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Development of Chinese duplex stainless steel in recent years

Zhi-gang Song*, Han Feng, Shao-mei Hu

Institute for Special Steels, Central Iron and Steel Research Institute, Beijing 100081, China

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ABSTRACT

The development in research, production, applications, and national standards of Chinese duplex stainless steel (DSS) in recent years was introduced in light of the worldwide development in the field of DSS. The results showed that the output of Chinese DSS increased greatly, and at the same time its grade gradually evolved into a collaborative developing series including the main grade type 2205 and other DSS types in recent years. Economical DSS and super DSS underwent rapid development, especially after 2010. In recent years, the application of Chinese DSS has been expanded further not only in traditional application areas such as the petrochemical industry, but also in diverse new fields such as oil and gas transportation, chemical tanker manufacturing, nuclear power plants, and construction. Moreover, due to the increase in output and improvement in quality, as well as applications in Chinese projects, Chinese DSS has also been exported to the Middle East, Eastern Europe, and other regions.

1. Characteristics and Development of Duplex Stainless Steel

Duplex stainless steel (DSS), which has the desired microstructure characteristic of the equal amount of two phases and the high alloy contents such as Cr, Mo and N, shows excellent performance of high strength and good corrosion resistance. The yield strength of DSS is approximately twice that of austenitic stainless steel, and it shows preponderant resistance to pitting corrosion and stress corrosion.

Since the first patent was filed in France in 1935, duplex stainless steel has underwent tremendous development over a span of three generations during the 20th century. The first generation of DSS is represented by the 329 steel, which was developed in the United States in 1940s, comprises high quantities of Cr and Mo, and has a good local corrosion resistance performance. 3RE60 developed in Sweden in the mid-1960s is an ultra-low carbon type DSS. Since the 1970s, the development of secondary refining technology and discovery of the importance of N in maintaining phase equilibrium and improving corrosion resistance constitute a milestone in the development of DSS. The second generation of DSS (ultra-low carbon, N-addition) was developed, among which 2205 was a typical grade. Based on the second generation, by further increasing the alloy contents and pitting resistance equivalent numbers (PREN) value, which is a measurement of the corrosion resistance of various types of stainless steel, the third generation of DSS (super DSS) was developed in the late 1980s. The PREN value of super DSS was greater than 40, and its typical grades included SAF2507, UR52N+, ZERON100, etc. Because of its higher contents of Cr, Ni, Mo, and N, as well as better phase balance, this type of DSS displayed better corrosion resistance and higher strength.

In the 21st century, hyper DSS and economical DSS became two important trends in the development of DSS. Due to its higher alloy content, hyper DSS possessed higher strength and better corrosion resistance[1]. For example, the PREN value of SAF 2707 developed by SANDVIK was 49 which enabled its application in rigorous chlorine-rich environment[2]. Economical DSS contained high Mn and N, low Ni, and no or only a small amount of Mo. SAF2304 developed in the 1980s, and AL2303, LDX2101, and LDX2404 developed after 2000 are all economical grade DSSs. 2101 gained obvious development and application focus because it contains low Ni content, about 5% Mn and 0.2%N, and a small amount of Mo content. The low production cost made economical DSS a strong competitor to

* Corresponding author. Prof., Ph.D.; Tel.: +86-10-62182495.
E-mail address: *songzhigang@nercast.com* (*Z.G. Song*).

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the austenitic stainless steel such as 304, 316, and even a candidate for 2205. In the meantime, economical DSS also became an important developing trend and growth point for DSS[3].

DSS alloy design emphasizes a balance between the austenite and ferrite both in ratio and performance. During the development of DSS, N alloying was one of the important approaches for DSS alloy design, which played a crucial role in balancing the ratio and performance of the two phases, improving the mechanical and corrosion resistance properties. N plays a significant role in promoting the strength and stability of austenite and in expanding the austenite phase area. N mainly dissolves in austenite, thereby increasing austenite content and maintaining phase equilibrium. More importantly, N dissolved in austenite phase increases the PREN value of the austenite phase and strengthens the austenite phase. This improves the corrosion resistance and strength of austenite phase and balances it with the ferrite phase rich in Cr and Mo. Thus, the overall mechanical and corrosion resistance properties of DSS are enhanced. Due to the development of N alloying, it was possible to increase and match the contents of Cr, Mo, and N simultaneously and to design DSS which has a balanced ratio and performance of the two phases, as well as higher corrosion resistance and strength[4,5].

After more than 80 years of development, the annual output of DSS production accounts for less than 1% of the overall stainless steel output. DSS has become an indispensable steel class that is as important as martensitic, ferritic, and austenitic stainless steels.

Moreover, DSS has unique microstructure characteristics of the same amount of austenite and ferrite phases, which requires reasonable element matching for austenite and ferrite forming elements in composition design, and may face the difficulties in the prevention of harmful phase formation, hot working and smelting resulting from over high alloying. In view of the three factors above, the DSS has developed to a relatively complete series today, which includes three generations of DSS, economical DSS, and hyper DSS. In developed countries in Europe and America, economical DSS and hyper DSS have achieved faster development, and have been applied more widely. Besides chemical and petrochemical industry, DSS has been successfully applied in marine, onshore, industrial, costal, urban, inland, etc.

Early in the 1970s, DSS was studied and developed in China, and the development focused on N-containing DSS. The development of Chinese DSS reflected that of international DSS and continuously narrowed the gap between them.

After 2000, the output of Chinese DSS increased gradually, and research, production, application, and national standard of DSS witnessed greater thrust in China.

2. Progress of Chinese DSS Research in Recent Years

Due to its high alloy content and microstructure characteristic of two phases, DSS is difficult to produce and achieve microstructure control. With the developing trend of DSS, attention on DSS research in China has increased continuously in recent years. With deepening the understanding of DSS, the direction of DSS researchers in China changed gradually. Significant progress in researches focused on N alloying control, hot ductility, and harmful precipitation phase has been made in recent years.

2.1. N alloying and its control of DSS

Since the importance of N in maintaining phase balance and improving the corrosion resistance as well as mechanical properties was first demonstrated in the 1970s, subsequently developed DSS all over the world contained N. N alloying and its precise control became an important factor in DSS development and production. Considering the development of stainless steel containing N in China, the size and amount of DSS production, as well as actual equipment and process of related enterprises, the smelting means of DSS in China included VIM (Vacuum Induction Melting), AIM (Air Induction Melting), EAF (Electric Arc Furnace)+AOD (Argon Oxygen Decarburization), or EAF+VOD (Vacuum Oxygen Decarburization). For normal and mass DSS production, the main smelting means used was EAF+AOD.

There are two N alloying approaches involved in the smelting methods: adding ferroalloy containing N and blowing N.

In the mass production of DSS, the N alloying as well as its control during the AOD refining process is particularly important. The N alloying was conducted by blowing nitrogen gas during the AOD process, which could be divided into two subprocesses comprising dissolution and the removal of nitrogen. During the early stage of AOD smelting, oxygen and nitrogen blowing was performed for complete saturation and dissolution of nitrogen. During the later stage of AOD smelting, based on the argon bubble refining theory, nitrogen gas was replaced by argon gas to complete the removal process of nitrogen. Nitrogen content was precisely controlled by controlling the flow rate and blowing accurate amount of argon gas[6-8].

2.1.1. Dissolution of nitrogen

During the early stage of AOD blowing, different proportions of nitrogen and oxygen were used. With the decrease in decarburization rate, the atom percent of