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Influence of Cr_{eq}/Ni_{eq} on pitting corrosion resistance and mechanical properties of UNS S32304 duplex stainless steel welded joints

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ABSTRACT

Pitting corrosion resistance and mechanical properties of 2304 duplex stainless steel with different Cr_{eq}/Ni_{eq} values after plasma-arc welding and welding thermal simulation were systematically studied. The results showed that the lower the Cr_{eq}/Ni_{eq} value in the experimental range, the better the microstructure after welding or welding thermal cycle. High pitting resistance equivalent number in the chemical composition brought in low weight loss rate and high critical pitting temperature for base metal. Furthermore, as the Cr_{eq}/Ni_{eq} value decreased, the degradation of pitting corrosion resistance after welding thermal cycle reduced.

1. Introduction

The success of modern duplex stainless steels (DSSs) is due to their weldability as well as their excellent mechanical properties and corrosion resistance. Compared with the earlier generation of duplex steels, weldability has been improved appreciably, by introduction of nitrogen as an alloying element and vacuum and argon oxygen decarburization (VOD and AOD) processes. The properties of DSS are dependent on the ferrite (α)-austenite (γ) phase ratio which in the base metal is designed to be approximately 1:1. Moreover, the precipitation of secondary phases including intermetallic phase (σ, χ) and nonmetallic compounds ($Cr_{23}C_6$, Cr_2N) has shown a detrimental influence on the properties especially the pitting corrosion resistance and toughness [1–6].

In the heat-affected zone (HAZ) and fusion zone (FZ), the microstructure strongly depends on thermal cycle and chemical composition. For DSS, among the parameters of welding thermal cycle, heat input is the most important one which determines the cooling rate of welding process directly. The lower the heat input, the faster the cooling rate. Low heat input brings on an extremely unbalance microstructure with excess of ferrite phase and also results in plenty of chromium nitrides precipitating in the interior of the ferrite grains or the interface of austenite and ferrite grains. Generally, a relatively high heat input is beneficial to the microstructure of welded joints with more austenite reformation during cooling stage and without chromium nitrides. However, intermetallic phases are easy to form when the cooling rate is too slow, especially for the high alloyed super duplex stainless steel. Therefore, it must be borne in mind that an upper limit to heat input is set by the prevention of intermetallic phase precipitation, and this risk increase with increased alloy element level [7–13].

As for the influence of chemical composition on welding of duplex stainless steel, a great number of investigations have carried out on the effect of alloying elements, especially the most effective nitrogen [14–23]. Ogawa and Koseki [24] had pointed out that both nitrogen and nickel could increase austenite content of the weld, but N increase the pitting corrosion resistance while Ni degrades the pitting corrosion resistance. Muthupandi and his coworkers [25,26] had investigated the influence of N and Ni on microstructure and mechanical properties of 2205 weld metals and the results that the addition of Ni and N could significantly improve the microstructure, phase balance and impact toughness, but it seems to have no appreciable influence on the hardness of the weld zone were obtained. Liou et al. [27,28] have carried out meaningful researches to prove the beneficial influence of nitrogen on microstructure and corrosion resistance such as pitting corrosion and stress corrosion cracking in simulated heat-affected zones of DSS. All these studies are focused on the influence of single alloying element. However, a more important parameter – the ratio of chromium equivalents (Cr_{eq}) and nickel equivalents (Ni_{eq}), which present the ability of stabilizing the ferrite and austenite structure from the angle of alloying elements, was less investigated. DSS contains ferrite stabilizing elements like Cr, Mo, Si and W as well as austenite stabilizing elements like Ni, Mn, C, N and Cu. Long and DeLong

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Table 1
Chemical composition of a series of 2304 duplex stainless steels.

Materials	Concentration of alloying elements (wt.%)										Cr_{eq}	Ni_{eq}	Cr_{eq}/Ni_{eq}	PREN
	Cr	Ni	Mo	N	Mn	C	Si	S	P	Cu				
2304-1	23.42	4.03	0.31	0.13	1.56	0.021	0.40	0.004	0.010	0.29	23.73	7.44	3.19	27.04
2304-2	23.54	4.60	0.31	0.13	1.67	0.011	0.41	0.005	0.010	0.31	23.85	7.66	3.11	27.16
2304-3	23.01	5.35	0.30	0.12	1.64	0.015	0.36	0.003	0.009	0.30	23.31	8.35	2.79	26.40
2304-4	23.66	4.87	0.71	0.16	1.49	0.030	0.37	0.005	0.007	0.31	24.37	9.20	2.65	29.20

Cr_{eq} = %Cr + %Mo + 0.7%Nb [14]. Ni_{eq} = %Ni + 35%C + 20%N + 0.25%Cu [14]. PREN = %Cr + 3.3%Mo + 20%N [4,5].

[29,30] suggested the effect of the elements on Cr_{eq} and Ni_{eq} with the following equations:

$$Cr_{eq} = \text{wt.\%Cr} + \text{wt.\%Mo} + 1.5\ \text{wt.\%Si} + 0.5\ \text{wt.\%Nb} \quad (1)$$

$$Ni_{eq} = \text{wt.\%Ni} + 0.5\ \text{wt.\%Mn} + 30(\text{wt.\%N} + \text{wt.\%C}) \quad (2)$$

In this paper the influence of Cr_{eq}/Ni_{eq} on corrosion resistance and mechanical properties of the 2304 welded joint including the practical plasma-arc welded (PAW) joint and simulated high temperature HAZ has been systematically studied. A series of 2304 duplex stainless steel base metal with different Cr_{eq}/Ni_{eq} values has been chosen as the studying object and the chemical composition of 2304 duplex stainless steel for the application was optimized through this study.

2. Experimental procedures

2.1. Materials

Four kinds of 2304 duplex stainless steels with different Cr_{eq}/Ni_{eq} value from 2.65 to 3.19, also with different pitting resistance equivalent number (PREN = %Cr + 3.3%Mo + 20%N), were investigated in this paper, and their composition and other important information were shown in Table 1. Here the Cr_{eq} and Ni_{eq} were calculated used the universe formulas according to WRC 1992 Constitution Diagram [17], which is more reasonable than the former formulas obtained by Long and DeLong in 1973 [29,30].

$$Cr_{eq} = \%Cr + \%Mo + 0.7\%Nb \quad (3)$$

$$Ni_{eq} = \%Ni + 35\%C + 20\%N + 0.25\%Cu \quad (4)$$

PREN is an experienced formula widely used to evaluate the pitting corrosion resistance of austenitic stainless steels and duplex stainless steels from the angle of chemical composition. A lot of alloying elements have the influence on the pitting corrosion resistance including beneficial effect and harmful effect. For example, Cr, Mo, N, Cu, etc. have the beneficial effect while Mn, S, P, etc. have the harmful effect. There is no universe formula for calculation of PREN. As we known that PREN = %Cr + 3.3%Mo + x%N only considering the beneficial effect of the major three element Cr, Mo and N, while the nitrogen factor x is in range of 16–30. Generally, x is chosen among 16, 20 and 30. A middle value 20 is the most widely employed to calculate the PREN value during the study for duplex stainless steels [4,5]. They were melted in a 50 kg vacuum furnace and then cast as a single square ingot. After removing the oxide skin, the ingot was forged into square bloom at the temperature ranging from 900 °C to 1200 °C and divided into several blooms with a dimension of 150 mm × 100 mm × 42 mm. The blooms were reheated at 1200 °C for 1 h and hot-rolled, using a laboratory hot-rolling mill, into 12 mm thick plates. After hot-rolling, DSS 2304 was solution-annealed at high temperature for 12 min and quenched in water. Due to the different chemical compositions, the annealing temperatures for 2304-1, 2304-2, 2304-3, 2304-4 were 1020 °C, 1040 °C, 1060 °C, 1100 °C respectively.

2.2. Welding and thermal simulation

Welding was performed using autogenous PAW without filler metal, and the corresponding parameters were listed in Table 2. Welding thermal cycle simulation was carried on DSS 2304 base metal through the Gleebe 3800 thermal–mechanical simulator. Fig. 1 shows the relationship between the temperature and the elapsed time registered by thermocouple during welding simulations. The rising rate was 350 °C/s; peak temperature was 1350 °C; holding time at peak temperature was 3 s; heat input was 1.5 kJ/mm.

2.3. Characterization

To observe microstructure, each specimen was electrochemically etched by 30%KOH solution at 2 V for 15 s. The ferrite volume fraction of the base metal, the welded joint, and the simulated high temperature HAZ was measured by Helmut Fischer MP3 Feritscope. The microstructure and the morphologies after pitting corrosion were observed by both optical microscope (OM) and scanning electron microscope (SEM).

The mechanical properties such as yield strength, tensile strength, and elongation of the PAW joints were measured while the impact toughness of the simulated HAZ specimens was charac-

Table 2
Welding conditions applied for PAW of duplex stainless steel DSS 2304.

Welding current (A)	165
Welding voltage (V)	50
Orifice gas nozzle diameter (mm)	3.2
Welding speed (cm/min)	27
Nozzle height (mm)	5–6
Plasma gas flow: Ar (L/min)	15
Shielding gas flow: Ar (L/min)	15

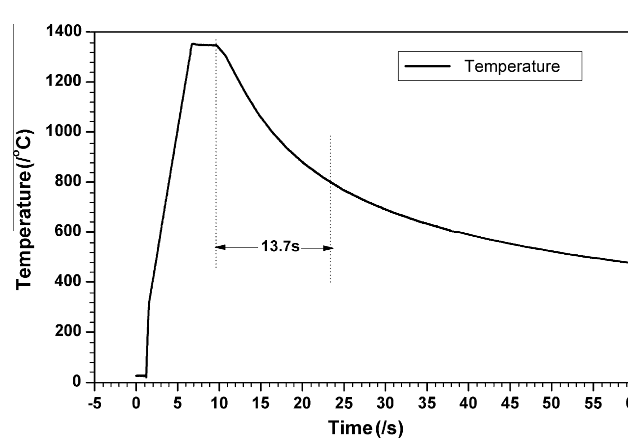

Fig. 1. Simulated welding thermal cycle curve of high temperature HAZ by thermo-mechanical simulator Gleebe 3800.