Development of DP28W™ duplex stainless

Special stainless steels are often used in high-pressure sections of today’s urea plants because ammonia carbamate, which is an intermediate product, is very corrosive. Type 316L modified (316L-UG) and UNS S31050 austenitic stainless steels are common grades used in the urea production process. Alternatively, duplex stainless steels containing a high percentage of alloyed chromium have been successfully used in Toyo Engineering Corporation’s urea process. This article deals with DP28W™, a duplex stainless steel with a high chromium and a low nickel content developed jointly by Sumitomo Metal Industries Ltd. and the Toyo Engineering Corporation. Its use has considerable advantages in such plants, namely it not only has high corrosion resistance, which naturally leads to a longer service life of the components, but it also has excellent re-passivation properties, which help to minimize the risk of active corrosion, and high mechanical strength.

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1. Introduction
In general, urea is produced by the chemical reaction of ammonia and carbon dioxide under high pressures and high temperature as shown below:

1st: reaction: \(2NH_3 + CO_2 = NH_4COONH_2\) (ammonia carbamate)
2nd: reaction: \(NH_4COONH_2 = NH_2CONH_2 + H_2O\)

Because ammonia carbamate, which is an intermediate product, is very corrosive, the materials used in the environments where it is present are required to have excellent corrosion resistance to urea-carbamate solution. Austenitic stainless steels such as type 316L modified (316L-UG) and UNS S31050 are the common grades used in the urea production process. However, in the case of TEC (Toyo Engineering Corporation)’s urea plants, duplex (ferrite-austenite) stainless steel with high chromium and low nickel content, “DP12” (UNS S31260) has been used, for more than twenty years, for the stripper and carbamate condenser, due to its excellent corrosion resistance to urea-carbamate solution and to chloride stress corrosion cracking. In addition, it has excellent re-passivation properties and high mechanical strength [1].

This paper describes the properties of DP28W™, focusing on its features and comparing it with conventional stainless steels for urea plants.
2. The alloying design of DP28W™

DP28W™ is designed to form a duplex phase structure as is conventional duplex stainless steel, DP12, which has been successfully used in TEC’s urea plants.

Table 1 shows the chemical requirements of DP28W™ compared to DP12 and conventional austenitic stainless steels used in urea plants. It is well known that increasing the chromium (Cr) content improves the corrosion resistances of stainless steels. To achieve excellent corrosion resistance, the Cr content of DP28W™ is controlled at higher values than those of conventional stainless steels for urea plants.

Lower molybdenum (Mo) and higher tungsten (W) contents are important features of DP28W™. Both elements are very beneficial in improving pitting corrosion resistance and some super duplex stainless steels with a high content of Mo and/or W have been developed for severe chloride containing environments [2]. According to our research, Mo and W are beneficial in improving the corrosion resistance in urea-carbamate solution, too. However, an increase of Mo content results in easier sigma phase precipitation at around 900°C, hence the worry of the HAZ (Heat Affected Zone) becoming brittle or leading to corrosion during the welding thermal cycle. It is known that addition of W does not affect the period before precipitation during heat treatment in super duplex stainless steel [2].

Table 1 shows that nickel (Ni) and nitrogen (N) which form the austenitic phase are controlled at higher values than DP12 to obtain well-balanced two-phase structure. Besides, higher N contributes to improving corrosion resistance in chloride containing environments.

3. Microstructure

The typical microstructure of DP28W™ in a longitudinal cross section is shown in Fig.1. It has a fine, two-phase structure with optimum balance maintained in both the base metal and the weld, which gives excellent corrosion resistance and high mechanical strength.

4. Mechanical properties

Table 2 compares the requirement of the tensile properties at room temperature of DP28W™ with conventional stainless steels for urea plants. In addition, Table 3 shows an example of the mechanical properties of seamless tubes for urea plants. Duplex stainless steels, DP28W™ and DP12 have a very high mechanical strength compared to those of austenitic stainless steels due to their fine two-phase structures.

DP28W™, especially, exhibits the highest mechanical strength among them, and 0.2% proof stress of DP28W™ is twice as high as that of type 316L.

Fig. 2 compares the tensile properties at elevated temperature up to 400°C between DP28W™ and DP12. Also, the tensile properties of DP28W™ are higher than those of DP12 at each temperature. Moreover, the higher mechanical strength of DP28W™ gives better allowance and more advantages in plant design.

Table 3 shows an example of the mechanical properties of seamless tubes for urea plants.

5. Formability

In spite of having a very high mechanical strength, DP28W™ exhibits good formability. Fig. 3 shows the appearance of seamless tubes after a flaring or flattening test. No crack is observed on the tube surface after flaring or flattening to the required size specified by ASTM standard.
6. Corrosion resistances

6.1. Corrosion resistance to boiling nitric acid (Huey test)

The Huey test according to ASTM A262 Practice C is commonly used to evaluate the corrosion resistance of materials for urea plants. This test was carried out on DP28W™ and compared with the results from DP12 as shown in Fig. 4. The base metal of DP28W™ exhibits a 35% lower corrosion rate than that of DP12.

Here, not only the base metal, but also the weld was tested to evaluate the effect of the welding thermal cycle on corrosion resistance. Firstly, a seamless tube of each material was TIG welded under the conditions shown in Fig. 5. Afterwards, the corrosion test sample was prepared from a weld of 35 mm length involving complete HAZ. The corrosion rate of the weld tended to increase by 11% when the base metal was DP28W™, and by 20% in DP12. However, no remarkable corrosion was observed in the welds after the corrosion test as shown in Fig. 6. The DP28W™ weld exhibits a 24% lower corrosion rate than the base metal of DP12 as shown in Fig. 4.

6.2. Corrosion resistance to urea-carbamate solution

The corrosion resistance of DP28W™ to urea-carbamate solution has already been proven in commercial plants. Practical experiences in this type of environment are very positive. Fig. 7 shows an example of the test results of DP28W™ compared to DP12 and type 316L in commercial plants. Here the Y-axis in the diagram refers to the equivalent corrosion rate compared with DP12. DP28W™ shows a lower corrosion rate than that of DP12 by 20%. This corrosion resistance results in a longer service life of components in a urea plant than usual.

6.3. Corrosion resistance to chloride solution

It is known that the pitting corrosion resistance of stainless steel in chloride-containing environments is improved with increasing the PREw value, calculated from the chemical composition as Cr+3.3(Mo+0.5W)+16N [3]. In the case of DP28W™, a higher Cr, W and N contents led to a higher PREw value. In general, duplex stainless steel has a higher resistance to stress corrosion cracking (SCC) in high-chloride containing environments than austenitic stainless steels that have the same Cr contents. Further, the high mechanical strength of DP28W™, is expected to improve SCC resistance.
6.4. Re-passivation properties in urea-carbamate solution

Duplex stainless steel, in particular DP28WM™, has a big advantage in re-passivation properties because of its high chromium and lower nickel content. DP28WM™ has the ability to form the passive layer that gives resistance to active corrosion, under conditions with very little dissolved oxygen. This property contributes to minimize the risk of active corrosion.

7. Weldability

DP28WM™ has good weldability. It has been designed to prevent sigma phase precipitation during the welding thermal cycle and also to keep an optimum ferrite-austenite balance in HAZ. Therefore, the alloying design of DP28WM™ can give excellent corrosion resistance not only in the base metal but also in the weld. Neither preheating nor post-weld heat treatment is necessary. Interpass temperatures are to be controlled below 150o. Matching filler metals are now being developed and will be available in the near future.

8. Standard

DP28WM™ has been registered as ASTM, UNS Design S32808 and ASME Code Case 2496.

9. Production experience

DP28WM™ has been applied mainly in the internal sections of TEC’s urea plants since 2002. It has shown an excellent performance. In 2004, it was nominated as one of the candidate materials to be used for a synthesis reactor in a plant in Japan, which had been considered to be replaced. The owner had the intention to operate the new reactor under the same operating condition as the existing one, which was fabricated with titanium. After a one year immersion test into the reactor, DP28WM™ was selected because it showed the best result among candidate materials. The corrosion rate is far lower than titanium. The Reactor which is fabricated with DP28WM™ has started into operation successfully since 2006 under the same operating condition as the case for titanium.

10. Conclusion

- DP28WM™ is shown to have excellent corrosion resistance to urea-carbamate solution, which is achieved by its two-phase structure and high Cr and W contents.
- Tungsten is selected as an additive to improve the corrosion resistance and to prevent σ phase precipitation after welding as substitution of Mo.
- DP28WM™ has very high mechanical strength and good formability, which give more advantages in plant design.
- The corrosion resistance of DP28WM™ is proven not only in the laboratory but also in a commercial plant, which will contribute to a longer service life of the components.
- The excellent re-passivation properties of DP28WM™ contributes to minimize the risk of active corrosion.

References