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Advance in Corrosion Protection and Its Material

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Abstract

Steel materials are extensively used in applications ranging from large structures that constitute social and industrial infrastructures such as building, civil structures, power and energy plants to objects which are close to our daily life such as automobiles, home electric appliances and cans. The conditions for which steel materials are used also range from mild ones to extremely severe ones. Therefore, corrosion resistance is one of the important performances required for steel. Particularly in recent years, needs for properties such as long durability and reduction of environment-affecting substances have grown to contribute to maintenance cost cuts and the building of recycle-oriented society. Nippon Steel has developed a number of corrosion-resistant steel and coated steel sheets.

1. Introduction

With the coming of the 21st century, a mission required for the industries is greatly changing with strong demands of the structuring of a recycle-oriented society, and compliance with global warming and an aging society. Steel products are used extensively as the important raw material of consumer and capital goods, and therefore expected to make a technical contribution toward the accomplishment of the above mission.

Corrosion-resistant material is used for many applications where the working conditions and requirement for corrosion resistance are ramified. Corrosion is an intrinsic problem for utility metals. In case of steel, stainless steel, galvanizing, electro galvanizing, and weathering steel of which corrosion can be prevented or moderated have been put to practical use. This has led to an increase in the volume of steel used along with the improvement in performance for corrosion resistance.

Japan has constructed and accumulated large-scale social and industrial infrastructures since the post-war high economic growth period. Thirty years have already passed since then, and the demand is growing for effective maintenance and a long service life of those infrastructures. On the other hand, in the fields of durable consumer goods and daily necessaries, public attention has been focused on 3 R (Reduce, Reuse, and Recycle) aiming at the improvement of a recycling rate and the reduction of wastes as a consequence of the enforcement of various environment-related laws, including the law for recycling of specified kinds of household electric appliances, and the green purchase law. Furthermore, in anticipation of the directive of EU (European Union), a move is rapidly being made toward the reduction in and the ban on the use of the environmental affecting substances, particularly lead and hexavalent chromium. As above-described, the changes in social needs and the progress of industrial technology have asked high technology for corrosion protection over a broad range of fields along with the request for high performance under severer working conditions.

Fig. 1 shows the outline of the market needs and the progresses in technology in respective fields. The horizontal-axis shows the applications in a variety of fields from daily necessaries and durable consumer goods with a comparatively short service life (in the order of several to 15 years) to social infrastructures for which a service life of over 100 years is required. In the field of daily necessaries and durable consumer goods, anti-rusting carries weight, and coating is applied. In the field of social and industrial infrastructures, a target is set for a long service life of over 50 years, and corrosion-resistant steel is mainly used. The main technical issue is how to make a service life longer, including how to maintain. Compliance with the en-

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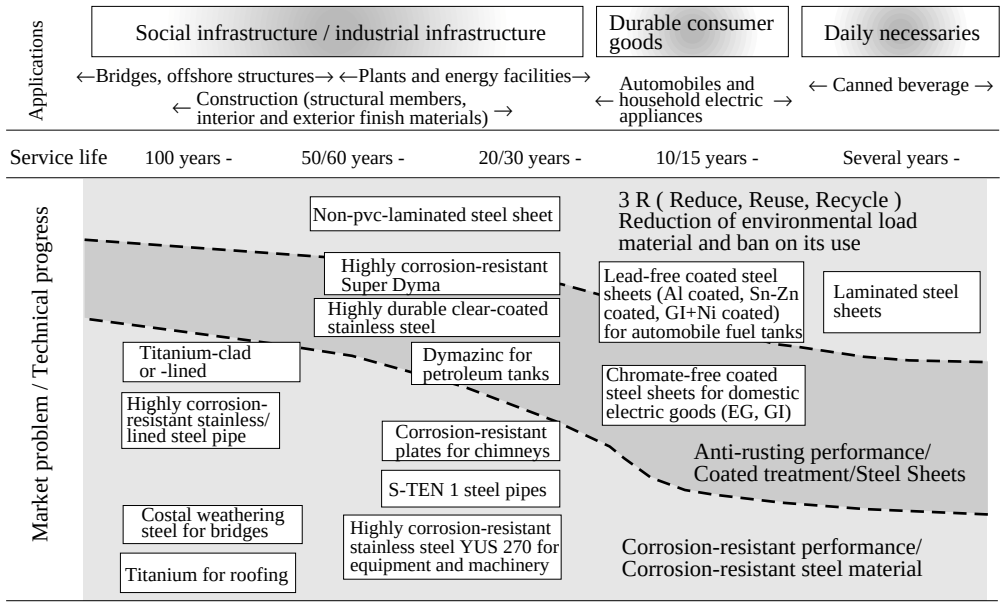

Fig. 1 Changes in social needs and recent progress in technology

vironment applies to all fields. Nippon Steel has so far succeeded in developing many corrosion-resistant steel and coated steel.

This paper, after supplementing the working environment and requirements for corrosion resistance, introduces the important development in corrosion-resistant materials and corrosion protection technology together with typical commercialized new products in recent years in Nippon Steel.

2. Working Environment and Request for Corrosion Resistance of Material

Fig. 2 shows an example of outlining the configuration of major equipments in respective fields in terms of temperature and the cor-

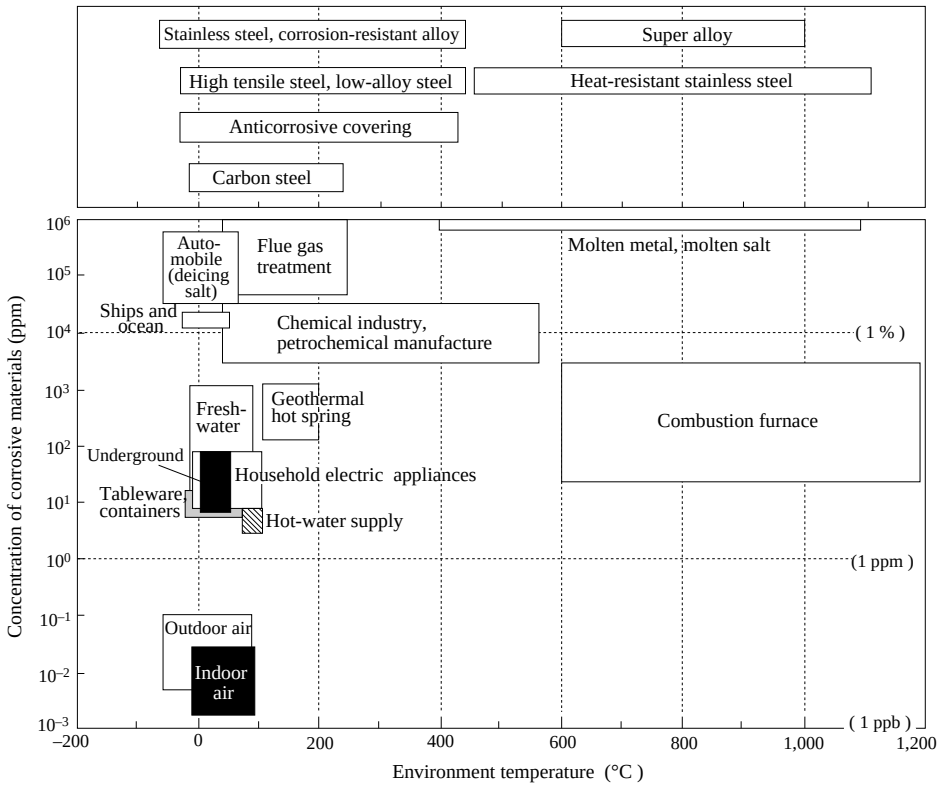

Fig. 2 An example of outlining the configuration of major equipment in respective fields in terms of material surface temperatures and corrosive condition (Edited by the National Institute of Resources, Science and Technology Agency: Rust close to us and its protection, partly revised by referring to 1986 edition)

rosive condition[1]. This figure is not an exact one, but reveals that the environment conditions are wide-ranging and the combination of materials is diversified. Corrosion resistance, though expressed in a word, is requested to have various performances, such as, for example, prevention of the rust of tableware familiar to us, control of the corrosion rate of steel plates for hull and offshore structures, and selection of corrosion-resistant materials harmless to food in the food processing plant.

The working environment for which freshwater is used, household electric appliances, and tableware, is comparatively less corrosive because these equipments and goods are used in the outdoor and indoor atmosphere. The environment slightly more corrosive is for hull and offshore structure use, and the still more corrosive one is found in hot water and hot springs where water is heated to a high temperature. Some chemical plants are classified into the latter category. Again, the environment for chemical and petrochemical plants, exposed to high temperature, and for automobiles, exposed to the highly salt-concentrated corrosive environment arising from the deicing salt, is classified into the highly corrosive category. Furthermore, the extremely corrosive environment is found in the exhaust system of an internal combustion engine, exposed to very high temperature, a hot-dipping tank for molten metals, and a fuel cell using molten salt.

As described above, although the corrosiveness in the specified environment and the requirements for corrosion resistance are diversified, it becomes possible to select appropriate materials available for practical use in almost all the fields at present, as a result of our efforts and accumulation of the technical understanding, collaborated with the users, on both the material and the working environment.

3. Recent Advance in Corrosion Resistance and Corrosion Protection technology

The development in ecology, medicine, life science, and economics have led to changing the stereotype of common sense in consideration of the material circulation on a global scale and the influence on organisms and a new concept of society is thus proposed, that is, structuring of a society with a less burden to the succeeding generation. Concretely, this comprises “Effective utilization of limited resources to a higher degree,” “Reduction in environmental burden,” “Enhancement of reliability,” and “Reduction in burden for the maintenance of the infrastructure.” In other words, in the corrosion resistance technology, the request of conformity with social needs is becoming all the more urgent in addition to a comparatively simple request for the control of rust and thinning. In addition to developing the basic techniques applicable to various surroundings, further investigation and research have been launched, and are still going on over various fields.

Table 1 shows the examples of steel corrosion problems in respective fields as well as the outlines of the corrosion-resistant steel materials and coated steel sheets, recently developed by Nippon Steel. Nippon Steel has developed the following steel materials:

1) In terms of effective utilization of resources, Dymazinc and Super Dyma, both of which can offer long-term anticorrosive performance and corrosion-resistant properties with a less coating

2) In terms of the reduction in environmental load materials, Al-coated steel sheet for fuel tanks, Sn-Zn coated steel sheets (Ecokote-T and Eco Trio), lead-free coated steel sheets, such as Silverzinc-NT, and chromate-free coated steel sheets, such as Zincoat 21 and Silverzinc 21

3) In terms of the enhancement of reliability, highly corrosion-resistant steel materials, such as titanium-clad steel and YUS270 Super-stainless steel

In terms of the reduction in burden for the maintenance of social infrastructures, Nippon Steel has developed various techniques that can contribute to the future application of steel as described below:

1) A technique of predicting the life expectancy of not only costal weathering steel enabling a long-term durability in the coastal area but also weathering steel and Dymazinc-thermal-sprayed steel for petroleum tanks on the basis of massive evaluation data and their multivariable volume analytical technique

2) A technique of real time monitoring of a corrosion condition by using advanced electrochemical technology

3) A new evaluation technique in compliance with the real condition[2]

4) A proposal for standardization of those evaluation techniques for JIS and ISO is also under way.

4. Requirements for Corrosion Resistance and New Technology in Respective Fields

(Those marked * are covered in this paper)

4.1 Construction and civil engineering structures

In this field with bridges, high-rise buildings and large steel structure, solutions for the prevention of corrosion from air and rain in terms of the reduction in burden for maintenance of social infrastructures are required. Weathering steel usually have been applied to bridges, but its application has been limited to an area not attacked by salt. For our country surrounded by the sea, the improvement of weathering steel has been requested for use in coastal areas. In response to this request, “Coastal weathering steel”* that decrease the infiltration of Cl ions with the addition of Ni has been developed, a kind of steel that have corrosion resistance in the presence of salt higher in concentration than usual. This steel can be applied in unpainted condition in coastal areas.

Furthermore, “Technique of predicting the corrosion of weathering steel”* has been developed that can predict the volume of corrosion of this weathering steel. This has enabled to assume the volume of corrosion by inputting the amount of air-borne salt and main meteorological data. We would like to utilize this technique in the future as a tool of selecting steel in the stage of bridge planning.

On the other hand, Zn coated steel sheets and Zn-Al coated sheets have so far been mainly applied to coated steel sheets for building materials. In terms of effective utilization of resources, however, Zn-Mg coated steel sheet “Dymazinc” and “Super Dyma”* with Al and Si added further have been developed and succeeded in realizing saving of Zn and improvement of corrosion resistance. In addition, the application of stainless steel and titanium, excellent not only in corrosion resistance but also in design, is under way for outdoor roofing materials.

4.2 Energy and chemical plants

Since this field covers large-scale pieces of equipment, including thermal and nuclear power plants and chemical plants, an accident, once it occurs, will have a large negative impact on our society. Furthermore, corrosion-resistant performance fit for use under the special environment is required where various acids, alkalis, and salts are handled along with a wide range of from-low-to-high working temperatures. It is a great task imposed upon us not only to secure the safety of those equipments as social and industrial infrastructures, but also to maintain them and reduce their burdens.

Heavy duty anticorrosion coating has so far been applied to petroleum and LNG tanks whose bottom plates and roofs are required

Table 1 Steel material-related problems (examples)

Field	Construction and civil engineering	Energy and chemical plant	Automobile	Household electric appliances, electronic equipment	Offshore structure, ship	Lifeline
Corrosion condition	·Atmospheric corrosion ·In-concrete reinforcing bar ·Corrosion ·Freshwater corrosion ·Salt damage corrosion	·Acid and alkali ·Salts ·High-temperature gas corrosion ·Hot water corrosion	·Atmospheric corrosion ·Salt damage corrosion ·Fuel tank corrosion	·Atmospheric corrosion ·Freshwater corrosion ·Salt damage corrosion	·Seawater corrosion ·Salt damage corrosion	·Soil corrosion (electric corrosion, natural corrosion, microbial corrosion)
Steel materials used so far	·Weathering steel ·Stainless steel ·Various coated steel sheets ·PVC-coated steel sheet	·Low-alloy steel ·Stainless steel ·S-TEN	·Highly corrosion-resistant coated steel sheet ·Stainless steel for exhaust system ·Chromate coated steel sheet ·Lead/tin-coated steel sheet for fuel tank	·Highly corrosion-resitant coated steel sheet ·Stainless steel ·Chromate coated steel sheet ·Lead/tin-coated steel sheet for household electric appliances	·Cathodic protection ·Heavy duty anticorrosion coating	·Coated steel pipe (polyethylene- or PVC-coated) ·Cathodic protection
Problems related to corrosion protection and antirust technology	·Security of social infrastructure ·LCC evaluation ·Security of long service life ·Replacement of PVC-coated steel sheet	·Measures against acid and alkali corrosion ·Measures against high-temperature corrosion ·Measures against stress corrosion cracking ·Cost reduction	·Simultaneous security of anti-corrosiveness, drawability and coat-ability ·Technique against corrosion free of environmental load materials, including lead and hexavalent chromium	·Techniques against corrosion free of environmental load materials, including lead and hexavalent chromium ·Omission of coating process at user's side	·Measures against seawater corrosion ·Measures against seawater corrosion of offshore structure ·Security of long service life and minimum maintenance	·Measures against soil corrosion ·PVC substitute-coated steel pipe
	Probability of the technique of evaluating optimal corrosion acceleration test methods (promotion of standardization of JIS and ISO)					
Newly developed steel and corrosion resistant technology	·Costal weathering steel for bridges* ·Technique of predicting weathering steel corrosion ·Highly corrosion-resistant stainless steel (YUS 270, YUS 220, etc.) ·Super Dyma, Titanium and titanium-clad ·PVC substitute-coated steel sheet ·Real time monitoring of corrosion condition ·HALS coated steel sheet	·Zn-Mg-coated steel sheet for tank bottom and roofing ·S-TEN steel pipe ·YUS 270 ·Water-corrosion-proof element steel sheet for LNG	·Al coated steel sheet for fuel tank, Sn-Zn coated steel sheet, GI+Ni coated steel sheet ·Chromate-free coated steel sheet (GA, Zincoat MZ) ·Various high tensile coated steel sheets	·Lead-free coated steel sheet (Ecokote T, Eco Trio) ·Chromate-free coated steel sheet (Zincoat 21, Silverzinc 21) ·Precoated steel sheet (Viewkote) ·Chromate-free precoated steel sheet	·Titanium-clad, titanium-lined steel pipes ·YUS 270-lined steel pipe	

* Steel capable of remaining corrosion resistance even in the presence of salt more concentrated than usual

to enhance their corrosion resistance. However, a high maintenance cost has resulted in a growing request to simplify or omit coating. To cope with this situation, a technique has been developed by which corrosion resistance can be enhanced by "coating or thermal spraying Zn-Mg"*, and this technique is under commercialization. Again, in thermal power plants and refuse incineration plants, corrosion resistance is required under extremely severe conditions, such as sulfuric acid dew corrosion of exhaust gas ducts and chimneys. With the development of products, including highly corrosion-resistant stainless steel such as "YUS270"*, high-chromium steel, and "S-TEN"*, it is becoming possible to select material according to the working environment and demand level. On the other hand, it is an important task for nuclear power plants to find out measures against stress corrosion cracking after due consideration of the influence of irradiation on pressure vessels and ancillary piping.

4.3 Automobiles

In this field, steel material is used in many parts, such as outer and inner plates. The demand for higher corrosion resistance of steel is growing stricter year after year. Steel material for automobiles is required to be resistant not only to atmospheric corrosion but also to salt corrosion from deicing salt. Therefore, Nippon Steel has developed stainless steel and coated steel sheets, more excellent in corrosion resistance. Particularly in recent years steel material is required to be excellent not only in corrosion resistance but also in other performances, such as drawability, coating adhesiveness, and weldability. This has led to developing various high-performance coated steel sheets. In addition, highly corrosion-resistant stainless steel has been developed for an exhaust gas system, including a muffler and an exhaust manifold.

To cope with the regulations for reduction of environmental load material, European and domestic customers have made a proposal

for its reduction. It was stipulated in Europe as the regulations of ELV (End of Life Vehicle) that lead, mercury, cadmium, and hexavalent chromium should not be used in principle in the sales of new automobiles after July, 2003. In the case of coated steel sheets for automobiles, lead/tin-coated steel sheets have so far been used for fuel tanks, and for zinc-coated steel sheets used in automobile parts and other car goods, chromate coated ones have been used. However, due to the above regulations, the use of environmental load materials, including lead and hexavalent chromium, will be limited. As alternative coated steel sheets, Al coated steel sheet for fuel tanks, Sn-Zn coated steel sheets, GI + Ni coated steel sheets, and chromate-free coated steel sheets have been developed and already supplied for many customers.

4.4 Household electric appliances, electronic equipment (electronics), and automated office equipment

Steel sheets for household electric appliances used indoors, as represented by refrigerators and washing machines, are used in a comparatively mild condition, and galvanized sheet is generally used. In this field, European directives, WEEE (Waste of Electrical & Electronic Equipment) and ROHS (Restriction on Hazardous Substances), have stipulated that a ban on the use of environmental load materials, including lead and hexavalent chromium, should be in effect after 2006. The manufacturers of household electric appliances and automated office equipment have gone ahead of other industries in the reduction of environmental load materials.

Nippon Steel has developed and commercialized the chromate-free coated steel sheets, “Zincoat 21” and “Silverzinc 21”, for the first time in the industry. It has also developed substitutes for lead/tin-coated steel sheets for soldering use, i.e., lead-free “Eco Trio” and “Ecokote T”, which are used among many manufacturers of household electric appliances and automated office equipment. What is more, the precoated steel sheet, “Viewkote”*, which serves to omit customer’s coating process, is also extensively used in this field. In response to customers’ demand and in succession to the indoor application, Nippon Steel has also realized hexavalent chrome-free precoated steel sheets that can be used outdoors as in out-of-room air controllers recently.

4.5 Offshore structures and ships

Steel plates for offshore structures and ships are used under a very severe environment as in and on the sea. To respond to the need of enhancing reliability, various corrosion-resistant steel and corrosion protection technology have so far been developed and applied. Cathodic protection is frequently applied to the submerged part. However, materials clad or lined with “titanium”* and highly corrosion-resistant stainless steel “YUS270”* are applied to a splash zone, the severest conditions. About 80 tons of this titanium-clad steel was used for the splash zones of Tokyo Trans-bay bridge piers. Offshore structures in which YUS270-lined steel pipes are used are also increasing in number. Application of those materials to jacket-type piers is also under study. Again, corrosion of the inner side of tanks in the VLCC (Very Large Crude Carrier) has recently become an important issue. The study of this mechanism is therefore going on by respective institutions.

4.6 Lifeline(Underground piping)

Since water supply and sewer pipes and gas pipes are mostly buried underground, it is necessary to pay attention to underground corrosion. Underground corrosion can be classified into electric corrosion due to a stray current in a railway, general soil or organism corrosion, and corrosion due to contact with a reinforcing bar in concrete. For corrosion protection of steel pipes, insulation, coating and cathodic protection of pipes are applied. Polyethylene painting is mainly applied for steel pipes as an excellent insulator.

5. Future Prospects

As above-described, the outline was introduced of new technology and new products, developed by Nippon Steel and applied by our customers. An optimal combination between materials and its working conditions, should be required for achieving excellent corrosion protection. Those new technology are developed by the plentiful technical experience and its accumulation for corrosion resistance collaborated with our users. Since social needs are greatly changing now, higher performance should be realized. Our Technical challenges should not be limited only to achieving the performance of corrosion protection of steel itself, but to developing corrosion protection technology including application in society. Concretely, they are:

(1) In the field of social and industrial infrastructures, corrosion protection technology including evaluation methods should be developed in terms of not only materials but members and structures, and contribute to improving a technology for maintenance of steel structures .

(2) In the field of durable consumer goods and daily necessaries, a corrosion protection technology should be developed in consideration of 3 R and environmental protection. At the same time, the excellent recyclability of steel should be taken advantage of.

(3) In addition, plentifully accumulated and wide-ranging knowledge of corrosion protection should be systematically organized so that it can be developed for the future.

References

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2) Example, Corrosion of Metals and Alloys Accelerated Cyclic Test. (Juridical Foundation) The Japan Iron and Steel Federation, etc., 2001