and transverse waves of the ultrasonic waves propagated in the samples shown in the horizontal axis and the Charpy impact value at room temperature (25°C) shown in the vertical axis. Along with the material becoming embrittled and the Charpy impact value being reduced because of the 475°C embrittlement, the average velocity for the longitudinal waves and transverse waves of the ultrasonic waves propagated in the sample becomes slower. The change in the velocity of the ultrasonic waves propagated in the sample is small at 1% for the large reduction by embrittlement in the impact energy value to about 1/8 of that for sound parts, but EMAR can evaluate minute changes in sound velocity with high precision; therefore, this evaluation curve is used to evaluate the presence or absence of 475°C embrittlement and the degree of the embrittlement in duplex stainless steel.

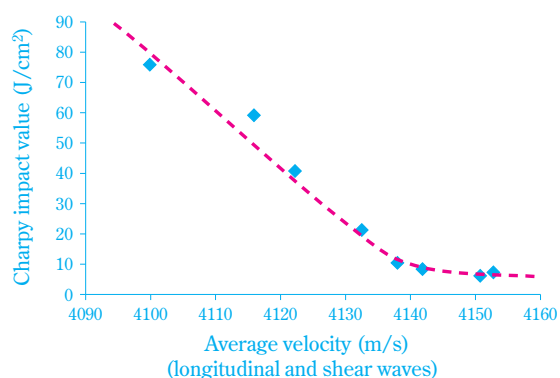


Fig. 11 Correlation between Average velocity and Charpy impact value

(2) Detection of hydrogen embrittlement

Titanium has superior corrosion resistance in a sea water environment. In Sumitomo Chemical, sea water is often used in the heat exchangers. However, the affinity of titanium to hydrogen is high and therefore the needle shaped hydrides like those shown in Fig. 12 form within the metal and embrittlement occurs when the hydrogen is stored. As a result, reduction in ductility is caused without evidence of corrosion and therefore the reduction in thickness occurs. Typically, if the hydrogen concentration in titanium is roughly 500 ppm or less, the reduction in mechanical characteristics at

normal deformation rates is small, but with rapid deformation as in Charpy impact tests, embrittlement manifests itself even at hydrogen concentrations of 100 ppm or less.

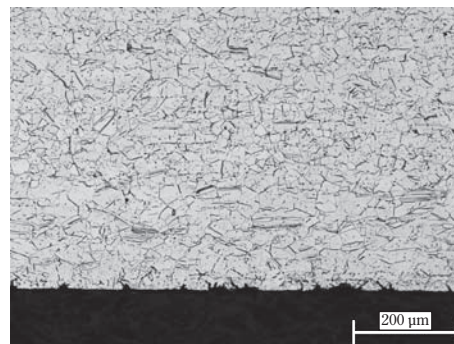


Fig. 12 Microstructure of titanium affected by hydrogen embrittlement

In terms of hydrogen storage, caution is naturally necessary in cases when process fluids contain hydrogen, but when the anticorrosion properties of titanium are not required on the shell side, titanium materials are mostly not used in baffle plates and tube plates that support the heat transfer tubes. Caution is necessary because there are examples of hydrogen that is generated by minute amounts of corrosion in these members being stored in the heat transfer tubes.

Since hydrogen embrittlement of titanium is caused by the formation of brittle needle shaped hydrides which can appear through changes in the material properties such as electrical conductivity, modulus of elasticity and hardness. The changes in these various properties can be detected in terms of changes in the velocity of longitudinal waves and transverse waves of ultrasonic waves propagated in samples. The relationship between the average velocity and the changes in electrical conductivity is shown in Fig. 13. EMAR is effective for the measurement of the velocity of sound waves propagated in samples. However, with minute amounts of hydrogen storage of 1000 ppm or less, the amount of changes in these parameters is extremely small and therefore clear determinations are difficult if there is a variation in the measurement data. Thus, we focused on the factors for hydrides inhibiting ultrasonic wave propagation and developed a method for detecting hydrogen embrittlement by measuring the attenuation rate of ultrasonic waves excited for a specific resonant frequency by the EMAT.⁷⁾ Fig. 14 shows the

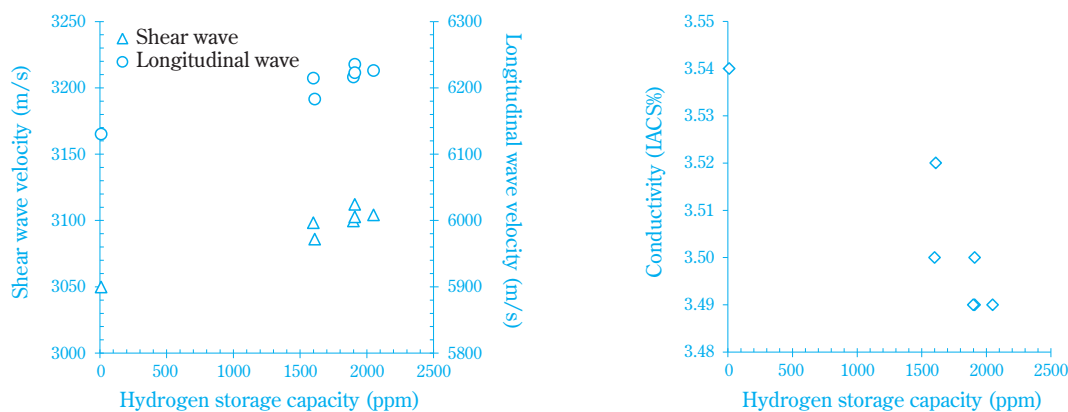


Fig. 13 Changes in ultrasonic velocity (left) and conductivity (right) due to hydrogen embrittlement

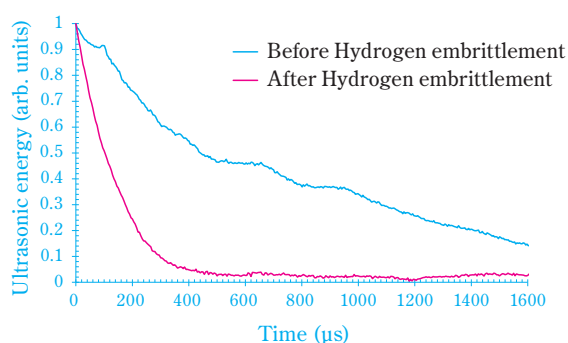


Fig. 14 Attenuation of ultrasonic energy in titanium

results of comparing attenuation rates of ultrasonic energy at 5.2 MHz, which is the fifth resonant frequency, for a healthy titanium sample and hydrogen stored titanium sample with hydrogen stored at approximately 300 ppm. With the healthy material, 1400 μsec were required for attenuation of energy to 20%, but in the hydrogen stored brittle material the attenuation occurred in 220 μsec. Hence, it can be concluded that detection of hydrogen storage is possible even for a minute hydrogen embrittlement by measuring the time a resonant state which can be maintained in this manner. However, this method is a partial inspection method that identifies inspection sites; therefore, when sites for hydrogen embrittlement cannot be identified in the direction of the tube axis in heat transfer tubes and other pipes, multipoint inspections must be carried out by determining a pitch to move in the axial direction. Since there is an overwhelming number of heat transfer tubes which are the objects of this inspection, a problem for the future is putting together a method that can carry out continuous inspections over the entire length of heat transfer tubes.

3. Applications in Corrosion Inspections for Contact Parts in Pipe Framing

As shown in Fig. 15 water from rain and other sources can easily accumulate at the contact parts in pipe framing, and coatings at the contact parts with the frame can easily peel off because of thermal expansion and contraction of the pipes. Therefore recoating and other maintenance are difficult at these sites where external corrosion can easily occur and progress.

On the other hand, the number of frames is proportional to the layout length of the pipes and is therefore immense. While corrosion and thinning are important inspection points, a large amount of time is required even for primary inspections centered on visual inspections. In addition, secondary inspections are carried out using non-destructive inspection methods such as ultrasonic tests at sites that are problematic during primary inspections, but incidental construction, such as removal of coatings on the surface of pipes, scraping of rust and surface polishing are required for carrying out ultrasonic inspection. While the progression of corrosion and thinning will make a dangerous situation for safety concerns, and also there is one more concern that the inspections will not be carried out in time. Thus, we carried out development of corrosion inspection techniques for the contact parts of pipe framing using the characteristic features of the electromagnetic acoustic wave technique that can excite ultrasonic waves without contact. EMAT has been developed not only to reduce the time required for secondary inspections by simplifying the pretreatment of sites to be inspected, but also consideration is given to the desire to increase the reliability of the contact parts of pipe framing. Here, we will describe the current state of the investigation into these techniques.

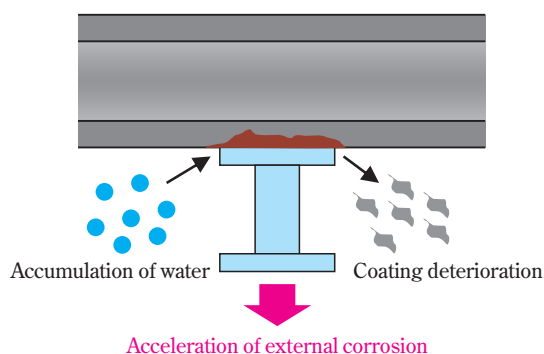


Fig. 15 Acceleration of external corrosion of pipe on a pipe support

The inspection technique forming the basis of this is the surface wave method for ultrasonic testing shown in Fig. 16.⁸⁾ The surface wave method of ultrasonic testing is carried out by setting up probes, which sandwich a framing part, for exciting and receiving the surface waves.

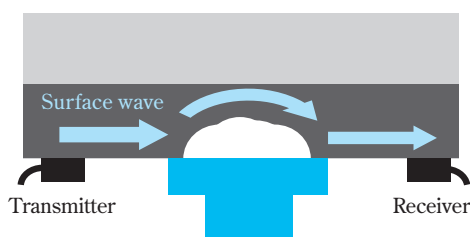


Fig. 16 Surface wave technique of ultrasonic testing

When the thickness of a pipe is reduced the arrival time of the surface wave is delayed by passing the part where the pipe is thinned out, and the amount of reduction in thickness is estimated from the time delay. Unlike the ultrasonic attenuation method, removal of liquids is unnecessary because the fluid inside has negligible effect on the time delay. The merit of this method is that when corrosion exists the amount of reduction in thickness is measured from the elongation of the propagation distance of the surface waves rather than a relative value such as attenuation. However, demerits are that surface treatment of parts where a probe is set up is necessary and the probe must be strongly pressed against the surface of the pipe to make a sizable inspection jig necessary.

It is important to resolve these demerits with the conventional surface wave method of ultrasonic testing. Hence, we decided to investigate using the EMAT which can excite ultrasonic waves within the material

without any contact. However, the energy conversion efficiency of EMAT is lower than that of piezoelectric probes. Therefore, the most important problem is excitation of ultrasonic waves with a superior S/N ratio which has the intensity required for measurements in the targeted objects. First of all, in terms of improvements related to devices, a wideband preamplifier was used for a wideband sweep of frequencies in EMAR used for degradation diagnostics in materials, but to narrow down the frequency band for exciting ultrasonic waves without resonance at flaws, therefore a narrow band preamplifier that only amplifies the signal in that particular band had been introduced. In addition, a bypass capacitor was put in place to eliminate high-frequency noise in the signal. In terms of the EMAT, a thick wire was used in the coil to increase the input voltage value, and in addition to that a variety of investigations had been carried out such as reassessing and optimizing the magnet arrangement. Fig. 17 shows the waveform of ultrasound during exciting and receiving with 60.5 mm outside diameter, 3.9 mm thick pipe as the target. Even if the distance between the probes was set at 50 cm or greater, envisioning the width of framing, exciting and receiving the signal required for the measurement could be possible. In the next step, we targeted improvements in measurement precision for the depth of reduced thickness in addition to current measurements for pipes with simulated reduced thickness and corroded pipes in actual equipment. Fig. 18 shows an example of a measurement on a corroded pipe with an outside diameter of 60.5 mm and thickness of 3.9 mm in actual equipment. We can see that the arrival time for the ultrasonic waves is delayed in the part with reduced thickness over that in the healthy part, and the amplitude is attenuated. The depth of the reduction in thickness estimated from the delay in arrival time is 1.6 mm,

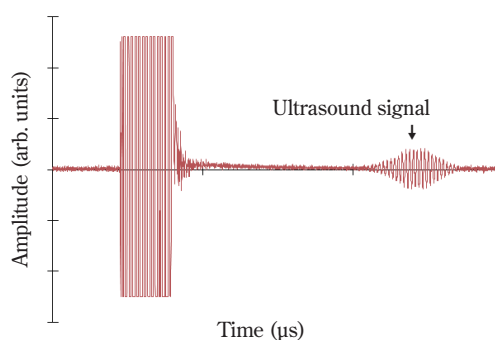


Fig. 17 Waveform of ultrasound in a non-defective steel pipe

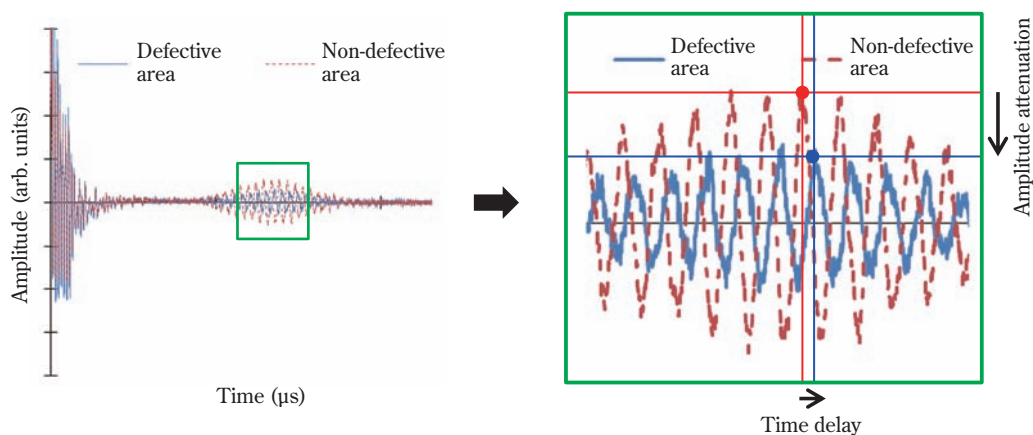


Fig. 18 Comparison between waveforms in defective and non-defective area of a steel pipe

and an excellent result for the depth of reduction in a thickness of 2.0 mm actually measured by an ultrasonic thickness measurement was obtained.

Along with further improving the performance of the EMAT in the future and developing an on-site jig for inspections, we will expand measurement data for pipes with simulated reductions in thickness and corroded pipes in actual equipment. Furthermore, we aim to improve the precision of the techniques for evaluating reductions in thickness after surveying the configurations of reductions in thickness due to corrosion in the actual equipment. In parallel with this, we will move forward with on-site data collection, make use of the knowledge obtained to improve the EMAT design and the jig for inspections and further improve measurement efficiency and measurement precision at actual sites.

Development of Carburization Measurement Technique and Portable Carburization Measurement Instrument

In the ethylene plants raw materials such as naphtha and ethane are fed inside the radiant tubes of a cracking unit to carry out thermal decomposition at a high temperature environment. Deposition of carbon known as coking occurs during the process on the inside surfaces of the radiant tubes which will lead to an increase in temperature of the tube wall. Cr and Si oxide films are formed on the inside surfaces of the tubes which inhibit the penetration of the carbon. However, as the performance of the oxide coating degrades or is destroyed by carbon deposition, carburization occurs and progresses according to the diffusion rate of the carbon. Carburization is a phenomenon in which chromium carbides, Cr_7C_3 is a typical form, are formed on the inside surface

of the tube. The cross-sectional microstructure of a radiant tube in which carburization has occurred is shown in Fig. 19. Here, the tube was immersed in a special etching fluid (Murakami's reagent), which stained the carburized locations with brown color. In this sample, it can be seen that local carburization had occurred. If carburization occurs ductility of the material will be almost entirely lost and the impact energy value will be reduced which creates an extremely brittle state in the material. In addition, because of expansion in volume, which is accompanied by carburization, tensile stress will arise in the healthy outer surface of the tube under high temperature use, and therefore deformation of the tube and creep damage may arise. Thus, the extent of carburization is the most important factor in determining the life of the radiant tubes.

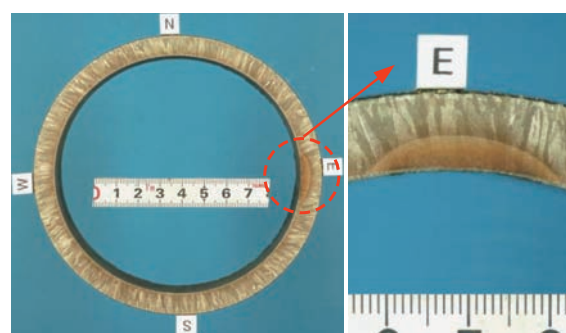


Fig. 19 Carburization of radiant tube

1. Principles for Measuring Carburization

Eddy current testing technique is used for carburization measurement. Generally the radiant tubes are non-magnetic materials, but when carburization occurs the amount of Cr in the basic composition of the material is

reduced and the balance of components changes due to the formation of Cr_7C_3 chromium carbides. Therefore, those parts in which carburization occur will be converted into ferromagnetic materials.

As is shown in **Fig. 20**, if a coil in which an alternating current flows is brought close to the outer surface of a radiant tube, an eddy current is generated in the direction of thickness of the radiant tube by the phenomenon of electromagnetic induction. Furthermore, the space between the carburized layer (ferromagnetic) and the coil is measured, in other words the non-ferromagnetic layer thickness is directly measured by this technique. Specifically, the thickness of the non-carburized layer is reduced as the carburization progresses in the direction of thickness. This change can be detected as a change in phase angle, which is one evaluation parameter, of the eddy current testing output signal. Therefore, the carburization evaluation curve, which is a calibration of the relationship between phase angle and the non-carburized layer thickness as shown in **Fig. 21**, is used to evaluate the thickness of the non-carburized layer. How-

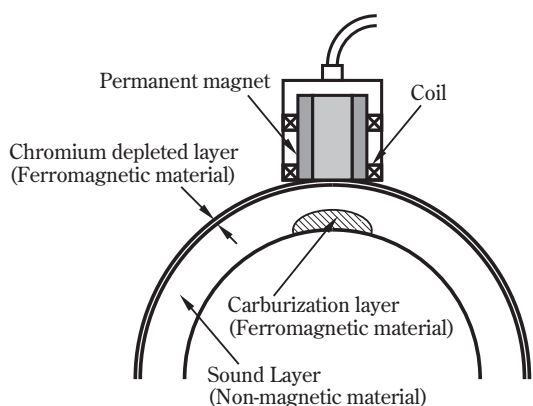


Fig. 20 Principle of carburization measurement

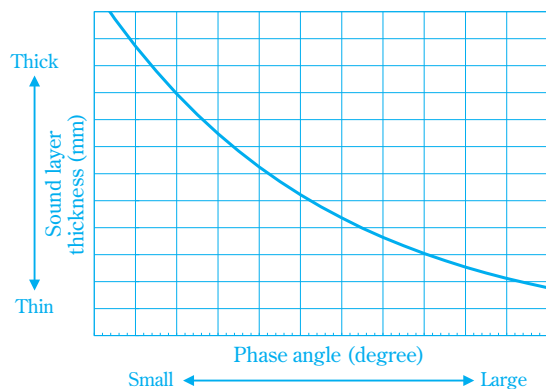


Fig. 21 Calibration curve for carburization measurement

ever, in radiant tubes made up of HP alloys (25% Cr–35% Ni) and 45% Ni alloys that have been used in recent years, chrome deficient layers will arise because of the oxidation that occurs on the outside surface of the tubes with use at high temperatures. Similarly, these parts will become ferromagnetic in the same manner as described above in case of carburization. Therefore, the eddy current generated on the outer surface will not be able to permeate through the thickness because of the skin effect, and hence carburization measurements are not possible with the eddy current testing technique.

With regard to this problem, at Sumitomo Chemical, after integrating a permanent magnet into the probe and reducing the effects of the magnetic layer of the outer surface layer part by magnetizing the part, we are measuring the thickness of the non-carburized layer using the carburization evaluation curve that calibrates the relationship between the phase angle of the signal obtained and the thickness of the non-carburized part. However, in this case, in terms of the measurement precision of this method the effects are shown in **Fig. 22** with the evaluation values for non-carburized layer thickness on the horizontal axis and actual measurement values for non-carburized layer thickness on the vertical axis. The actual measured values are within a range of ± 1 mm from the evaluation values, and hence carburization measurements could be carried out with high precision.

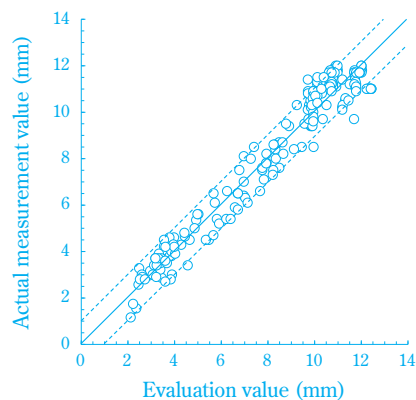


Fig. 22 Carburization measurement accuracy in 45% Ni alloy

2. Handling of Nitride Layers

Resistance to carburization can be increased if the radiant tube material is upgraded to 45% Ni alloy and this makes long-term use possible, but a layer (called nitridation layer in the following) made up of a com-

pound (Cr_2N) of nitrogen and chromium is formed in air as shown in **Fig. 23** on the inside of an oxide layer on the outer surface of the tubes when they are used for a long time at high temperatures. If the nitridation layer progresses approximately 1–2 mm, a layer with the same magnetic properties as with carburization is formed on the outer surface. The changes in electromagnetic properties with the formation of this thick nitridation layer are large and the precision of carburization measurements will be reduced. Specifically, non-carburized parts are also erroneously diagnosed as having occurrences of carburization and the thickness of the carburization is overestimated.

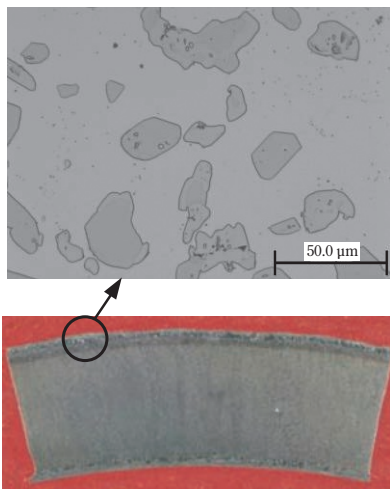


Fig. 23 Nitridation of radiant tube (outer surface)

We can consider a method in which a strong magnetic field is applied from the outside and magnetic saturation created in the same manner as with magnetic layers due to oxidation of the outside surface of the tubes, but if magnetization is carried out to the extent that reduces the effects of the thick nitridation layer, the evaluation of the carburized layer progressing from the inside surface of the radiant tube is also affected. Therefore, we investigated the method for evaluating the presence or absence of a nitridation layer from the changes in the properties of an eddy current signal due to the nitridation layer on the outside tubes. Using the radiant tube samples from the actual equipment, we measured the carburization of the samples and also carried out cross-sectional structure observations to evaluate the absence or presence of nitridation and carburization.

Fig. 24 adds the results of cross-sectional structure observations to results showing the phase angle for eddy current test data for the samples on the horizontal

axis and amplitude on the vertical axis. There is an increase in both the phase angle and amplitude of the eddy current signal at carburized parts over the healthy parts, but at the nitrided parts only the phase angle increases and no changes are observed in the amplitude. In addition, when nitridation and carburization are combined the intermediate characteristics are displayed. Based on these results, we developed a method⁹⁾ for dividing and determining carburization, nitridation, combined nitridation and carburization regions by solid line A-B and dashed line C-D as shown in **Fig. 25**.

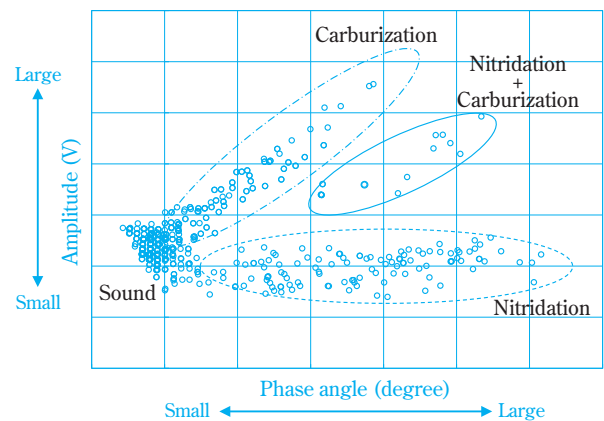


Fig. 24 Correlation between amplitude and phase angle

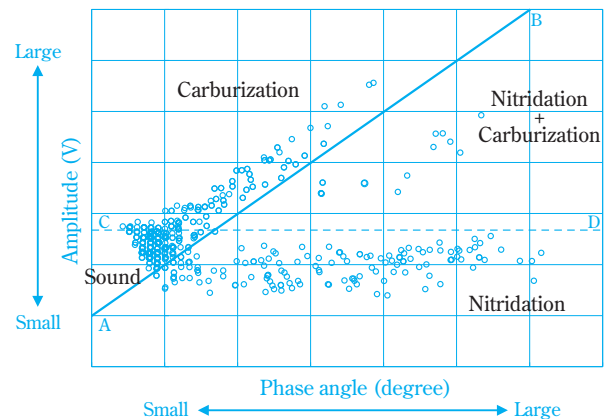


Fig. 25 Determination procedure of nitridation layer

In addition, with regard to the problem of overestimation of carburization thickness because of the combination of nitridation and carburization, we came to understand that there is an approximately 2 mm overestimation of the actual carburization thickness if nitridation and carburization are combined as a result of investigations based on the results of carburization

measurements and cross-sectional structure observations in the samples. Therefore, when a combination of nitridation and carburization is determined, 2 mm is subtracted from the measurement value of the carburization thickness in order to estimate the actual carburization thickness. Moreover, we will improve the reliability of data by conducting destructive investigations on the samples in the future.

3. Development and Application of Portable Carburization Measurement Instrument

With the Sumitomo Chemical carburization measurement technique, carburization thickness can be evaluated with high precision while considering the effects of nitridation. However, even though the eddy current testing equipment, data recorders, etc., for carburization measurements have become smaller and lighter in weight, it cannot be said that they can be easily taken inside cracking furnaces for inspections. In addition, calibration of equipment, and analysis of data obtained are special techniques requiring adequate knowledge, and measurements by certified eddy current testing personnel is necessary.

In Sumitomo Chemical plants in Japan it has been possible to have inspections carried out by certified personnel, but at affiliated overseas companies, starting with the Middle East, it is difficult to carry out inspections at the same level. Therefore, we developed portable carburization measuring instrumentation that combines a lightweight, compact and robust measurement instrument body and a tablet PC on which a software version of the data analysis know-how is installed. In addition to assuring measurement precision by this means, measurement technology that improves operability at the actual site and does not require knowledge of specialists can be provided.

Fig. 26 shows the configuration of the portable carburization measuring instrumentation.

The instrumentation is made up of the carburization measurement device a tablet PC, a carburization measurement probe, a probe connector, a USB cable and a standard test piece. The size of the carburization measurement device is 110 mm (W) × 210 mm (L) × 24 mm (H), with a weight of 480 g (including AA nickel metal-hydride batteries), and five hours of continuous measurements are possible.

Fig. 27 shows the tablet screen during a carburization measurement. A state in which it is possible to carry out carburization measurements on radiant tubes

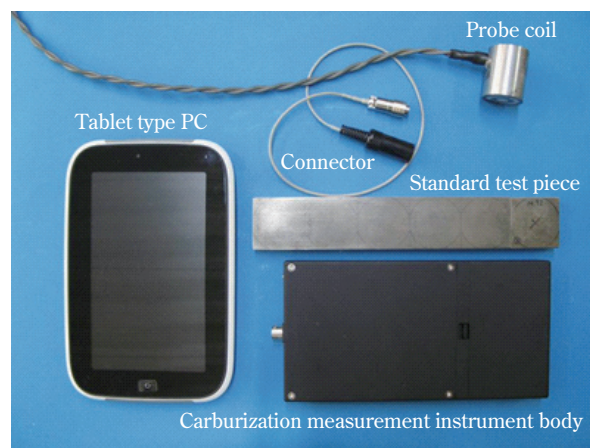


Fig. 26 Portable carburization measuring instrument

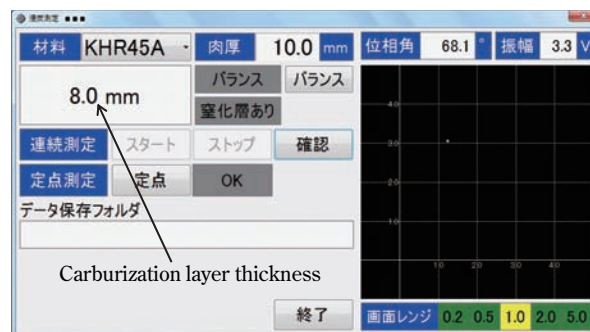


Fig. 27 Screenshot of portable carburization measuring instrument

is reached approximately 1 minute after starting up the software for carburization measurements by carrying out a simple calibration using the standard test piece. The presence or absence of a nitridation layer and the depth of carburization are displayed on the screen just by bringing the probe into contact with the surface of the radiant tube. Storage of measurement data is also simple, and in the continuous measurement mode, the carburization measurement data is continuously stored in the PC, and at the same time, the maximum carburization measurement value is displayed on the screen.

Since the instrumentation is lightweight, compact and battery-powered, it does not require a power supply to be assured inside the furnace, and since the equipment is easily carried around, the efficiency of on-site operations is greatly improved. In addition, we are able to reduce the immense time required for data analysis to almost zero. Moreover, we also prepared an English version of the software in which all of the text on the screen is in English to handle use in overseas plants.

Summary

In this article we have introduced inspection and diagnostic techniques developed with low cost, high speed, high quality as keywords. Magnetic eddy current flaw testing in heat transfer tubes made of magnetic materials, such as nickel and duplex stainless steel, has reached the same level of inspection quality as eddy current flaw testing in nonmagnetic material pipes. In addition, even with reactor tubes made of ferromagnetic materials such as carbon steel, it has become possible to detect and evaluate local reductions in thickness such as those which exist below the baffle plates. Above all, this method is being applied as a high-speed inspection technique and can be an alternative to IRIS. EMAR can evaluate the thermal aging embrittlement of duplex stainless steel and hydrogen embrittlement of titanium. In addition, making the characteristic ability to excite ultrasonic waves without contacting the target material, we are moving forward with development of a corrosion inspection technique on the contact parts of pipe framing. By application of eddy current for the carburization measurement, it has become possible to evaluate carburization depth with high precision including evaluations of nitridation layers which has been accompanied by long-term use. Furthermore, we have developed a portable carburization measuring instrumentation that improves operability in the actual field, and does not require a specialist to operate it. The portable instrument has been in use for measuring carburization depth at our plants both in Japan and overseas.

Continuation of plant safety and stable operations are not only assuring stable and continuous earnings for

Sumitomo Chemical, but also plant operations without accidents and without disasters are our minimum responsibility as a corporation to the regions and societies with which we coexist. To carry out a suitable maintenance at suitable timings for facilities that will be aging even more in the future will become an even greater responsibility for those of us in the field of facility maintenance. Starting with the techniques that are introduced in this article, we truly want to develop and investigate the maintenance techniques that will be even more necessary in the future and contribute to the continuing safety and stable operation of plants.

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