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Effect of Solution Treatment Temperature on Microstructure and Pitting Corrosion Resistance of S32760 Duplex Stainless Steel Postprint

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Abstract

The effects of solution temperature on the microstructure of S32760 duplex stainless steel hot-rolled plates and the distribution characteristics of alloying elements were investigated using OM, EPMA, SEM, EDS, TEM, etc., and the pitting corrosion resistance of the material was measured via an electrochemical workstation. The results indicate that during high-temperature solution treatment above 1080 ℃, nitrogen diffuses from the γ phase to the δ phase in S32760 duplex stainless steel. Upon slow cooling after solution treatment, nitrogen atoms migrate back to the γ phase; however, with water cooling after solution treatment, nitrogen atoms do not have sufficient time to diffuse and instead precipitate in-situ as dispersive Cr2N particles within the δ phase. The quantity of Cr2N particles is determined by the solution temperature prior to quenching, increasing with higher temperatures. As the solution temperature rises from 1100 ℃ to 1300 ℃, the nitrogen solubility in the δ phase increases rapidly, and its microhardness improves from 281 HV to 345 HV; concurrently, the nitrogen concentration in the γ phase also increases indirectly due to the decreased phase proportion, raising its microhardness from 290 HV to 314 HV. Additionally, due to the presence of W in the experimental steel, σ phase precipitates in S32760 duplex stainless steel hot-rolled plates during heat treatment below 1040 ℃, resulting in a relatively narrow solution treatment and water cooling temperature range, with the optimal solution temperature being 1060 ℃. After holding at this temperature for 60 min followed by water cooling, the specimen exhibits no precipitates, a Brinell hardness of 249 HBW, a pitting potential of 1068 mV, and a passive current density of 1.48$×10^{-4}$ A/cm^2.

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Effect of Solution Temperature on Microstructure and Pitting Corrosion Resistance of S32760 Duplex Stainless Steel

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Abstract

The microstructural characteristics and alloy element distribution of S32760 duplex stainless steel hot-rolled plates were investigated using optical microscopy (OM), electron probe microanalysis (EPMA), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM). The pitting corrosion resistance was evaluated through electrochemical measurements. The results demonstrate that during high-temperature solution treatment above 1080 °C, nitrogen diffuses from the austenite (γ) phase into the ferrite (δ) phase. Upon slow cooling after solution treatment, nitrogen atoms migrate back to the γ phase. However, with water quenching, nitrogen atoms lack sufficient time for diffusion and precipitate in situ within the δ phase as finely dispersed Cr_2N particles. The quantity of Cr_2N precipitates is determined by the solution temperature prior to quenching, increasing with higher temperatures. As the solution temperature rises from 1100 °C to 1300 °C, the nitrogen solubility in the δ phase increases rapidly, elevating its microhardness from 281 HV to 345 HV, while the γ phase hardness also increases from 290 HV to 314 HV due to an indirect nitrogen concentration increase associated with phase ratio changes. Additionally, owing to tungsten addition, σ phase precipitation occurs in S32760 duplex stainless steel hot-rolled plates when heat-treated below 1040 °C, resulting in a narrow optimal solution temperature window. The optimal solution temperature is 1060 °C, which after 60 min holding and water cooling yields a specimen free of precipitates, with a Brinell hardness of 249 HBW, a pitting potential of 1068 mV, and a passive current density of 1.48$\times$10^{-4}$ A/cm^2.

Keywords: duplex stainless steel, solution treatment, precipitation, pitting corrosion resistance

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Introduction

Super duplex stainless steels (SDSS) exhibit superior corrosion resistance compared with conventional duplex stainless steels, as evidenced by a pitting resis-

tance equivalent number exceeding 40 [?]. These steels typically contain over 20 wt% Cr along with specific amounts of Mo and N, offering higher strength, hardness, and corrosion resistance than austenitic stainless steels of comparable performance grades while significantly reducing noble Ni consumption [?]. UNS S32760 is a novel super duplex stainless steel with minor additions of W and Cu, providing enhanced resistance to localized corrosion for applications in harsh environments such as petroleum, chemical, military, and paper industries [?, ?].

Due to their high alloy content and diverse elemental composition, super duplex stainless steels are susceptible to precipitate formation under improper heat treatment conditions, including σ, , Cr_2N, and $M_{23}C_6$ phases [?], which substantially degrade corrosion resistance and mechanical properties [?, ?]. Lacerda et al. [?] investigated the phase ratio, nitride quantity, and morphology of UNS S31803 duplex stainless steel after heat treatment at 1060, 1200, and 1300 °C, analyzing their effects on fatigue performance. Migiakis et al. [?] observed microstructural and corrosion resistance changes in S32760 duplex stainless steel during plasma arc welding, noting that high cooling rates in the fusion zone and heat-affected zone altered the phase balance, reducing corrosion resistance and mechanical strength. Elsabbagh et al. [?] measured impact absorption energy of S32760 duplex stainless steel after aging at 350–950 °C, finding values significantly lower than those after solution treatment at 1150 °C, indicating severe toughness degradation by precipitates. Xiang et al. [?] studied precipitation behavior in cast S32760 duplex stainless steel after solution treatment and aging at various temperatures, observing residual σ phase even after aging at 950 °C.

Current research on S32760 duplex stainless steel remains limited [?, ?], particularly regarding the influence of W on solution and precipitation behavior. Therefore, clarifying the microstructural evolution and corrosion performance of S32760 duplex stainless steel after solution treatment at different temperatures is crucial for optimizing heat treatment processes, enhancing material performance, and developing this new steel grade.

Experimental Procedures

The experimental material was a 12 mm-thick S32760 hot-rolled steel plate with chemical composition conforming to ASTM A789 standards (Table 1). Specimens measuring 10 mm × 10 mm × 6 mm were sectioned from the plate mid-thickness and subjected to solution treatment in an SRJX-8-13 box-type electric furnace at temperatures ranging from 1000 °C to 1300 °C in 50 °C increments, with 60 min holding followed by water quenching.

Microstructural observation was performed using a DM 2500M optical microscope (OM) after electrolytic etching in oxalic acid or etching in aqua regia. Precipitate element distribution was examined with a JEOL JXA-8100 electron probe microanalyzer (EPMA). Microhardness of δ and γ phases was measured using a VMHT 30M micro-Vickers hardness tester. Phase composition and pre-

cipitate chemistry were analyzed with an EVO 18 scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). Precipitate morphology and crystal structure were characterized using a JEM-2100F transmission electron microscope (TEM). Brinell hardness of solution-treated specimens was measured with an XHB-3000 hardness tester. Polarization curves for specimens solution-treated at various temperatures were obtained using a PS-168C electrochemical measurement system. Pitting potential tests followed GB/T 17899-1999 in 3.5 wt% NaCl solution at (30$±$1) °C, with a saturated calomel electrode (SCE) as reference, graphite as auxiliary electrode, and a scan rate of 20 mV/min.

2.1 Effect of Solution Temperature on Microstructure

Figure 1 [Figure 1: see original paper] presents optical micrographs of S32760 hot-rolled plate after solution treatment and water quenching. The microstructure consists of dark gray δ ferrite, light gray γ austenite, and bright white and black dispersed precipitates. After solution treatment at 1000 °C, numerous undissolved bright white σ phase particles remain visible (Fig. 1a). The microstructure after 1050 °C solution treatment and water cooling comprises only δ and γ phases without observable precipitates (Fig. 1b). For solution temperatures of 1100–1300 °C, fine black dispersed precipitates appear within δ grain interiors, with quantity increasing progressively with temperature (Figs. 1c–g). Figure 1h shows the microstructure after furnace cooling from 1300 °C to 1100 °C followed by water quenching. Compared with direct water quenching from 1300 °C (Fig. 1g), the dispersed precipitates within δ grains decrease significantly to a level comparable to that after 1100 °C solution treatment (Fig. 1c), indicating that the pre-quenching temperature determines precipitate quantity. Figure 1i reveals that after 1100 °C solution treatment and air cooling, δ grains contain virtually no intragranular precipitates, with only minor granular precipitates at grain boundaries. This demonstrates that cooling rate governs precipitation extent: rapid cooling induces substantial intragranular dispersion, while slow cooling reduces precipitation. Consequently, precipitates form during rapid cooling rather than during high-temperature holding.

Figure 1g also reveals precipitation-free zones (PFZ) around δ grain boundaries, particularly pronounced after high-temperature quenching (e.g., 1300 °C). These PFZs result from quenched-in vacancies [**?**]. According to vacancy concentration calculations, $C = A \cdot exp(-Uv/kT)$ (where C is vacancy concentration, A is a constant coefficient estimated at 1–10, Uv is the formation energy of a single vacancy, k is the Boltzmann constant, and T is thermodynamic temperature) [**?**], vacancy concentration at high temperatures far exceeds that at room temperature. During water quenching, this high vacancy concentration is retained. However, grain boundaries and phase interfaces act as sinks for excess vacancies during cooling, causing rapid vacancy diffusion to these interfaces and resulting in lower vacancy concentrations near boundaries compared to grain interiors. Reduced vacancy concentration impedes precipitation, and when it falls below

the critical level required for precipitate nucleation, PFZs form. The PFZ width depends on vacancy concentration: faster cooling allows less vacancy diffusion to grain boundaries, yielding narrower PFZs [**?**].

EPMA elemental mapping results for the matrix and σ phase are shown in Figure 2 [Figure 2: see original paper]. The σ phase is enriched in Cr, Mo, and W but depleted in Ni, indicating that W addition alters the chemical composition of σ phase in duplex stainless steel and influences its precipitation behavior. The presence of substantial σ phase after 60 min at 1000 °C (Fig. 1a) demonstrates that W enhances σ phase stability, promoting its formation and hindering dissolution.

2.2 Cr_2N Precipitation and Nitrogen Diffusion in δ and γ Phases

Unlike conventional duplex stainless steels, S32760 retains significant σ phase after quenching from 1000 °C (Fig. 1). Deep electrolytic etching and SEM examination of this specimen reveal granular precipitates 3–5 m in diameter distributed within the δ phase matrix and at δ/γ phase boundaries, with surrounding pits (Fig. 3a [Figure 3: see original paper]). EDS analysis of various phases in Fig. 3a (Table 2) identifies these granular precipitates as austenite based on chemical composition. The eutectoid decomposition reaction $\delta \rightarrow \sigma + \gamma_2$ suggests that pits around γ_2 phase result from σ phase detachment during electrolytic etching. Xiang et al. [**?**] observed that increased nitrogen content enhances austenite phase pitting resistance, causing corrosion to initiate preferentially at austenite-ferrite boundaries and within ferrite grains. Corrosion pits expand within ferrite grains, eventually surrounding and detaching austenite particles, consistent with the microstructure shown in Fig. 3a. In contrast, the specimen solution-treated at 1300 °C and quenched exhibits numerous fine dispersed precipitates within the original δ phase that have mostly detached after etching, leaving regular square pits less than 1 m in size, with no precipitates observed near grain boundaries, phase boundaries, or within the γ phase (Fig. 3b). The precipitate morphology at 1300 °C differs markedly from that at 1000 °C.

Since the dispersed precipitates persist even at 1300 °C and increase with both temperature and cooling rate, their precipitation mechanism differs from conventional aging precipitation. TEM analysis of a specimen solution-treated at 1250 °C and quenched (Fig. 4 [Figure 4: see original paper]) reveals precipitates approximately 100 nm in size with a near-square morphology, consistent with the square pits observed via SEM. Selected-area electron diffraction (SAED) pattern indexing (Fig. 4b) identifies a simple hexagonal structure. The measured interplanar spacings of 0.19034, 0.21305, and 0.116 nm for three crystal planes show deviations of 0.77%, 2.23%, and -1.49% from standard Cr_2N PDF card values. The measured angle between (0006) and (1012) planes is 63.4°, deviating by -0.8% from the standard value, confirming the precipitates as Cr_2N. The orientation relationship between Cr_2N particles and the δ phase matrix is $[1230]Cr_2N//[001]\delta$, differing from the $[0001]Cr_2N//[001]\alpha$ relationship reported

for aged precipitation [?]. Thermodynamic analysis indicates Cr_2N precipitation occurs at 700–1000 °C [?], not above 1100 °C or at 1300 °C. The experimental results show slower cooling reduces Cr_2N precipitation, suggesting that Cr_2N forms during water cooling. Nitrogen, highly soluble in the δ phase at elevated temperatures, becomes supersaturated during rapid quenching due to drastically reduced room-temperature solubility, leading to in situ Cr_2N precipitation within the δ phase.

Extensive research on duplex stainless steels considers nitrogen a γ-phase stabilizing element with significantly higher solubility in austenite than in ferrite, resulting in predominant nitrogen distribution in the γ phase. For instance, Garfias-Mesias et al. [?] assumed δ-phase nitrogen content at room temperature saturation to be approximately 0.05% in their study of S32550 duplex stainless steel, then determined γ-phase nitrogen content through mass balance calculations based on measured high-temperature phase ratios for pitting resistance equivalent calculations. However, the variation in Cr_2N precipitation quantity after solution treatment at 1100–1300 °C and water quenching in this study reveals dramatic changes in nitrogen solubility in the δ phase within this range. As temperature increases, nitrogen solubility in the δ phase rises rapidly, accompanied by nitrogen diffusion from the γ phase to the δ phase. Nitrogen atoms that diffuse into the δ phase can return to the γ phase during slow cooling, but precipitate as fine Cr_2N dispersion during rapid quenching.

Microhardness analysis of both phases corroborates nitrogen diffusion into the δ phase at high temperatures. Although both phases exhibit linear hardness increases with solution temperature, the δ phase shows a greater enhancement rate. After 1100 °C solution treatment and water quenching, the γ phase is harder than the δ phase (290 HV vs. 281 HV). Above 1200 °C, the δ phase becomes harder than the γ phase. From 1100 °C to 1300 °C, γ-phase hardness increases by only 24.6 HV, whereas δ-phase hardness increases by 63.5 HV. Hardness variations originate from changes in alloy element solubility. Since nitrogen atoms are much smaller than Fe atoms, they occupy interstitial sites in the Fe matrix octahedral interstices, creating asymmetric lattice distortion and resulting in interstitial solid solution strengthening [?]. Zhao et al. [?] confirmed that as solution temperature increases, the compositional differences of Cr, Mo, Si, and Ni between δ and γ phases in 00Cr25Ni7Mo4N duplex stainless steel diminish, reducing the disparity in substitutional solid solution strengthening from these elements. Interstitial solid solution strengthening from nitrogen is approximately two orders of magnitude greater than substitutional strengthening from Cr, Mo, and Ni [?]. Therefore, microhardness variations in S32760 duplex stainless steel primarily reflect nitrogen content changes in both phases. The simultaneous increase in hardness of both phases with temperature indicates elevated nitrogen concentrations in each. In the γ phase, increased nitrogen concentration stems from the transformation of γ to δ phase, leaving higher nitrogen in the residual γ phase due to its lower solubility. In the δ phase, the nitrogen increase results from diffusion from the γ phase. The concurrent increase in δ-phase volume fraction and hardness confirms nitrogen migration

from γ to δ phase.

2.3 Effect of Solution Temperature on Pitting Corrosion Resistance

For ultra-low carbon (<0.03%) super duplex stainless steels, carbide precipitation is unlikely [**?**]. However, S32760 duplex stainless steel, containing high nitrogen, chromium, and molybdenum, is prone to σ and Cr_2N precipitation after high-temperature heat treatment. These precipitates create Cr-depleted zones, degrading pitting corrosion resistance. As established, Cr_2N particles exist within δ grains after solution treatment above 1100 °C, while σ phase persists at 1000 °C and below. Therefore, identifying an optimal solution temperature that eliminates all precipitates is essential.

Specimens were solution-treated at 20 °C intervals from 1040 °C to 1100 °C for 60 min and water-quenched (Fig. 5 [Figure 5: see original paper]). At 1040 °C, σ phase remains incompletely dissolved, with sizes of 2–5 m (Fig. 5a). At 1060 °C, the matrix is clean and precipitate-free (Fig. 5b). At 1080 °C, Cr_2N precipitation initiates within δ grains (Fig. 5c). Thus, the optimal solution temperature for the S32760 hot-rolled experimental steel is determined to be 1060 °C.

According to ASTM A789 and ASTM A240 specifications, the Brinell hardness of solution-treated S32760 duplex stainless steel tubes and plates should be below 300 and 270 HBW, respectively. All specimens solution-treated at 1040–1100 °C for 60 min and water-quenched meet these requirements. At 1040 °C, incomplete σ phase dissolution yields a relatively high hardness of 260 HBW. The precipitate-free specimen at 1060 °C exhibits the lowest hardness of 249 HBW. Further temperature increases to 1080 and 1100 °C result in progressive hardness increases to 254 and 256 HBW, respectively, due to Cr_2N precipitation.

Polarization curves for specimens solution-treated at 1040–1100 °C and water-quenched (Fig. 6 [Figure 6: see original paper]) demonstrate high pitting potentials and wide passivation ranges, with all tested specimens maintaining passivity between 50–1000 mV. Within this range, S32760 duplex stainless steel forms a dense passive film, providing good corrosion resistance in Cl^--containing solutions [**?**].

Figure 7 [Figure 7: see original paper] shows the pitting potential (E_b) and corresponding passive current density (i) for each heat treatment temperature. The 1040 °C solution-treated specimen exhibits a relatively low E_b of 1003 mV due to undissolved σ phase. At 1060 °C, E_b reaches a maximum of 1068 mV with i = 1.48$×10^{-4}$ A/cm^2. Further temperature increases produce minimal E_b variation (~1065 mV) but a linear increase in i, indicating deteriorating pitting corrosion resistance. Consequently, the 1060 °C solution-treated and water-quenched specimen demonstrates optimal pitting corrosion resistance with the highest E_b and lowest i, establishing 1060 °C as the optimal solution treatment temperature.

Conclusions

1. During high-temperature solution treatment of S32760 duplex stainless steel hot-rolled plate, nitrogen diffuses from the γ phase to the δ phase. Upon subsequent slow cooling, nitrogen atoms migrate back to the γ phase. However, water quenching after solution treatment prevents nitrogen diffusion, causing supersaturation in the δ phase and resulting in in situ precipitation of finely dispersed Cr_2N particles. The quantity of Cr_2N precipitates is determined by the solution temperature prior to quenching.

2. As solution temperature increases from 1100 °C to 1300 °C, nitrogen concentration in the δ phase rises rapidly, while the γ phase experiences an indirect nitrogen concentration increase due to phase ratio changes. Consequently, δ-phase microhardness increases sharply from 281 HV to 345 HV, and γ-phase hardness rises from 290 HV to 314 HV.

3. Due to its high nitrogen content, S32760 duplex stainless steel exhibits Cr_2N precipitation after solution treatment above 1080 °C followed by water quenching. Additionally, tungsten addition results in undissolved σ phase precipitation up to 1040 °C. Therefore, the optimal solution temperature is 1060 °C, yielding a precipitate-free microstructure with a Brinell hardness of 249 HBW, a pitting potential of 1068 mV, and a passive current density of 1.48$×10^{-4}$ A/cm^2.

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