CORROSION SCIENCE AND TECHNOLOGY, Vol.31, No.3(2002), pp.198~202

Application of Stainless Steels for Environments in Korea

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This paper covers the introduction of demand, supply and consumption pattern for stainless steel in Korea. Recently, stainless steel has a potential to become a more attractive environmental friendly material because of its intrinsic corrosion resistance and hygienic properties. This paper also introduce the application of developed stainless steels to Korea industry for clean energy and environments, such as automotive exhaust pipe system, FGD (Flue Gas Desulphurization) in power plants and structural & weathering materials in construction. Recently, the development of stainless steels for the use of energy and environmental industry can be divided into two aspects of research trends. One is to save the natural resource without using expensive alloying elements or replaced by environment-friendly alloying elements. The other research trend is to develop the high performance of stainless steels by improving the properties such as strength, heating & corrosion resistance etc. Especially, the application of new developed stainless steels to the Korea industry is described in detail.

Keywords : *stainless steel, environmental friendly, high nitrogen stainless steel*

1. Introduction

Entering the new millennium, environmental protection in the world is becoming an important issue. It is, therefore, inevitable for the steel company to develop an efficient energy process and environmental friendly materials. Recently, stainless steel is thought as the most environmental friendly materials. The environmental benefits provided by stainless steels in the development of a sustainable society must be balanced against the environmental of its manufacture and use. In this context, it has been recently reported that the environmental benefits and impacts of stainless steels are presented as credits and debits.[1)] Traditionally, stainless steel has a very strong "credit", based on its intrinsic corrosion resistance, hygienic, no painting and low leaching. The general public perceives stainless as a ideal material for the applications where cleanliness is essential. The fact that there is an increasing demand for stainless steel in pollution processes, like flue gas cleaning and desalination or waste water treatment, as well as for higher alloyed stainless grades closed loop recycling of chemicals in the process industry. Lately, both stainless steel industry and market have realized that these materials exhibit some very interesting mechanical properties. Highly formable, ultra-high strength stainless steels provide very attractive weight savings in the automotive, transport and construction sectors. Thus, less energy will be consumed during usage of the products and less material will have to be produced for each application. For an example, high nitrogen stainless steels has been actively developed. Due to its advantageous effects on corrosion resistance, strength and toughness, nitrogen emerged as the potential alloying elements which could replace the expensive nickel alloy. In the present paper, the current status of POSCO stainless steel industry and high nitrogen stainless steels and high purity ferritic stainless steels are introduced and application of the developed stainless steels to Korea industry for clean energy and environments are also described in detail.

2. Current status of POSCO stainless steel industry

POSCO is the unique integrated stainless steel mill in Korea. Total crude stainless steel production at present was about 1.2 million tons since POSCO began production of stainless hot bands in 1989. After finishing the 3rd phase expansion of stainless steel production, the POSCO production will be about 1.7 million tons in 2003. By the time, POSCO will be one of the largest stainless steel producer in the world. The growth of stainless steel production in the world during the last 25 years has been increased markedly compared to that of carbon steel production, as shown in Fig. 1. The rapid growth of stainless steel industry is due to requiring a large amount of stainless steels to the use of various industry application

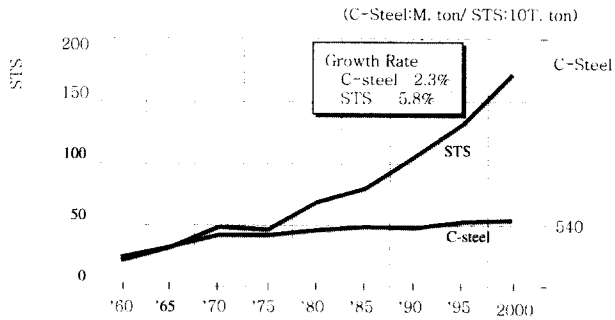


Fig. 1. Trends for Growth of Stainless Steel Industry

Table 1. World Market Share of Stainless Steels (unit : T. ton)

	EU	Japan	Aisa	USA	Etc.	Total
'84 (%)	2,120 (36)	1,300 (22)	650 (11)	1,350 (23)	470 (8)	5,900
'00 (%)	4,760 (34)	1,670 (16)	4,380 (24)	2,300 (18)	1,400 (8)	14,510

Table 2. Usage of Stainless Steel Products (unit : %)

	Home Appliance	Construction	Industry	Transportation	Electronic	Etc.
World	29.9	23.4	19.4	14.9	6.7	5.7
EU	26.8	22.4	27.4	11.3	6.6	5.5
Japan	22.5	25.6	18.5	18.2	7.5	7.7
Korea	34.8	34.8	11.6	8.7	3.2	6.9

such as construction and engineering plants. The portion of stainless steel production and consumption in the world are shown Table 1. Especially, stainless steel consumption in Asia has rapidly increased in the past 14 years. The consumption pattern for stainless steels in Korea is shown in Table 2. It is projected that as developing the Korea industry, stainless steel consumption will increase in the fields of engineering, transportation and electronics in order to keeping the same trend as the stainless steel consumption in Japan and Europe.

3. Development of Ni-Saving stainless steels

3.1 High nitrogen stainless steels

Nitrogen is becoming as a potential alloying element which could replace the expensive nickel, due to its advantageous effects on corrosion resistance, strength and toughness. High nitrogen stainless steels are, therefore, a new class of high alloy martensitic, austenitic or duplex grades with up to 0.9 mass% of N in solid solution for saving the nickel alloying. They also provide another advantage of recycling in the environmental protection point of view, as results of reducing the energy and SOx gas in the nickel refining process as shown in Fig. 2.

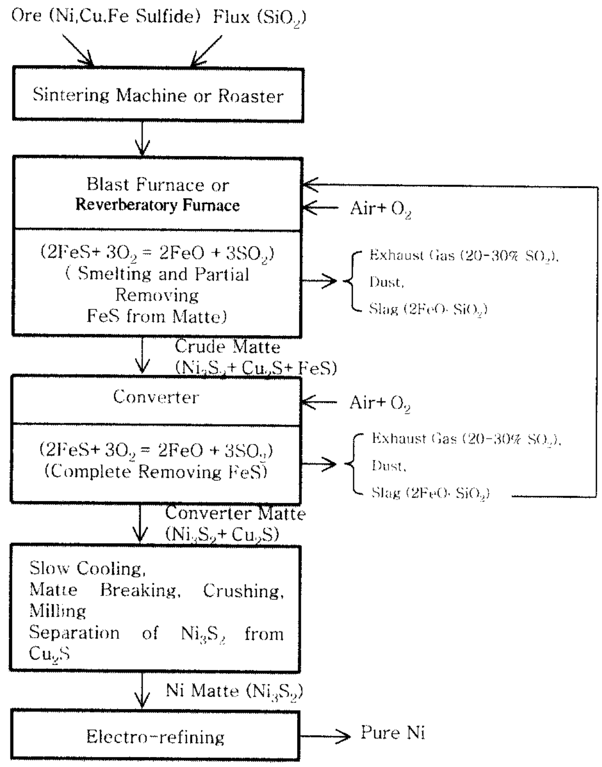


Fig. 2. Pyrometallurgical Process of Ni

Nitrogen addition gives several beneficial effects on the properties of stainless steels such as strength, toughness and corrosion resistance. The effects of nitrogen on pitting corrosion of stainless steels have been studied and a number of different mechanism have been proposed for the effect of nitrogen on pitting corrosion related to observe synergistic interactions with Mo in the alloy.[2] There is a fairly consistent agreement that N addition improves the pitting corrosion resistance of stainless steels by dissolution of nitrogen during active corrosion forming ammonium ions, which passivate the pits and crevices.[3] Nitrogen also improves the heat resistance and creep strength by locking the dislocation movement at high temperatures, although it is an interstitial element as carbon.

3.2 High purity ferritic stainless steels

High chromium ferritic stainless steels without containing Ni have higher corrosion resistance and lower production cost than those of austenitic stainless steels. Also, another benefit of the ferritic stainless steel is a view point of environmental protection because SOx gas and slag are not produced in the Ni refining process. However, high Cr ferritic stainless steels containing high residual elements (C,N,S,O) concentrations are limited to use the

Table. 3. Guideline of Stainless Steel & Nickel Alloy Selection for FGD Equipment

<table>
<tr><td colspan="2" rowspan="2">CHLORIDE (ppm) / pH</td><td>MILD</td><td colspan="2">MODERATE</td><td colspan="2">SEVERE</td><td colspan="3">VERY SEVERE</td></tr>
<tr><td>~500</td><td>~1,000</td><td>~5,000</td><td>~10,000</td><td>~30,000</td><td>~50,000</td><td>~100,000</td><td>~200,000</td></tr>
<tr><td>MILD</td><td>6.5</td><td colspan="2">TYPE 316L STAINLESS STEEL</td><td colspan="2"></td><td></td><td rowspan="3">SUPER AUSTENITIC S.S.</td><td>NICKEL ALLOY 625ETC.</td><td></td></tr>
<tr><td>MODERATE</td><td>4.5</td><td></td><td colspan="2">TYPE 317LMN S. S.</td><td colspan="2" rowspan="2">SUPER DUPLEX S.S.</td><td colspan="2" rowspan="3">NICKEL ALLOY C276 etc.</td></tr>
<tr><td>SEVERE</td><td>2.0</td><td>TYPE 317LM S.S.</td><td></td><td>DUPLEX S.S</td></tr>
<tr><td>VERY SEVERE</td><td>1.0</td><td>TYPE 317LMN S.S.</td><td colspan="3">SUPER AUSTENITIC S.S.</td><td>NICKEL ALLOY 625ETC.</td><td></td></tr>
</table>

applications because they influence the pitting corrosion and inter-granular corrosion susceptibility as well as toughness in BCC metals. In order to solve these problems, stabilizing elements (Nb, Ti) and Al are added to prevent the formation of chromium carbides and to reduce the oxide inclusions, respectively. Also, removal of residual elements by advanced refining technology of AOD and VOD process can be reduced to improve toughness. High chromium ferritic stainless steel, STS 447 (30%Cr-2%Mo) has been developed that increasing quantities of chromium and molybdenum in ferritic stainless steels improve the corrosion resistance. This steel is used for the roof material of Kansai international airport. It has been reported[4)] that if the impurity elements (C,N,O,S,P) of a ferritic stainless steel is reduced to less than 100ppm, pitting corrosion resistance improves very much as a result of increasing pitting potential rapidly. It is expected that the corrosion resistance of 20% Cr ferritic stainless steel, if it has the impurity elements of less than 100 ppm, can reach to the equivalent corrosion resistance of 30% Cr stainless steel. Therefore, the development of technology for production of high purity ferritic stainless steels is an important research task for the purpose of saving the natural resources and environment protection as well.

4. Application of environment-friendly stainless steels

4.1 Ferritic stainless steels for automotive exhaust systems

As the need to meet the regulation of reducing exhaust emission gas and fuel consumption limitation has been increased, the materials for having excellent corrosion and heat resistance, as shown in Table 3 are required to developed for the purpose of weight reduction, better fuel efficiency, low pollution and long life. High performance of ferritic stainless steels such as 436L and 429EM has been used as muffler and exhaust manifold, respectively. Cast-iron manifold and aluminized steel for exhaust pipes are replaced by these ferritic stainless steels. In order to increasing the exhaust emission efficiency, ceramic catalytic converter has been replaced by newly developed metallic converter as a alloy composition of 25%Cr-5%Al-REM. The material of this metallic converter with honeycombed foil and plates is required to have excellent high temperature strength and hot corrosion resistance. The replacement of cast-iron manifold by stainless steel manifold contributes to reduce both 30% weight reduction and 15% HC gas emission due to increasing the temperature of catalysis after engine-start.[5)]

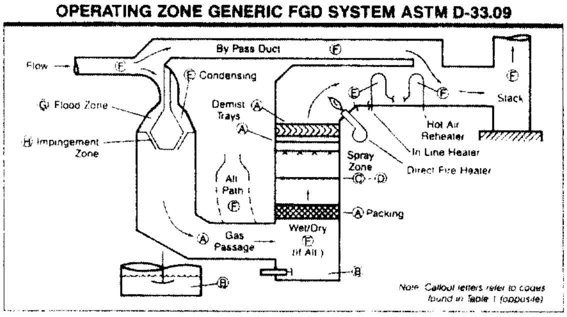
4.2 Duplex stainless steels for FGD in power plant

Due to the environmental legislations for the coal power plants in domestic, the FGD (Flue Gas Desulphurization) process is required to adopt for all coal power plants. A typical FGD process, wet limestone SOx scrubber system used in the power plants is shown in Fig. 3. The environment in this system is severe corrosion condition such as low PH, high chlorides, high temperatures and high abrasives as shown in Table 4.[6)] The materials used in severe corrosive conditions are required to have excellent properties of pitting corrosion resistance, SCC and strength. Duplex stainless steel and super austenitic stainless steel are the most suitable steels for the use of FGD plants because of its excellent corrosion resistance and high strength. The excellent SCC property and strength of duplex stainless steel is due to having the microstructures of 50% austenite and 50% ferrite, and to increasing strength by nitrogen addition, respectively. This type of 22% Cr duplex stainless steel recently produced by POSCO is applied to use for FGD in power plant and chemical carriers.

Table 4. Development Trends for Automotive Exhaust pipes

Name of ports	Backgrounds	Properties Requirements	Materials
Exhaust Manifold (950 ~ 850℃)	• Weight Reduction • High Engine power	• High Temperature oxidation • High Thermal Fatigue	Cast Iron → 429EM, 430J1L
Front pipe (800 ~ 600℃)	• High Engine power • High Temperature of Exhaust Gas	• High Temperature oxidation • High Thermal Fatigue	409L → 429EM, 430J1L
Flexible pipe (650℃ Below)	• Long Life	• Hot Corrosion Resistance • Formal	304 → XM15J
Catalytic Converter (1,100℃ ~ 600℃)	• High Gas Emission Regulation	• High Temperature oxidation	Shell : 409L - 429M Converter : ceramic → 20Cr-5Al
Muffler	• Long Life Guarantee (2 ~ 5 ~ 10 years)	• Condensed Aqueous Corrosion Resistance	Al coated steel → 409L, 436L, Al coated STS

OPERATING ZONE GENERIC FGD SYSTEM ASTM D-33.09



QUANTIFICATION OF OPERATING ZONES

	CHEMISTRY	MECH. ENVIRONMENT (ABRASION LEVEL)	TEMPERATURE
MILD	pH 3-8 H_2SO_4	AGITATED TK WALLS DUCTS THICKENER	AMBIENT TO 150°F
MODERATE	pH 0.1-3 8-13.9 H_2SO_4 0-15%	SPRAY ZONE TANK BOTTOMS	AMBIENT TO 200°F
SEVERE	pH < 0.1 > 13.9 H_2SO_4 15%	HI ENERGY VENTURI IMPINGEMENT TURNING VANES TARGETS	AMBIENT TO 360°F

Source ASTM STP 837

Fig. 3. FGD Process and its corrosion environments

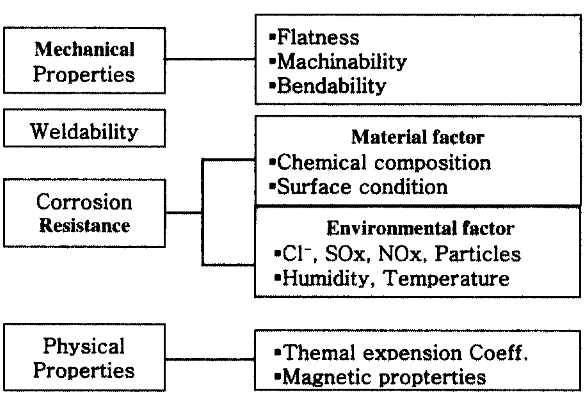


Fig. 4. Requirement of Properties for Architecture Exteriors

4.3 Stainless steels for building exterior and water reservoir

The ministry of construction and transportation in Korea recommended to use the high performance of construction materials with an aim to activating the construction of environmental friendly buildings. Stainless steels are suitable materials for environmental friendly construction because they have excellent corrosion resistance and offer the significant aesthetics. However, the selection of materials for use of buildings in marine areas should be considered as the factors of properties and environments such as Cl, SOx gas in Fig. 4. Recently, high corrosion resistance high-Cr ferritic stainless steels, 445(22Cr-1.5Mo) and 446(26Cr-2Mo) have been developed and adopted in many constructions as maintenance-free roofing material because the use of type 304 stainless steel for roofing material in coastal areas has the rust problems. Typical applications of these steels for roofing of buildings in domestic are the roofing of Young jong-do new international air port terminal and the ASEM convention center. The materials used for water reservoir are stainless steel, painted steel, plastic and cement. Among them, the use of stainless steel for water reservoir has been increased for improvement of cleanliness of water. However, occurrence of rust under different water conditions is one of problems for use of stainless steels. Table 5 shows the classification of corrosion types for the stainless steels.[7] 90% of total corrosion for stainless steels is local corrosion such as SCC, pitting and crevice corrosion. SCC is major corrosion for heat exchange and pipes in the use of high temperature, while pitting corrosion is often observed for water tank in the use of room temperatures. Type 444 ferritic stainless steel instead of austenitic stainless steel has often been used in hot water tank material because austenitic stainless steel is low resistance to stress corrosion cracking (SCC) in hot water environments. Upper part of hot water tanks has a highly corrosive environment due to chlorine ions. Therefore, type 329 duplex or 444 ferritic stainless steels with strong resistance to SCC are adopted for the material of choice for the boilers and hot water tanks.

4.4 Anti-bacterial stainless steels for kitchen ware

As customer are keen interested to the cleanliness and their health, the anti- bacterial materials are increasing for the use of kitchen ware and electrical appliances. The demand for anti-bacterial stainless steels for the use of medical utensil and home appliances is, therefore, expected to be increased rapidly. Anti-bacterial stainless steels containing Cu mainly is required to have good corrosion resistance and formability with maintaining a property of anti-bacteria. The mechanism of anti-bacteria can be explained that Cu on the surface of the stainless steel is reacted with water to Cu ion and then, Cu ions are activated to have anti-bacteria.[8] The bacteria of making a diarrhea is normally increased by ADP as nutrition reacted with HS as catalysis. However, in case that the HS-CoA is reacted with Cu ion in the stainless steel, a number of bacteria has been reduced. Although Cu added 304 stainless steel is used for high formable applications, Cu ions are hard to dissolved in solution by Cr oxide passive film and so, the action of anti-bacteria by Cu ion is not effective. In order to improving the efficiency of anti-bacteria effect on the stainless steel, precipitation of ϵ -Cu phase on the steel surface is need to be accelerated by heat treatment.

5. Summary

Stainless steel has a potential to become a more attractive construction material in the development of a sustainable future. Fig. 5 summarizes the environmentally significant debits and credits for stainless steel. There is a significant market opportunity for stainless steel in a sustainable society. To be able to reap the benefits of this opportunity, we need to make strong efforts to reduce and use of energy and consumables during manufacturing by using the light weight-corrosion resistant features of stainless steel. Typical types of these stainless steels are high nitrogen stainless steel and high chromium ferritic stainless steel. High performance of high nitrogen stainless steel and high purity ferritic stainless steel are needed to develop for expanding their applications in various industries. The relationship between microstructure and properties such as corrosion resistance, strength and formability should be, therefore, more investigated by many metallurgist for clarifying unknown phenomena and mechanisms.

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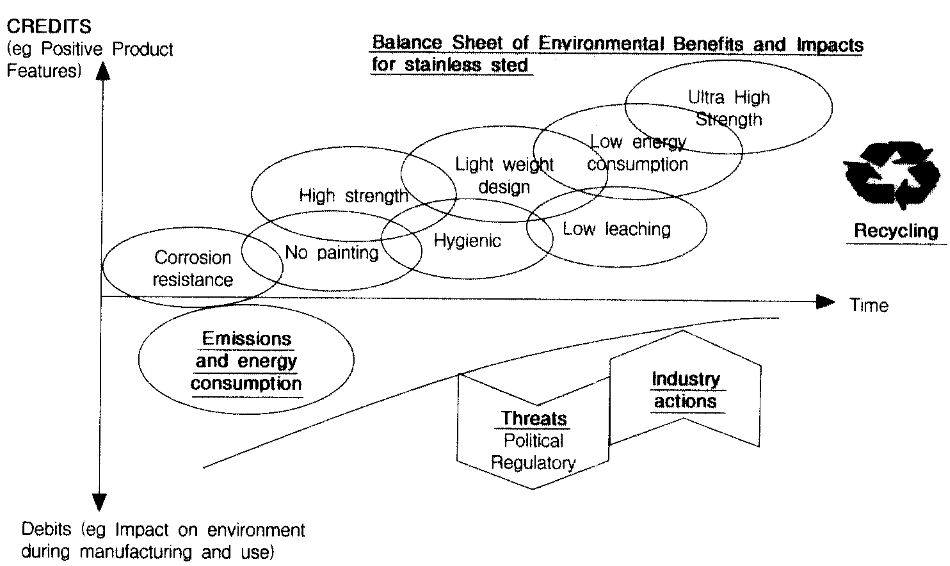

Fig. 5. Balance Sheet of Environmental Benefits and Impacts for Stainless Steel