TOYO ENGINEERING NIPPON STEEL

DP28W™

Super Duplex Stainless Steel for Urea Applications

<Technical Information>

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1. BASIC INFORMATION

Introduction

Toyo Engineering Corporation (TOYO) and Sumitomo Metal Industries (the current Nippon Steel Corporation) developed a new super duplex stainless steel DP28W™ specially for application in urea synthesis section. DP28W™ has been used in commercial urea plants since the early 2000s because of a number of remarkable advantages. DP28W™ shows excellent corrosion resistance even in weld metal and HAZ because of optimized alloying design of base metal and welding material. Furthermore, DP28W™ can be easily passivated with little oxygen concentration in urea-carbamate solution. High mechanical strength is also one of the remarkable advantages of DP28W™. DP28W™ has been successfully applied for urea high pressure equipment for many years and provided great benefits to plant owners.

In conclusion, DP28W™ is the best material for applications in urea synthesis section thanks to excellent corrosion resistance, passivation properties and mechanical properties.

Available Products

DP28W™ is registered as UNS S31808 and approved by ASME Code Case 2496 for ASME Sec.VIII Div.1 and Sec.VIII Div.2. Standard product forms are tube, pipe, plate, forging and bar. Material specifications of these product forms are listed below.

1) Tube: ASTM A789 / ASME SA-789 “Seamless and Welded Ferritic/Austenitic Stainless Steel Tubing for General Service”
2) Pipe: ASTM A790 / ASME SA-790 “Seamless and Welded Ferritic/Austenitic Stainless Steel Pipe”
3) Plate: ASTM A240 / ASME SA-240 “Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General Applications”
4) Forging: ASTM A182 “Forged or Rolled Alloy and Stainless Steel Pipe Flanges, Forged Fittings, and Valves and Parts for High-Temperature Service”
5) Bar: ASTM A479 “Stainless Steel Bars and Shapes for Use in Boilers and Other Pressure Vessels”

Physical Properties

Physical properties of DP28W™ are shown below.

◆ Density: 7860 kg/m^3

◆ Coefficient of thermal expansion

Temperature Range [°C]	**RT-100**	**RT-150**	**RT-200**	**RT-250**	**RT-300**	**RT-350**	**RT-400**
Coefficient [x10^{-6}/°C]	13.7	13.9	14.0	14.2	14.4	14.5	14.7

◆ Thermal conductivity and specific heat

Temperature [°C]	Thermal Conductivity [W/m·K]	Specific Heat [J/kg·K]
20	12.4	458
100	15.0	519
150	16.1	547
200	17.2	570
250	18.2	586
300	19.2	607
350	20.2	627
400	21.7	651

◆ Modulus of elasticity

Temperature Range [°C]	**RT**	**100**	**150**	**200**	**250**	**300**	**350**	**400**
Modulus of Elasticity [GPa]	191	186	183	180	176	172	168	164

Chemical Composition

Chemical composition requirement of DP28W™ is shown in **Table 1-1**. Excellent corrosion resistance is achieved by an optimum alloying design such as high chromium content, addition of tungsten and optimum balance of ferrite-austenite structure. A feature of DP28W™ is that tungsten (W) element is added to increase the corrosion resistance of HAZ during welding thermal cycle, and the phase stability, preventing from precipitation of sigma phase. The well-balanced composition of "Mo + W" is optimized to increase the corrosion resistance of base metal. Corrosion resistance of heat affected zone (HAZ) is deteriorated during welding thermal cycle if chemical composition of "Mo + W" is not optimized.

Table 1-1 Chemical composition requirement of DP28W™

	C	**Si**	**Mn**	**P**	**S**	**Ni**	**Cr**	**Mo**	**N**	**W**
DP28W™	Max. 0.030	Max. 0.50	Max. 1.10	Max. 0.030	Max. 0.010	7.00 -8.20	27.00 -27.90	0.80 -1.20	0.30 -0.40	2.10 -2.50

[wt %]

Mechanical Property

DP28W™ has remarkable mechanical properties. Mechanical properties requirements of DP28W™ as per material specification are shown in **Table 1-2** and typical results of tensile test and hardness test in comparison with other stainless steels are shown in **Table 1-3**. It is indicated that DP28W™ has high mechanical strength compared with other austenitic stainless steels such as 25Cr-22Ni-2Mo, and 316L. It provides great advantages for mechanical

design of equipment.

Typical tensile properties at elevated temperatures and typical impact properties are shown in **Figure 1-1** and **Figure 1-2** respectively. DP28W™ has good impact properties both at room temperature and at low temperature. The ductile - brittle transition temperature of DP28W™ is below -100 °C.

Table 1-2 Mechanical properties requirement of DP28W™

	Yield Strength [MPa]	Tensile Strength [MPa]	Elongation [%]	Hardness
Tube, Pipe (t<10 mm)	≧550	≧800	≧15	≦310 HB ≦32 HRC
Plate, Forging, Bar, Pipe (t≧10 mm)	≧500	≧700	≧15	≦310 HB ≦32 HRC

Table 1-3 Typical mechanical properties of DP28W™ in comparison with other stainless steels

	Yield Strength [MPa]	Tensile Strength [MPa]	Elongation [%]	Hardness [HV]
DP28W™	647	934	42	281
DP12	610	822	42	251
25Cr-22Ni-2Mo	352	676	50	173
316L	234	518	52	144

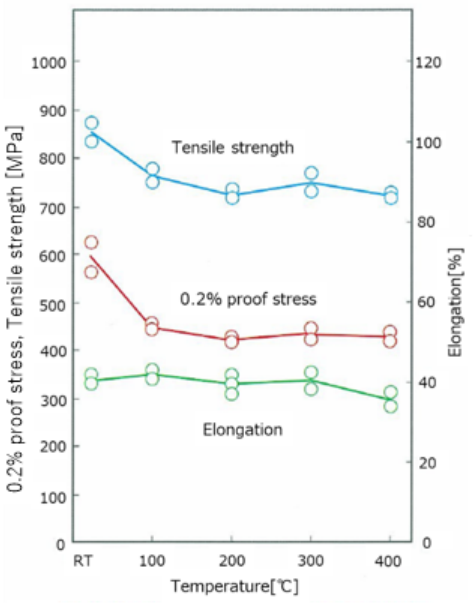


Figure 1-1 Typical tensile properties of DP28W™ at elevated temperatures

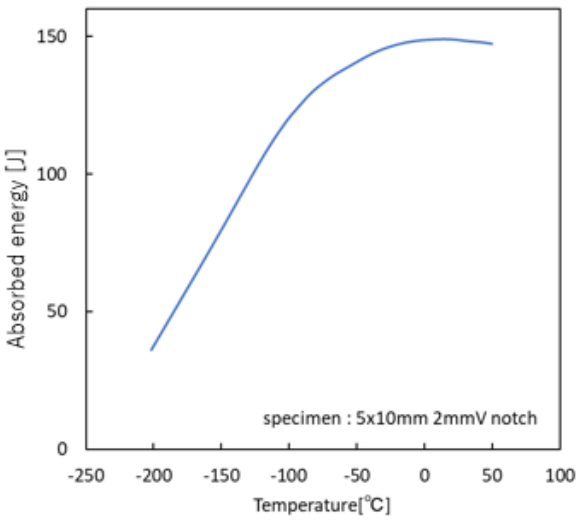


Figure 1-2 Typical impact properties of DP28W™

Microstructure

Typical microstructure of DP28W™ is shown in **Figure 1-3**. DP28W™ has a well-balanced ferrite-austenite duplex structure to improve both corrosion resistance and mechanical properties.

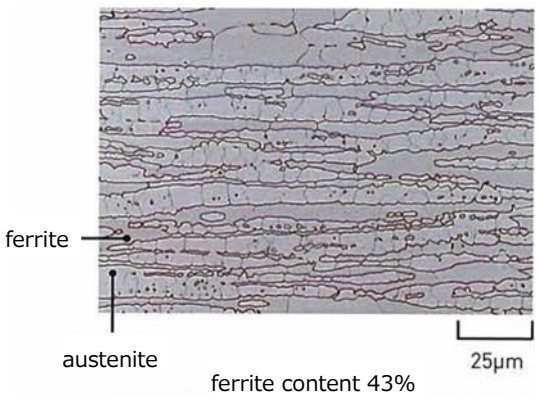


Figure 1-3 Typical microstructure of DP28W™

2. CORROSION PROPERTIES

Corrosion Resistance

Ammonium carbamate (NH_2COONH_4) is an intermediate product formed by the reaction of NH_3 and CO_2 in urea synthesis section. It is highly corrosive to not only carbon steels but also stainless steels at elevated temperatures. Only limited types of stainless steels can be used to deal with the corrosive environment. This paragraph focuses on the corrosion resistance of DP28W™ in urea synthesis section.

◆ Corrosion resistance in boiling nitric acid

Boiling nitric acid test, also known as huey test, is commonly performed to evaluate the corrosion resistance of the materials used in urea plant since the corrosion mode in boiling nitric acid is similar to that in ammonium carbamate solution. This test was carried out on DP28W™ and compared with the results of DP12*1) as shown in **Figure 2-1** and **Figure 2-2**. Both weld joint and all weld metal of DP28W™ exhibit approximately 35% and 50% lower corrosion rate than that of DP12, respectively.

*1) DP12 is a 25Cr duplex stainless steel specialized for urea plant application

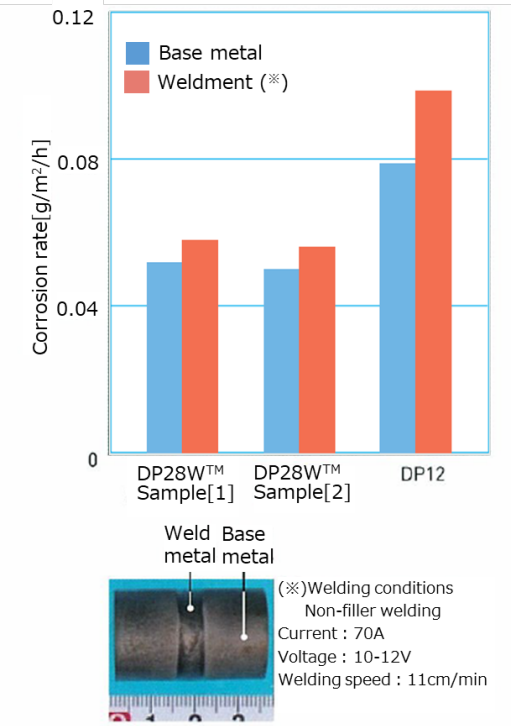


Figure 2-1 Huey test results of weld joint of DP28W™ and DP12

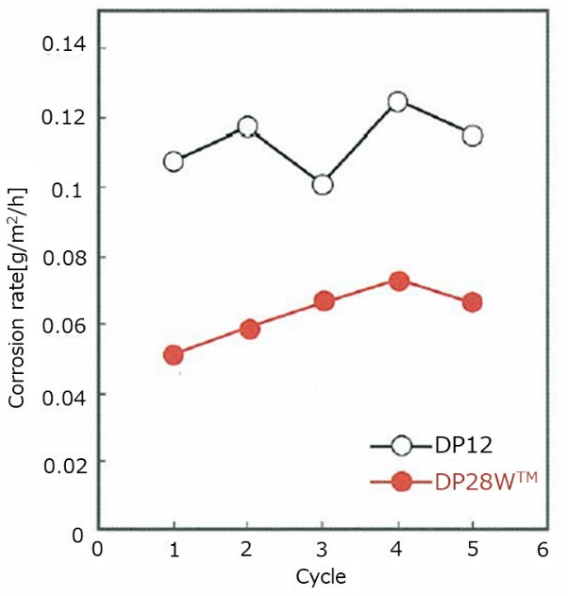


Figure 2-2 Huey test result of all weld metal of DP28W™ and DP12

◆ Corrosion resistance in commercial urea plant

The corrosion resistance of DP28W™ to ammonium carbamate has already been proven in commercial urea plants. **Figure 2-3** shows an example of the test results of DP28W™ compared to DP12 and type 316L Urea Grade (316L-UG) in a commercial urea plant. Corrosion rate refers to the equivalent one compared with DP12. DP28W™ shows a lower corrosion rate than that of DP12 by 20%. This result shows that DP28W™ contributes to longer service life of components in a urea plant than DP12 and type 316L-UG.

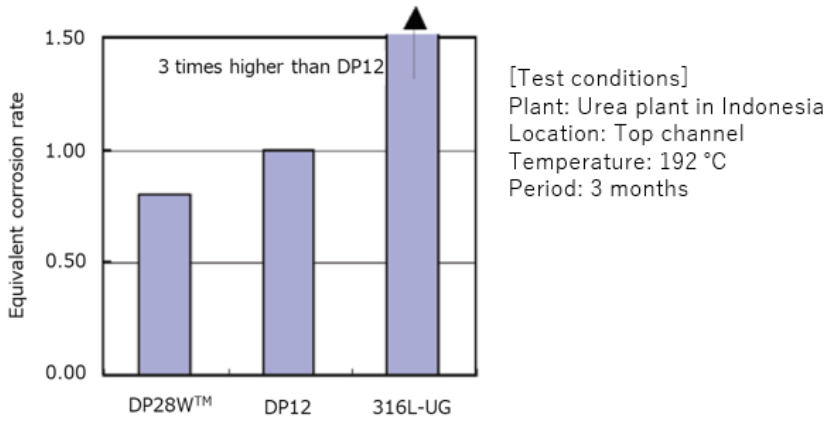


Figure 2-3 Equivalent corrosion rates in a Stripper (CO_2 stripping process)

Another immersion test was carried out in a commercial Reactor of total recycle process. The reactor has operated at 195°C with passivation air concentration equivalent to 550 ppm O_2 in CO_2 feed. Corrosion rates of the base metal of DP28W™ were 0.03 mm/year at the bottom side and 0.04 mm/year at the top side of the reactor, as shown in **Figure 2-4**, which proves that corrosion resistance of DP28W™ is superior to that of other urea grade stainless steels and titanium.

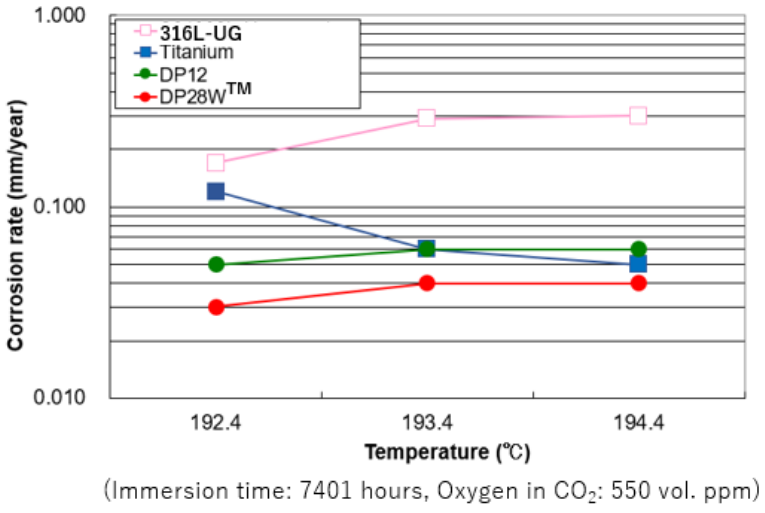
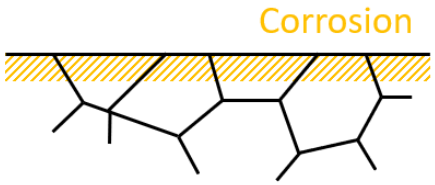
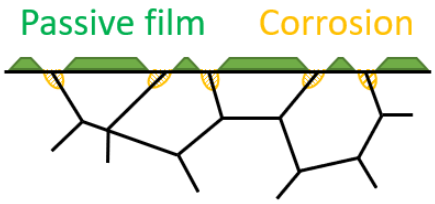


Figure 2-4 Corrosion rates in a Reactor (total recycle process)

Passivation Property

Corrosion mechanism in ammonium carbamate is classified into two types, active corrosion and intergranular corrosion as shown in **Table 2-1**, except erosion which tends to occur on titanium. Active corrosion will happen if no protective oxide film, called as passivation film, is formed on metal surfaces due to insufficient oxygen. If active corrosion happens, corrosion rate would be very high. Active corrosion rate of 316L can be 60 mm/year in urea carbamate solution. In urea synthesis loop, small amount of air is intentionally introduced to maintain a passivation film, which prevents stainless steels exposed to ammonium carbamate solution from active corrosion. Intergranular corrosion (passive corrosion) occurs even though a sufficient amount of oxygen is introduced. However, the corrosion rate with passivation film is quite low. Oxygen concentration required for passivation in ammonium carbamate mainly depends on chemical composition of metals.

Table 2-1 Types of corrosion in urea carbamate solution

Type	Characteristics	Schematic
Active corrosion	Lack of oxygen, high temp. No passivation film High corrosion rate (unacceptable)	
Intergranular corrosion (Passive corrosion)	Sufficient oxygen, high temp. Passive to transpassive potential Generally low corrosion (acceptable)	

DP28W™ is easily passivated with less dissolved oxygen in ammonium carbamate solution. ESCA (Electron Spectroscopy for Chemical Analysis) performed on DP28W™ after exposure to ammonium carbamate solution at high temperatures with little oxygen shows that tungsten oxide is present as a part of the passivation film on its outermost surface. Also, there is metallic nickel which remains insoluble just under the tungsten oxide. Notably, nickel is enriched to approximately two times concentration of original DP28W™ composition. Those results prove that tungsten contained in DP28W™ enhances passivation film in ammonium carbamate solution as shown in **Figure 2-5**. Passivation air, which restricts process efficiency due to lower conversion in the synthesis section and ammonia loss in the recovery section, etc. can be positively reduced using DP28W™. **Figure 2-6** shows minimum required oxygen concentration in CO_2 for passivation of DP28W™ and 316L-UG. Application of DP28W™ to whole ACES21®(*) synthesis section can reduce oxygen requirement in CO_2 to 500 ppm. The reduction of oxygen requirement to 500 ppm drastically reduces inert gas (nitrogen & oxygen supplied as passivation air) in urea process. It contributes to urea process improvement and cost reduction such as reduction in power consumption in CO_2 compressor, increase in CO_2 conversion into urea, reduction in ammonia consumption (less ammonia emission), equipment downsizing and process simplification in synthesis and recovery sections. The reduction in passivation air also contributes to safer operation by minimizing explosive limits in urea process.

(*) ACES21® is advanced technology to realize low investment cost and low energy consumption for urea production.

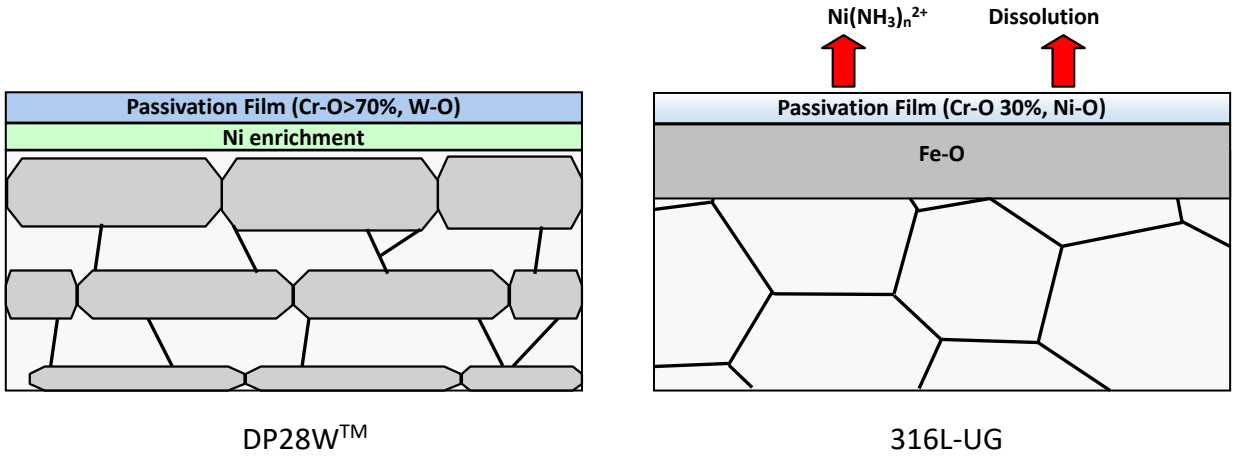


Figure 2-5 Comparison of corrosion behaviour between DP28W™ and 316L-UG in urea carbamate solution with little oxygen

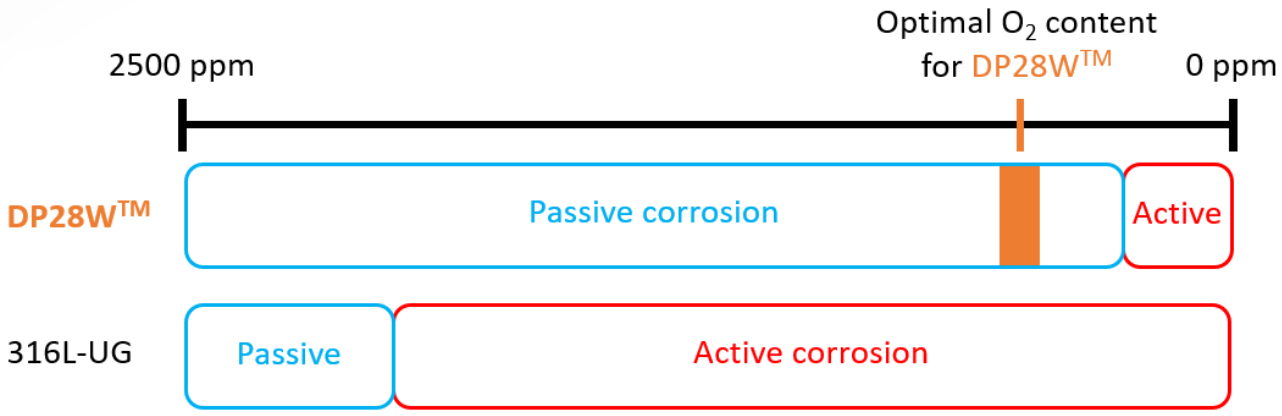


Figure 2-6 Oxygen concentration in feed CO_2 required for passivation

3. WELDING

Weldability

It is reported that general types of duplex stainless steels have sometimes experienced accelerated corrosion in weld metal and HAZ. This accelerated corrosion is caused by unbalanced ferrite/austenite phase ratio and/or precipitations of carbides/intermetallic compounds. DP28W™ has overcome this problem by optimizing chemical composition of base metal and by developing special welding material. Appropriate ferrite-austenite balance is kept even in the HAZ under the favorable addition of austenite formers. Optimized addition of molybdenum and tungsten prevents sigma phase precipitation during thermal cycles. This gives DP28W™ good corrosion resistance in the HAZ. It is important to properly control interpass temperature and heat input to ensure the good corrosion resistance of weld joints. For example, interpass temperature and heat input is typically limited to max. 100°C and max. 25000 J/cm for lining welds respectively.

Welding Consumables

TOYO and welding consumables suppliers have developed specially designed welding consumables for DP28W™. Chemical composition has been suitably designed to exhibit excellent corrosion resistance in urea plant application. Qualified welding consumables are listed in **Table 3-1**.

Table 3-1 Qualified welding consumables of DP28W™

GTAW	ESW (Strip)	SMAW	Supplier
YT- DP28W	NSSW NS-DP28W (STRIP) x NSSW YF-15E (FLUX)	-	NIPPON STEEL WELDING & ENGINEERING CO., LTD.
WEL TIG 28W (Manual) WEL Auto TIG 28W (Auto)	WEL ESS 28W (STRIP) x WEL ESB F-28W (FLUX)	WEL 28W	NIPPON WELDING ROD CO., LTD.

Inner Bore Welding

Inner-bore welding (IBW) is applied to tube-to-tubesheet welding of Vertical Submerged Carbamate Condenser, one of the critical synthesis equipment of TOYO's ACES21®. IBW is a Gas Tungsten Arc Welding (GTAW) without filler metal. DP28W™ has good corrosion resistance even in non-filler weld joints because of the optimized chemical composition of base metal. Appearances of IBW during manufacturing and cross-sectional observation are shown in **Figure 3-1**.

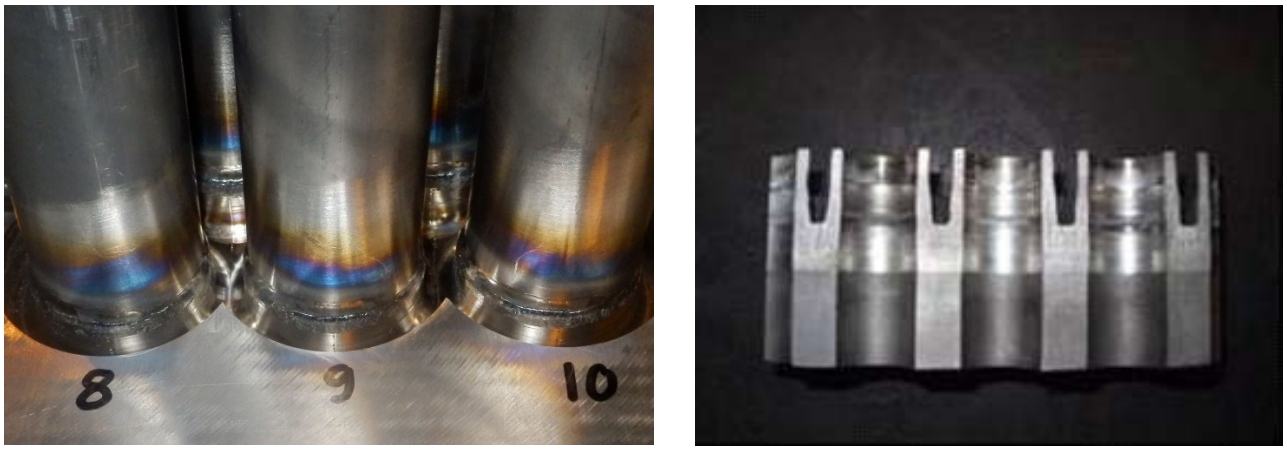


Figure 3-1 Appearance of IBW with DP28W™

4. APPLICATION TO HIGH PRESSURE EQUIPMENT

Introduction

DP28W™ has been used for corrosion resistant material of urea high pressure equipment since the 2000s. Since DP28W™ has excellent corrosion resistance and passivation property, it has been applied to critical parts which are exposed to severely corrosive environment. Several inspection results of commercial urea plants indicate that lining plates, heat exchanger tubes and internal parts made of DP28W™ show no severe corrosion and have still good appearance even in welds after more than 10 years operation.

History of Toyo Urea Plant Material

Figure 4-1 shows history of materials selection in TOYO's urea process. From the 1960s to 1970s, titanium was widely used for urea plant of total recycle process because titanium has high corrosion resistance and good passivation property at low amount of oxygen. However, erosion-corrosion resulted in aggressive thinning occurred on titanium by turbulent flow therefore the maintenance cost and time had been a problem for decades. Since the early 1980s when TOYO developed CO_2 stripping process (former "ACES" Process), TOYO has been mainly using duplex stainless steels for its equipment because duplex stainless steels generally have excellent corrosion resistance and passivation property although austenitic stainless steels such as 316L Urea Grade and 25Cr-22Ni-2Mo have been partially used for the equipment in less corrosive environment. In the 2000s, TOYO and Sumitomo Metal Industries (the current Nippon Steel Corporation) jointly developed duplex stainless steel DP28W™ for urea plant application. DP28W™ possesses excellent corrosion resistance, passivation property and high strength. Because of these advantages, DP28W™ has been used for highly corrosive environment such as tubes of Stripper and Carbamate Condenser for more than a decade.

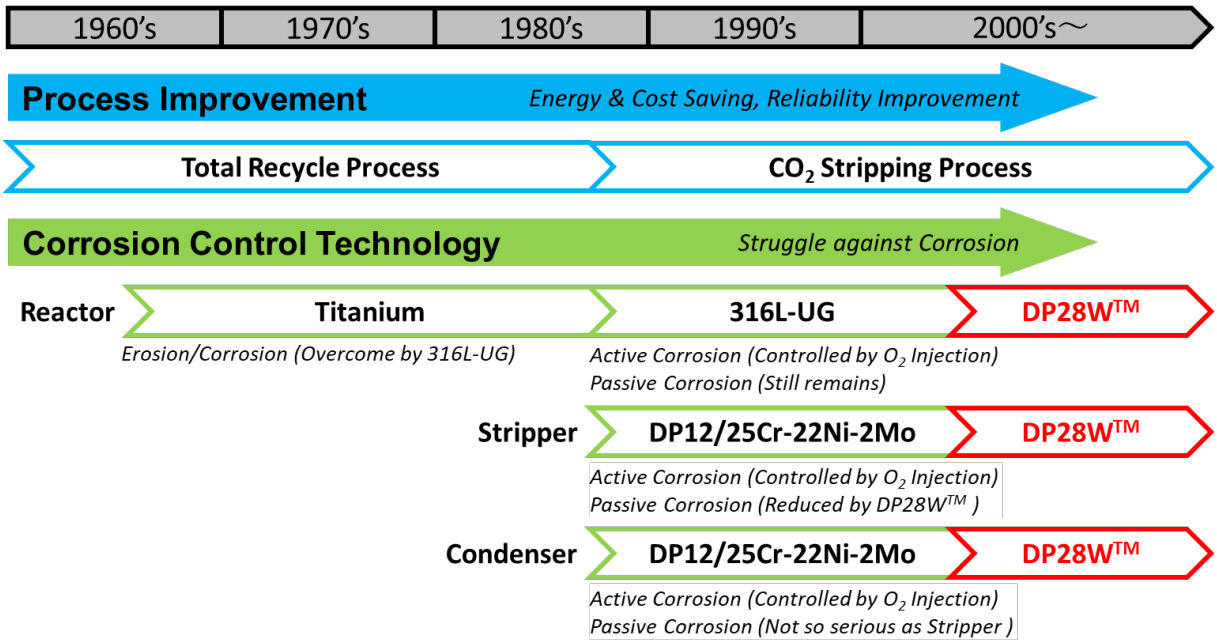


Figure 4-1 History of Material Selection in TOYO's Urea Process

DP28W™ in Urea High Pressure Equipment

It has been more than 10 years since DP28W™ was extensively applied to TOYO urea plants. TOYO specialists have joined turnaround of urea plants and assessed the condition of urea high pressure equipment in synthesis section. The inspection results of DP28W™ applied to a urea plant which has been in operation for more than 10 years are introduced below.

◆ Lining plates

Visual inspection of lining plates shows that no abnormal corrosion such as active corrosion or accelerated corrosion is observed in both base metal and welds as shown in **Figure 4-2**. It is confirmed that corrosion resistance of welds of DP28W™ has been drastically improved compared with conventional duplex stainless steels.

Figure 4-2 Appearances of lining welds of DP28W™

◆ Tubes

DP28W™ has been applied to Stripper/Carbamate Condenser tubes. Inner bore welding (IBW) is applied to Carbamate Condenser of ACES21® process. **Figure 4-3** shows the appearance of U-tube and tube to tubesheet welds of DP28W™. Even after more than 10 years operation, no severe corrosion is observed and no repair work is still required. It has been confirmed that DP28W™ shows excellent corrosion resistance, which enhances maintainability in tube to tubesheet welds.

Tube to tubesheet weld

IBW U-bend tube for Carbamate Condenser

Figure 4-3 Appearances of U-tube and tube to tubesheet welds of DP28W™

DP28W™ for Refurbishment of Aged Urea Equipment

TOYO has constructed a number of urea plants all over the world based on TOYO's proprietary urea technologies since the 1960s. Before shift into CO_2 stripping process in the 1980s, TOYO's primary technology was total recycle process. Many of urea plants with the total recycle process are still under operation in far over 20 years operating life. In those plants, plant owners are trying to minimize production losses caused by unexpected shutdowns due to leakages from lining plates, and to reduce maintenance cost of periodical repair works. In addition, urea plants with ACES CO_2 stripping process (ACES process) also have been operated over 20 years. Under such circumstances, refurbishment of urea high pressure equipment may be necessary for reliable operation. It is important for plant owners to establish a refurbishment strategy of aged urea equipment or internal parts. Advantages of DP28W™ used for refurbishment are discussed below.

◆ Replacement of titanium-lined Reactor

In the original reactor of the total recycle process, titanium lining plate has been used. Due to lower erosion-corrosion resistance of titanium, aggressive thinning of titanium lining plates is observed, therefore extensive repair at annual turnaround is carried out to prevent unexpected shutdown, which led to an increase in maintenance costs. The best solution against the erosion-corrosion of titanium is to replace titanium lining plates with DP28W™ ones. Reactor of the total recycle process is operated under a high temperature with less passivation air, because titanium can be passivated with small amount of oxygen. Therefore, an immersion test in a commercial urea plant of the total

recycle process was conducted to confirm whether DP28W™ can be passivated under this condition. The test result has indicated that DP28W™ has excellent corrosion resistance and passivation property in such a severe operating condition. Consequently, one plant owner of the total recycle process has decided to replace titanium-lined Reactor with a new one lined with DP28W™ (see **Figure 4-4**).

It is notable that the actual corrosion rate of DP28W™ has been far lower than titanium. The new reactor fabricated with DP28W™ lining plates has been operating successfully since it was put into operation in 2006 and the owner has reduced its maintenance cost drastically by 90% as shown in **Figure 4-5**. The maintenance activity during each turnaround has been mainly visual inspection only and there have been no major repairs caused by the material.

The advantages of replacement of Reactor lined with DP28W™ are:

- to be able to operate without design change in operating condition from original one
- to avoid unexpected shutdown because of high reliability in weld joints
- to reduce maintenance cost

Figure 4-4 New Reactor lined with DP28W™

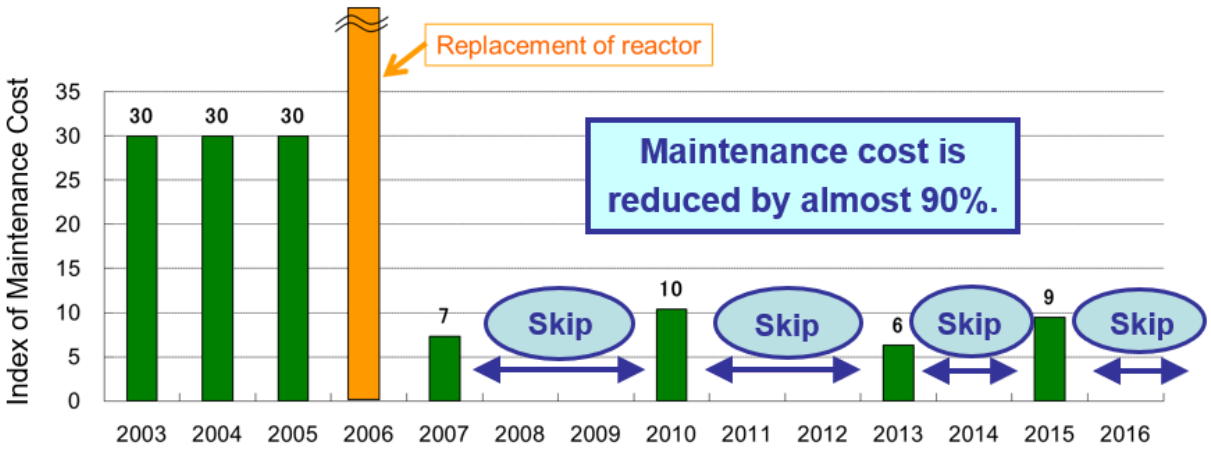


Figure 4-5 Maintenance cost before and after Reactor replacement

◆ Refurbishment of ACES process

Some of urea high pressure equipment composed in ACES process are using DP12 as a corrosion resistance material. After 10-20 years operation, weld joints of DP12 are gradually corroded because corrosion resistance of HAZ and fusion line is lower than base metal. Therefore, plant owners need to consider the necessity of refurbishment or repair of the high pressure equipment for more reliable operation. Application of DP28W™ for the high pressure equipment in the ACES process contributes enhancing the reliability of weld joints as well as base metal because of higher corrosion resistance in both weld joints and base metal. Some plant owners have replaced the existing high pressure equipment with new one using DP28W™ material for components (e.g. lining plate, tube, internal parts) and it has been successfully operated for years.

The advantages of refurbishment with DP28W™ are:

- to extend lifetime because of higher corrosion resistance both in welds and base metal
- to avoid unexpected shutdown because of high reliability in weld joints
- to reduce maintenance cost

APPENDIX 1 TECHNICAL PAPERS ABOUT DP28W™

- Y. Kojima, et al.: ACES21® Process Demonstrated in a World-Scale Urea Plant in China, Nitrogen + Syngas 2005
- E. Nagashima, et al.: Duplex Stainless Steel DP28W™ Enhances Safety and Economy of Urea Plants, Nitrogen + Syngas 2007
- E. Nagashima, et al.: Use of DP28W™ Reduces Passivation Air in Urea Plants, Nitrogen + Syngas 2010
- E. Nagashima, et al.: Use of DP28W™ to Reduce Passivation Air in Urea Plants: Technology Improvement, Nitrogen + Syngas 2011
- D. Ishikawa, et al.: Recent Updates on DP28W™: Metallurgical Study on Welding Joint Properties and Successful Experiences in Commercial Plants, Asian Nitrogen + Syngas 2012
- M. Takahashi, et al.: Lifecycle Solution to Enhance Reliability of Urea Plants, Nitrogen + Syngas 2014