

Progress in weldability research of super and hyper duplex stainless steels

Aiguo Liu*

School of Materials Science and Engineering, Shenyang Ligong University, Shenyang 110159, China

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Abstract

Super duplex stainless steels (SDSSs) and hyper duplex stainless steels (HDSSs), with more alloying elements content, are more corrosion resistant than the standard grades. Progresses of research works on weldability of SDSSs and HDSSs in recent years are reviewed in this paper. If proper heat input is provided, SDSSs and HDSSs can be welded with most fusion welding processes, while tungsten inert gas welding is the most popular process. SDSSs and HDSSs are more prone to secondary phases precipitation than the standard and lean grades, and heat input for SDSSs and HDSSs welding is restricted to a smaller range. Matching filler materials are usually recommended for SDSSs and HDSSs welding, rather than Ni-riched ones for standard and lean grades. Nitrogen addition in shielding gas is always beneficial. Post weld heat treatment with slow cooling rate will be harmful. Hot cracking tendency of SDSSs and HDSSs joints is not high, but sometimes they can suffer from hydrogen induced stress cracking.

Keywords Weldability, Super duplex stainless steel, Hyper duplex stainless steel, Phases balance, Secondary phase, Cracking

1 Introduction

Duplex stainless steels (DSSs) were invented in the 1930s. Since the 1980s, a lot of research works have been done to improve corrosion property of DSSs by increasing the content of alloying elements or adding new alloying elements [1]. The modern DSSs can be divided into four groups, the lean, the standard, the super and the hyper DSSs. The super and hyper DSSs are DSSs with higher Cr, Ni, Mo, and N contents and corresponding pitting resistance equivalent number (PREN) [2]. The PREN is a measure of a material's resistance to pitting corrosion. It can be determined from the material's primary alloying element composition such as Cr, Mo, N, and W, which significantly affect pitting corrosion resistance of stainless steels. The most commonly used equations are shown in Eqs. (1)–(3) [1, 3–4].

$$\text{PREN} = \text{Cr} + 3.3\text{Mo} + 16\text{N} \quad (1)$$

$$\text{PREN}_w = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 16\text{N} \quad (2)$$

$$\text{PREN}_w = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 30\text{N} \quad (3)$$

The formula of PREN_w is used for stainless steels that contain W [1]. While, Eq. (2) is claimed valid for austenitic stainless steels (ASSs) and the austenitic phase in DSSs, but not for DSSs. The PREN coefficient for N content in DSSs should be roughly doubled, as shown in Eq. (3) [4].

The super duplex stainless steels (SDSSs) were developed to compete super ASSs and nickel base alloys in very aggressive environments, such as chloride-containing acids. The hyper duplex stainless steels (HDSSs) were developed as a complement to SDSSs with increased strength for use in even more aggressive conditions, such as in “sour” crude [1], hot seawater, acidic chloride solutions and organic acids [2]. Demands of these aggressive environments and high costs of high nickel materials promote development of SDSSs, HDSSs and associated manufacturing processes, including welding, to meet these challenging requirements. Progress in weldability research of SDSSs and HDSSs is re-

* **Corresponding author:** Aiguo Liu (1969–), Ph.D, Professor. Mainly engaged in new welding processes. E-mail: aiguoliu@tom.com

viewed in this paper.

2 Welding processes for SDSSs and HDSSs

Typical SDSSs and HDSSs are shown in Table 1 [5]. DSSs can be welded using most welding processes [6]. Almost all these welding processes, like tungsten inert gas welding (TIG) [4, 7–21], metal inert/active gas welding

(MIG/MAG) [20, 22], flux-cored arc welding (FCAW) [9, 20, 23–26], shielded metal arc welding (SMAW) [1, 27], submerged arc welding (SAW) [23], laser beam welding (LBW) [28–30], friction stir welding (FSW) [31–33], have been used in welding of SDSSs and HDSSs. TIG, MIG/MAG, FCAW, SMAW, and SAW are all recommended processes for SDSSs welding, while for HDSSs welding, only TIG and SAW are recommended [5].

Table 1 Typical SDSSs and HDSSs [5]

Steels	UNS No.	EN No.	Common designation	Main alloying elements						
				Cr	Ni	Mo	N	Cu	W	Co
SDSS	S32520	1.450 7	2507Cu	25	7	3.5	0.25	1.5		
	S32750	1.441 0	2507	25	7	4	0.27			
	S32760	1.450 1	Zeron 100	25.4	6.9	3.8	0.27	0.7	0.7	
	S32808		DP28W	27.5	7.7	1	0.35		2	
	S32906	1.447 7	SAF2906	29	7	2.3	0.35			
	S39274		DP3W	25	7	3.2	0.26	0.5	2	
	S39277		AF918	25.5	7.3	3.8	0.26	1.7	0.9	
HDSS	S32707		SAF 2707 HD	27	6.5	4.8	0.4			1
	S33207		SAF 3207 HD	32	7	3.5	0.5			

3 Weldability of SDSSs and HDSSs

3.1 Precipitation of secondary phases

SDSSs and HDSSs are more corrosion resistant than standard DSSs, for the content of alloying elements, like Cr, Mo, N, and W in them is high. As a consequence of high alloying element contents, it is much easier for secondary phases to precipitate in SDSSs and HDSSs than in lean and standard DSSs. Among all the secondary phases found in DSSs, σ phase, χ phase, chromium nitrides Cr_2N and CrN , and secondary austenite γ_2 , are the most important ones. Fig. 1 shows the effect of individual alloying elements on a time temperature transformation (TTT) diagram of DSSs [1]. With increase of alloying elements, boundary curve of precipitation of these secondary phases expands to shorter time and higher temperature. Second phases in SDSSs and HDSSs will precipitate in larger temperature and cooling rate ranges than in lean and standard grades of DSSs. Due to the high alloying elements content, the HDSSs are more sensitive to secondary phase precipitation than the SDSSs [2].

Fig. 2 shows a section of the isopleth diagram of a HDSS as a function of temperature based on CALPHAD equilibrium calculation, where nitrogen content is 0.4% [34]. The phases volumetric fraction is shown in Fig. 2 as a function of temperature. The σ phase begins to precip-

itate when the temperature is below 1 105 °C, and the fraction of it increases rapidly with temperature decrease, reaches 40% at 800 °C. The χ phase begins to precipitate from 800 °C, and its volume fraction reaches a maximum of 19% at 550 °C at the expense of the σ phase. Cr_2N can precipitate from over 1 000 °C.

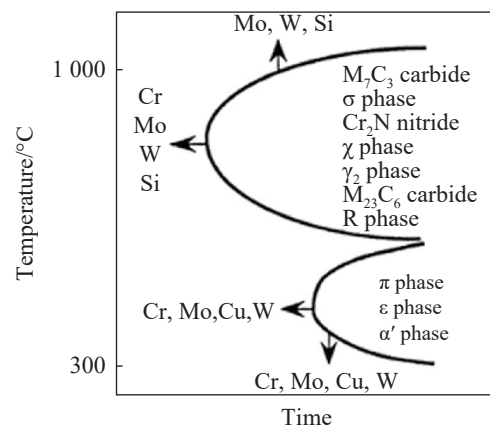


Fig. 1 Effect of alloying elements on shape and position of the TTT diagram of duplex stainless steels [1]

3.1.1 Precipitation of σ phase

σ phase is the predominant precipitate in the highly alloyed DSS. It can be seen in Fig. 2 that, the σ phase is stable below 1 105 °C, and its volume fraction increases

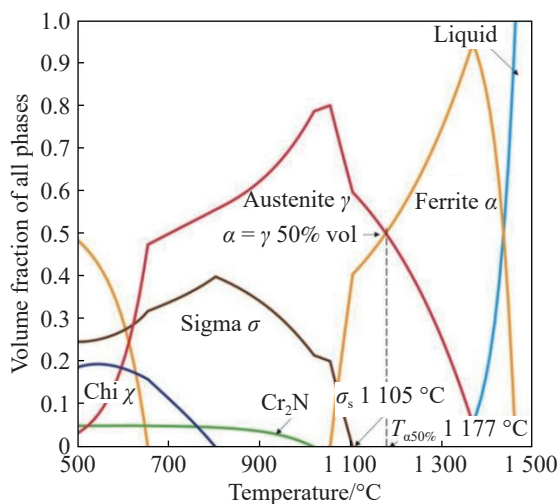


Fig. 2 CALPHAD equilibrium calculation (TCFE11 database), phases volumetric fraction as a function of temperature [34]

rapidly with temperature reduction, reaching maximum of 40% at 800 °C. Constant cooling rate conditions calculated using this CALPHAD model suggest a minimum cooling rate of 4 °C/s as the threshold for the σ phase to form [34].

σ phase is a hard intermetallic phase enriched in Cr and Mo with a complex tetragonal structure [35], which has very low dislocation mobility, reducing the toughness [34]. As shown in Fig. 1, the quickest σ phase precipitation rate occurs between 800 and 900 °C. Elements like Cr, Mo, W, and Si promote precipitation of the σ phase. With increasing the content of Cr, Mo, W, and Si, the driving force for σ formation increases, and the curve shifts to a higher temperature, affecting the processing of DSSs [36]. Lean DSSs are very safe in terms of σ formation during welding, while SDSSs and HDSSs are very much prone to σ formation. The total volume fraction of σ phase increases with increase of Cr and Mo concentration, while Ni reduces the total amount of σ precipitation [3].

σ phase formation as a function of temperature and time has been described using the Johnson-Mehl-Avrami-Kolmogorov kinetic calculation equation, as shown in Eq. (4) [34].

$$f = 1 - e^{(-kt^n)} \quad (4)$$

where f is the transformed σ volume fraction ($0 < f < 1$), t is the transformation time, n is the Avrami's exponent related to the rate of nucleation and growth, and k is related to the energy barrier for the σ phase formation.

High nucleation sites of the σ phase are ferrite/ferrite

boundaries and ferrite/austenite boundaries with high interfacial energy [3, 36], twin boundary presented in the austenite phase is considered the most favorable site [3]. It nucleates at interfaces and grain edges and grows into the ferrite consuming Cr and Mo from the ferrite. As a consequence, the Cr and Mo-depleted neighboring phases have reduced corrosion resistance [34]. The ferrite is transformed to σ and secondary austenite γ_2 due to eutectoid reaction $\delta \rightarrow \gamma_2 + \sigma$ [3]. Fig. 3 shows the microstructures of HDSS specimens isothermally heat treated at 904 °C utilizing a Gleeble 3800 physical simulator [34].

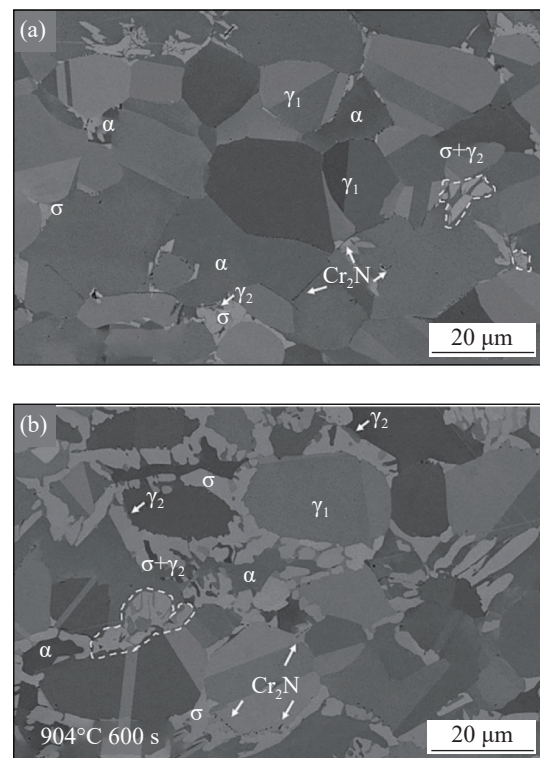


Fig. 3 Microstructural comparison of HDSS isothermally heat-treated samples at 904 °C: (a) Heat treated for 100 s, presenting interfacial nuclei and σ phase precipitates growth with secondary austenite formation, (b) Heat treated for 600 s with extensive σ phase precipitates growth at the expense of ferrite [34]

When the specimen was heated for 100 s, small σ interfacial nuclei are present, and some cells of $\sigma + \gamma_2$ clusters begin to appear (circled by dashed white line in Fig. 3a). When the specimen was heated for 600 s, extensive σ phase precipitates grow at the expense of ferrite (circled by dashed white line in Fig. 3b).

Acuna et al. [34] have identified a double-stage kinetics mechanism for σ phase formation. The first stage is eutectoid precipitation and interfacial-controlled growth occurring before 250 s, and the second stage is diffusion-

controlled growth, occurring after 250 s. Shorter time heat treatment usually produces blocky σ phase grains with some secondary austenite in between. In specimens heat treated for longer time, σ/γ_2 lamellar structure resulting from the eutectoid ferrite decomposition $\delta \rightarrow \gamma_2 + \sigma$ can be found. Fig. 4 shows the σ/γ_2 lamellar structures in a SDSS specimen isothermally heat treated utilizing a Gleeble 3800 physical simulator [37]. This kind of lamellar structures are found mainly in longer times, diffusion-controlled kinetics, at temperatures below 950 °C. At temperatures beyond 950 °C, mainly blocky σ phase grains are formed consuming the ferrite from one γ/α interface to the other [34].

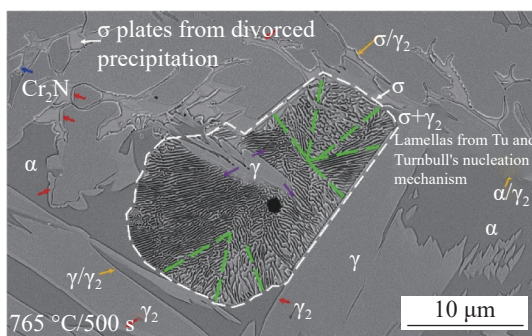


Fig. 4 σ/γ_2 lamellar structures in a SDSS specimen heated for 500s at 765 °C [37]

Acuna et al. [37] have compared σ phase formation kinetics in the as-welded microstructure of SDSS and HDSS. The results show that σ phase formation kinetics is the same for SDSS and HDSS up to 1% volume fraction, despite the higher Cr and Mo content in HDSS. The growth rate to 5% and 10% σ phase volumes is slightly higher in HDSS.

3.1.2 Precipitation of χ phase

Composition of χ phase is similar to that of σ phase, with low or non Mo content. σ phase is present in the binary Fe-Cr system, while χ phase appears only in the Fe-Cr-Mo ternary and in the Fe-Cr-Ni-Mo and Fe-Cr-Ni-Ti quaternary systems [38]. χ phase belongs to the topologically closepacked (TCP) phases and precipitates as a ternary compound containing Fe, Cr and Mo, with a wide range of stoichiometry extending from $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ to $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_3\text{Ti}_7$ [39].

As shown in Fig. 2, χ phase precipitates at lower temperatures and in smaller amounts than σ phase. The χ phase becomes stable below around 800 °C, and its volume fraction reaches a maximum of 19% at 550 °C. Fig. 5 shows χ phase found in a HDSS specimen isothermally heat-treated for 500 s at 830 °C utilizing a Gleeble 3800 physical simulator [34].

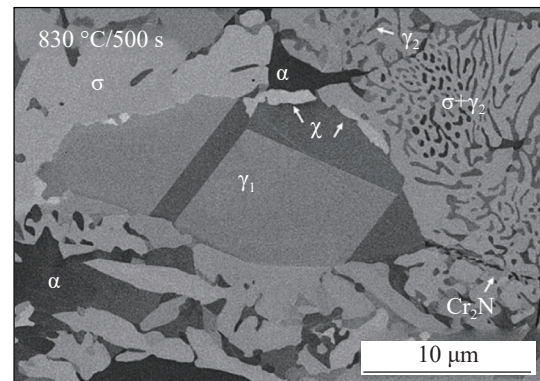


Fig. 5 χ phase found in a HDSS specimen heated for 500 s at 830 °C [34]

3.1.3 Precipitation of chromium nitrides

The precipitation of chromium nitrides is because of ferrite's saturation with nitrogen [3]. The precipitation can be intragranular or intergranular, as shown in Fig. 6 [4] and Fig. 7 [40].

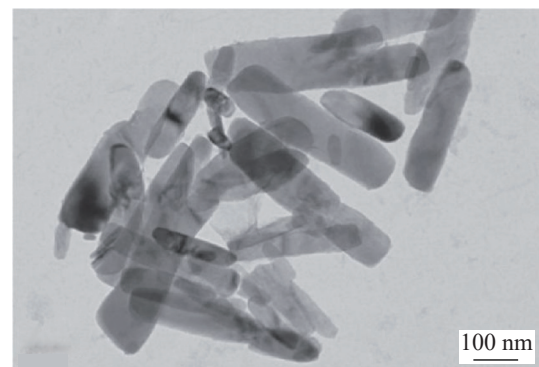


Fig. 6 Cr_2N precipitated in a HDSS weld [4]

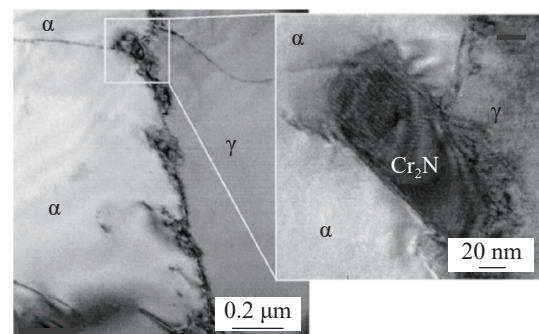


Fig. 7 Cr_2N precipitation at α/γ interface in UNS S32550 [40]

Nitrogen is an important alloying element in SDSSs and HDSSs, so it is not feasible to eliminate chromium nitrides precipitation in the weld by reducing or remov-

ing nitrogen from the base metal or the filler metal. In fact, the precipitation of chromium nitrides is usually caused by high ferrite phase content [4], resulted from fast cooling rate or loss of nitrogen. The high nitrogen alloying content in SDSSs and HDSSs is reduced during welding due to its limited solubility in the liquid metal [34]. Nitrogen is a strong austenite stabilizer, can ensure austenite formation at the end of solidification of SDSS and HDSS weld [37]. Solubility of nitrogen in austenite is much higher than that in ferrite, so high austenite volume fraction means low nitrogen content in ferrite and less tendency to form chromium nitrides. SDSSs and HDSSs are usually recommended to be welded with nitrogen addition in the shielding gas [4, 8–10, 13, 30].

3.1.4 Precipitation of γ_2

The austenite precipitates during reheating is called secondary austenite (γ_2), to differ from that precipitates during the initial weld cooling, which is called primary austenite (γ_1) [40]. Maurya et al. [3] have proposed three mechanisms by which γ_2 precipitates from ferrite. The first is by a eutectoid reaction ($\delta \rightarrow \sigma + \gamma$) in the temperature range of 700–900 °C. The σ/γ_2 lamellar structures shown in Fig. 4 are formed in this way. The second is by Widmanstätten precipitates in the temperature range of 650–800 °C. And the third is via a martensitic shear process, which appears below 650 °C.

Ramirez et al. [40] have proposed a co-precipitation mechanism of chromium nitrides and γ_2 at the α/γ_1 interfaces, as shown in Fig. 8.

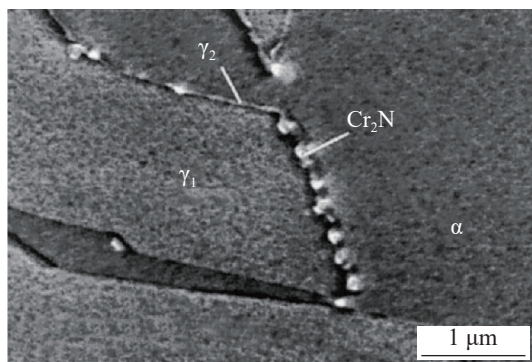


Fig. 8 γ_2 and chromium nitride precipitation in UNS S32550 at original α/γ interface during reheating treatments [40]

With reheating going on, the α/γ interface advances and leaves the chromium nitrides behind, as shown in Fig. 9. These chromium nitrides will dissolve later when the reheating time is long enough.

γ_2 can also nucleate heterogeneously at a composite

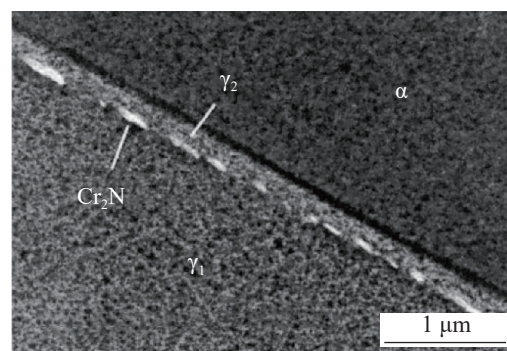


Fig. 9 Advancing of α/γ interface leaves chromium nitrides behind in UNS S32550 [40]

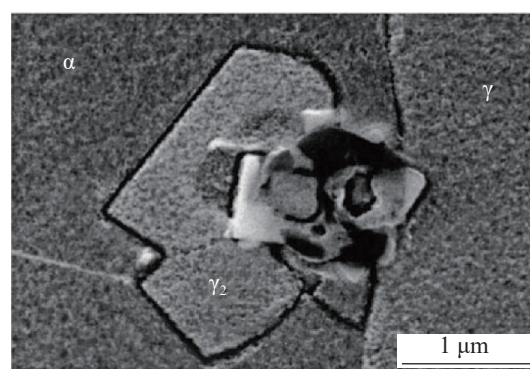


Fig. 10 Heterogeneous nucleation of γ_2 at O, Al, Mg and Ce composite inclusion during reheating at 1 000 °C for 1 s in UNS S32760 [40]

oxide inclusion, as shown in Fig. 10 [40].

3.2 Balance control of ferrite/austenite phases

As same as standard DSSs, proper ferrite/austenite phase ratio around nearly 1:1 is also critical for SDSSs and HDSSs to possess excellent corrosion resistance, high strength, and high toughness. The phases balance in joints of SDSSs and HDSSs can be controlled in the same way as in those of standard DSSs [6], with some cautions.

As mentioned before, SDSSs and HDSSs, with higher alloying elements content, are more prone to secondary phases precipitation than the standard grades. When considering phases balance control with filler materials [6], precipitation secondary phases must be taken into account. Some researchers claim that the over-alloyed Ni-based filler metals may be preferred for welding SDSSs, while others address that the over-alloyed filler metal is not suitable with SDSSs welding because the weld metal's sensitivity to precipitation of many intermetallic phases [41]. SDSSs are commonly welded with matching filler materials [5].

As for phases balance control with heat input, precipitation of secondary phases must be taken into account, too. In general, for obtaining proper phase proportions in DSS, 0.5–2.0 kJ/mm heat input is recommended,

while, 0.5–1.5 kJ/mm is recommended for SDSSs to control the deleterious phases [41]. The filler materials and heat input used for SDSSs and HDSSs in some literatures are summarized in Table 2.

Table 2 Filler materials and heat input used in some literatures

Base metal	Filler material	Welding process	Heat input/(kJ·mm ⁻¹)	Reference
UNS S32760	25 9 4 NL	TIG	0.85–1.2	[11]
UNS S32906	Sandvik 29.8.2.L	TIG	1.19–1.87	[12]
UNS S32750	ISO 25 9 4 NL	TIG	1.48–2.06	[9]
	ISO 25 9 4 NL	FCAW	0.77–1.25	
UNS S32750	ER2553	TIG		[17]
	ERNiCrMo-4	TIG		
2507	—	TIG	0.37–0.87	[18]
UNS S32750	25. 9.4 NL	MIG	0.8–2.0	[22]
UNS S32750	—	TIG	0.47–1.08	[19]
UNS S32750	E 2593-16	SMAW	0.81–1.06	[27]
UNS S32750	Inox 2509 MoW B	MIG	0.65–1.07	[20]
	Inox 2509 MoW B	TIG	0.745	
	ER2209T-1	FCAW	0.665	
UNS S32750	—	TIG	0.47–1.08	[21]

SDSSs and HDSSs are usually recommended to be welded with nitrogen addition in the shielding gas, to compensate nitrogen loss in welding process and to inhibit secondary phases precipitation. Nitrogen added in the shielding gas also promotes austenite and improves phases balance in the joints. Jang et al. [4] have investigated effect of shielding gas composition on the phase transformation and the mechanism of pitting corrosion HDSS welds in highly concentrated chloride environments. The results show that, ferrite volume fraction in the HDSS tube welded with 5 vol.% N₂ addition in argon decreases to 56 vol.% from 59 vol.% in that welded with pure argon. The resistance to pitting corrosion is increased due to a decrease of the PREN difference between the γ -phase and the α -phase in the weld metal and the heat affected zone. Kim et al. [10] have investigated the effects of solution heat treatment and nitrogen in shielding gas on the ferrite content and the resistance to pitting corrosion of HDSS welds. The results show that the ferrite content in the HDSS weld metal welded with Ar + 5% N₂ decreases to 56 vol.% from 58 vol.% in that welded with pure argon. With further solution heat treatment, the ferrite content decreases to 47.5 vol.%.

Saravanan et al. [28] have welded UNS S32750 with pulsed Nd: YAG laser. Ferrite content of 64% has been observed in as-weld joint with heat input of 150 J/mm.

After heat treated in an INDFUR furnace for two hours at a temperature of 1 050 °C and followed by furnace cooling, ferrite content in the joint has been found to decrease.

Zhang et al. [7] have investigated effects of short-time heat treatment on the microstructure evolution and pitting corrosion behavior of UNS S32750. The as-weld specimens are heated in a muffle furnace at 1 020, 1 050, 1 080 and 1 100 °C for a holding time of 3 minutes, followed by water quenching. The results show that, after short-time heat treatment, the excessive ferritization in the heat-affected zone has significantly alleviated. The highest pitting corrosion resistance of the welds has been obtained at 1 080 °C.

While Udo et al. [42] have drawn some different conclusion from investigation on how the microstructure and fatigue strength of a welded UNS S32750 joint is affected by post-weld heat treatment. σ phase has been found when the specimens cool from the solution treatment temperature of 1 323 K at rates below 10 K/s, and its fraction reaching 20% at rates as low as 0.1 K/s. Fatigue properties of the joints are deteriorated correspondingly to the amount of the σ phase. Post weld heat treatment on weldments of UNS S32750 is not suggested by the authors.

3.3 Hot cracking

SDSSs and HDSSs are more resistant to hot cracking than austenitic alloys with austenitic-ferritic or fully austenitic solidification [43]. But precipitation of secondary phases can sometimes invoke hot cracking. Park et al. [24] have carried out a flux cored arc multi-pass welding using a super duplex stainless steel as a filler metal. The weld metal has been aged for 30 min at 850 °C, followed by water quenching. A hot cracking is found in the weld, as shown in Fig. 11. The crack is the intergranular crack that occurs in the α/γ grain boundary, and the end of the crack is the curve type. The exposed area on the surface of the crack fracture plane is oxidised. The precipitation of σ of the adjacent area to the crack was measured to be higher by about 12 wt.% than the non-adjacent area to the crack.

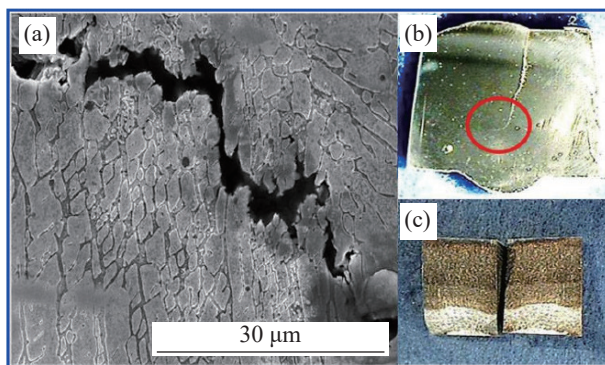


Fig. 11 Features of hot cracking: (a) Intergranular crack, (b) Tip of crack, (c) Fracture surface at crack [24]

3.4 Hydrogen induced stress cracking (HISC)

HISC [15] is a commonly used expression in the offshore community when referring to hydrogen embrittlement (HE), a phenomenon that the material's toughness reduces when atomic hydrogen interacts with the microstructure. Occurrence of HISC requires three essential factors, which are tensile stress, high ferrite contents and the presence of atomic hydrogen. Diffusivity of hydrogen is much higher in ferrite than in austenite, and solubility of hydrogen is much higher in austenite. So as the ferrite content in the DSS increases, cracking susceptibility becomes higher. Silva et al. [15] have investigated HISC of as-received and welded UNS S32750 tubes under hydrogen charging condition. The results show that the microstructural changes induced by welding increase diffusivity of hydrogen, and increase susceptibility of HISC.

Meinhardt et al. [31] have evaluated the susceptibility to HISC under cathodic protection of FSW welded UNS

S32760. Fracture toughness tests in synthetic sea water under cathodic protection indicate that the microstructure of the stir zone is actually less sensitive to HISC than the microstructure of the base metal.

3.5 Unmixed zone (UZ)

The UZ occurs in dissimilar joint, neighboring the fusion boundary. It is reconsolidated base metal without properly mixed with filler metal [3]. The UZ reduces the joint's mechanical properties and remains unaffected after heat treatment. Zhou et al. [16] have investigated dissimilar TIG welding of SDSS 2507 to super-austenitic stainless steel 6Mo using nickel-alloy filler materials ERNiCrMo-13 and ERNiCrMo-3 as well as SDSS filler material ER2594. UZs have been observed close to the fusion boundary of both the 2507 side and the 6Mo side in the root and middle of the dissimilar welded joints with nickel-alloy fillers, as shown in Fig. 12. While no UZ has been found in the joint welded with SDSS filler.

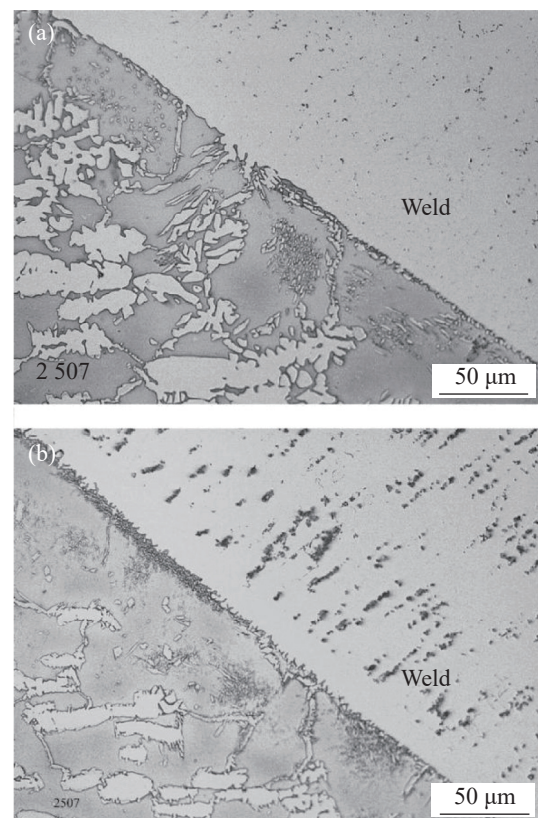


Fig. 12 UZ using nickel-alloy filler material of ERNiCrMo-3: (a) On the 2507 side, (b) On the 6Mo side [16]

4 Conclusions

Weldability problems of SDSSs and HDSSs are reviewed in this paper, and conclusions are drawn as follows.

(1) SDSSs and HDSSs can be welded with most fusion welding processes if proper heat input is provided. TIG welding is the most popular process.

(2) SDSSs and HDSSs are more prone to secondary phases precipitation than the standard and lean grades, and heat input for SDSSs and HDSSs welding is restricted to a smaller range.

(3) Matching filler materials are usually recommended for SDSSs and HDSSs welding, rather than Ni-riched ones for standard and lean grades. Nitrogen addition in shielding gas is always beneficial. Post weld heat treatment with slow cooling rate will be harmful.

(4) Hot cracking tendency of SDSSs and HDSSs joints is not high, but sometimes they can suffer from HISC.

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Author contributions

The author finished the paper alone.

Conflict of interest

The author declares that he has no conflict of interest.

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