

Article



The Isolated Austenite Forming during High-Temperature Cooling and Its Influence on Pitting Corrosion Resistance in S32750 Duplex Stainless Steel

Xiaohan Wu^{1,2}, Zhigang Song^{2,*}, Jianguo He², Zhiyi Bao², Han Feng², Wenjie Zheng² and Yuliang Zhu²

- School of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China
- ² Central Iron & Steel Research Institute, Beijing 100081, China
- * Correspondence: zhigangsongnercast@163.com

Abstract: The formation mode of isolated austenite (IA) formed during high-temperature cooling and its effect on pitting corrosion resistance of S32750 DSS were investigated. As the structure formed during the high-temperature cooling process after hot rolling in S32750 duplex stainless steel (DSS), the precipitation of isolated austenite (IA) can be considered as the combined production of temperature and cooling rates. IA generated at the ferrite (α) grain boundaries or internal α and performed the K-S crystallographic relation with the α N element enriched in IA. The redistribution of elements not only increased the concentration gradient between α /IA, but also reduced the pitting resistance equivalent number (PREN) of original austenite (γ). Scanning Kelvin probe (SKP) and Gaussian fitting proved that with prolonged corrosion time, the potential difference enlarged and local corrosion aggravated. Measured by the weight loss method, pitting resistance decreased to one-third of the solid solution state due to the existence of IA; following, the quantities, sizes, and depth of corrosion pits increased significantly. In addition to α/γ boundaries and α/α boundaries, corrosion pits preferred to initiate around IA. The IA that appeared at α grain boundaries deteriorated the pitting corrosion resistance severely. Furthermore, original austenite with decreased PREN tended to be corroded. In general, the order of pitting occurrence is displayed as follows: α - γ -IA.

Keywords: pitting corrosion; elemental redistribution; duplex stainless steel; scanning Kelvin probe; specific interface

1. Introduction

S32750 duplex stainless steel (DSS) contains approximately equal proportions of ferrite (α) and austenite (γ) and has superior integration of advanced mechanical properties with excellent corrosion resistance [1,2]. The pitting resistance equivalent number (PREN) is greater than 40 due to its high mass fraction of Cr (25–27%) and Mo (3–4.5%), and medium mass fraction of N (0.24–0.32%), especially the local pitting resistance in high-chloride environments, which brings wide applications to the marine and petrochemical industries. Undesired secondary phases such as M₂₃C₆, M₇C₃, Cr₂N, σ -phase and χ -phase formed in S32750 severely deteriorate the pitting resistance [3]. The secondary phases above have been studied thoroughly and could be well-avoided in the production process. However, different from the pancake-like austenite, the tiny-sized dispersed spherical austenite is often observed in the water-cooling process after hot rolling, which is named "isolated austenite (IA)" through its morphological character. As a metastable structure, the appearance of IA is speculated to bring several problems to the production and development of DSS, while its formation and influence on properties remain ambiguous.

Pitting corrosion, accelerated dissolution of the passive film on the local metal surface, is known to be a common corrosion phenomenon in DSS. The corrosion pits distribute unevenly and snugly, with the corrosion depth being generally larger than the surface



Citation: Wu, X.; Song, Z.; He, J.; Bao, Z.; Feng, H.; Zheng, W.; Zhu, Y. The Isolated Austenite Forming during High-Temperature Cooling and Its Influence on Pitting Corrosion Resistance in S32750 Duplex Stainless Steel. *Metals* **2022**, *12*, 1316. https:// doi.org/10.3390/met12081316

Academic Editor: Soran Birosca

Received: 12 July 2022 Accepted: 1 August 2022 Published: 5 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). area, which can induce stress corrosion cracking and corrosion fatigue cracking. Therefore, mainly affected by materials (element composition, impurities, and precipitated phases) and environment (corrosive medium and corrosion temperature), pitting corrosion resistance has always been one of the important parameters to evaluate the durability of DSS [4]. Forming at a relatively fast cooling rate from high temperatures (approximately 1200 °C), elements in IA have inadequate time to diffuse, which tends to cause the segregation of elements and the formation of local, relatively weak areas that may be affecting the pitting corrosion resistance. Therefore, it is necessary to study the behavior of IA during the corrosion process.

The scanning Kelvin probe (SKP) can measure potential distribution on the surface of samples without damage, which is extremely sensitive to slight changes [5,6]. The present investigation is therefore devoted to exploring the precipitation mechanism of isolated austenite and its influence on the pitting corrosion resistance of S32750 DSS, carried out with the aid of SKP and weight loss methods, which guides the production and development of duplex stainless steel.

2. Material and Methods

The chemical composition of the S32750 hot-rolled strip (in wt.%) was: 0.03C, 0.4Si, 0.7Mn, 25.2Cr, 6.8Ni, 3.8Mo, 0.27N, 0.2Cu, and balance Fe. Referring to the previous research [7], a near-perfect duplex structure without other second phases was obtained by the following method: The as-received material was isothermally treated at 1150 °C for 1 h, then furnace-cooled to 1100 °C and held for 1 h, then water quenched, and was named as state R. Another part of the hot-rolled strip was held at 1100 °C for 1 h then water-quenched to gain quantities of isolated austenite distributed in the structure and ensure the equivalent α/γ phase ratio in the meantime, which was named as state I.

The pitting corrosion resistance of S32750 DSS was evaluated by the weight loss method according to the ASTM-G48 standard. Each three corrosion specimens sampled from state R and state I were immersed in 6% FeCl₃ + 5% HCl solution at a constant temperature of 50 °C for 24 h. The weight loss of the specimens was measured and the average value was calculated. According to the SKP experimental conditions, the surface potentials of state R and state I, corroded for 12 h and 24 h, were tested. To verify the stability of the SKP tip during long time measurements, the calibration was controlled before and after each experiment. The samples were rinsed in de-ionized water and dried in air. A 3000 μ m² scan with a step size of 50 μ m was taken along the surface of the samples. The vibration amplitude of the probe was 30 μ m, and the average distance from the sample surface was controlled within 50 μ m. The measurements were performed in air at an ambient temperature of 25 ± 1 °C with 50–60% relativity humidity (RH), which were defined as laboratory conditions. The time delay between the end of cathodic charging and the start of potential measurements using SKP was about 5 min. Origin 9.0 software (OriginLab, Northampton, MA, USA) was used for data analysis and graphing of 3D surface color maps.

The microstructures of samples were characterized using electron backscattered diffraction (EBSD, FEI Quanta 650, FEI Company, Hillsboro, OR, USA), with 1 µm step size and 20 mm working distance at 20 kV. The specimen preparation was described elsewhere [8]. A transmission electron microscope (TEM, FEI Tecnai G2 F20, FEI Company, Hillsboro, OR, USA) was used for the microstructural and elemental examination. The TEM specimens were prepared by referring to the existing article [7]. The element contents of each phase were detected by the electron probe X-ray microanalysis (EPMA) in model JXA-8530F (JEOL Ltd., Tokyo, Japan). Three test points were randomly selected from the same phase and the average value was calculated. The corrosion pits were observed with an optical microscope (OM, Leica MEF4M, Leica, Wetzlar, Germany) and a scanning electron microscope (SEM, FEI Quanta 650, FEI Company, Hillsboro, OR, USA). A thermal scanning electron microscope (CSLM, Coherent Inc., Santa Clara, CA, USA) was used to measure the depth of pits.

3. Results

In state R, the classical pancake-liked austenite (γ) and ferrite (α) elongates parallel to the rolling direction alternately (Figure 1a). Tiny-sized isolated austenite disperses in α with approximately spherical morphology, as dyed red in Figure 1b. Two typical precipitation positions of IA are observed in the inverse pole figures (IPF) (Figure 1c), meaning the interior α grains (Figure 1d) and the grain boundaries of α (Figure 1e). The crystallography relationship between α and IA precipitated from the two positions above is calibrated as follows:



Figure 1. Optical morphologies of state R (**a**) and state I (**b**) in S32750 DSS, two precipitation positions of isolated austenite presented by IPF map (**c**), and band contrast: interior ferrite (**d**) and grain boundary of ferrite (**e**).

IA from interior α grains (Figure 2a):

$$(\overline{1}0\overline{1})_{bcc}//(111)_{fcc}, \ [\overline{1}\ 1\ 1]_{bcc}//[0\ \overline{1}\ 1]_{fcc}$$

IA from grain boundaries of α (Figure 2b):

$$(01\overline{1})_{bcc} / / (\overline{111})_{fcc}, [1\ 1\ 1]_{bcc} / / [01\ \overline{1}]_{fcc}$$

The orientation relationships above are both fulfilled with the K-S orientation relationship (Figure 2) [9]. Image-pro software (Image-pro6.0, Reachsoft, Beijing, China) was used to examine 10 metallographic images of 1000 mm² fields in state R and state I, respectively. The phase fractions of γ are approximately 49.4% and 49.1% in R and I; that is, the volume ratio of γ/α in R and I are close to 1:1. The proportion of IA is about 4.5%. In addition, no other precipitates appear in the microstructure. Figure 3 shows EPMA test points of original austenite in state R (γ_R), state I (γ_I), IA, and α , with the element contents for each listed in Table 1. It is noteworthy that N enriches in IA, which induces N content in γ_I , and affects the content of other elements (Cr, Ni, Mo, Si). The pitting corrosion resistance equivalent number (PREN) is proposed to characterize the pitting corrosion resistance of materials. PREN is mainly affected by Cr, Mo and N contents [10], which are generally expressed in Equation (1):

$$PREN = Cr + 3.3\%Mo + 20\%N$$
 (1)



Figure 2. TEM morphologies of the Isolated austenite precipitated at α/γ boundary (**a**) and interior α (**b**).



Figure 3. Test points of EPMA: (a): γ_R ; (b): γ_I ; (c): IA; (d): α .

	Cr	Ni	Мо	Ν	Si	Mn	Fe	PREN
$\gamma_{ m R}$	24.93 ± 0.02	8.44 ± 0.02	2.96 ± 0.003	0.57 ± 0.012	0.31 ± 0.05	0.74 ± 0.01	62.11 ± 0.06	46.10
γ_{I}	24.63 ± 0.06	8.60 ± 0.01	2.94 ± 0.009	0.48 ± 0.002	0.18 ± 0.02	0.78 ± 0.02	60.65 ± 0.16	43.93
IA	23.91 ± 0.04	8.26 ± 0.03	2.98 ± 0.006	0.72 ± 0.01	0.20 ± 0.04	0.79 ± 0.01	60.56 ± 0.18	48.14
α	26.78 ± 0.03	5.54 ± 0.02	4.16 ± 0.02	0.00 ± 0.002	0.24 ± 0.03	0.73 ± 0.02	59.52 ± 0.09	40.51

Table 1. Element contents of γ_R , γ_I , IA and α (mass. %).

The higher the PREN value, the greater the pitting corrosion resistance [11]. As can be inferred from Table 1, the element redistribution associated in state I not only results in a higher PREN value of IA, but also affects the PREN of original austenite.

The Kelvin potential distribution of state R and state I immersed in 6%FeCl₃ + 5%HCl solution for 12 h and 24 h are displayed in Figure 4. The Gaussian distribution function (Equation (2)) was adopted to fit the potential distribution above. The fitting results are listed in Figure 5 and Table 2.

$$E = E_0 + \frac{A}{w\sqrt{\pi/2}} e^{-2\frac{(x-x_c)^2}{w^2}}$$
(2)

where A is a constant; E_0 is the ordinate (potential) offset; x_c is the concentrated distribution potential; and w is the concentration of potential distribution. The smaller the w value, the more concentrated the potential distribution on the x_c .



Figure 4. Kelvin potential profiles measured after pitting corrosion in state R (**a**,**b**) and state I (**c**,**d**): (**a**): R 12 h; (**b**): R 24 h; (**c**): I 12 h; (**d**): I 24 h.



Figure 5. Gaussian fitting curves of pitting corrosion at different times.

Table 2. SKP potential and Gaussian fitting results.

	Potential Range/mV	$\Delta E/mV$	x_c/mV	w^2
R 12 h	-342~-220	122	-287.14	$(38.81)^2$
I 12 h	$-369 \sim -155$	214	-250.68	$(67.21)^2$
R 24 h	$-302 \sim -28$	274	-146.45	$(86.30)^2$
I 24 h	-299~29	328	-133.92	$(129.87)^2$

When corroded for 12 h, the surface potential distribution of state R is uniform (Figure 4a) with no obvious cathode and anode partition in the 2Dmapping. Exhibiting negative initial potential, its highly concentrated surface potential is basically distributed around -287.14 mV. The potential range is -342 mV ~ -220 mV and the potential difference (ΔE) is 122 mV. For the 12 h-immersed sample in state I, the surface potential disperses slightly with potentials ranging from -369 mV ~ -155 mV and ΔE 214 mV. Compared with state R, although the anode distribution increases, the anode/cathode distribution still performs apparent randomness in general. After being immersed for 24 h in state R, the positively shifted corrosion potential dispersedly distributes ranging from -302 mV to -28 mV, resulting in the ΔE increase to 274 mV. Meanwhile, the anode and cathode areas appear apparently. The surface potential moves more positively, and the distribution displays further dispersion in state I. An obvious potential peak is observed in the anode area, and the ΔE is 328 mV. Accordingly, the corrosion degree rises significantly after conducting for 24 h.

Corrosion weight loss rate refers to the rate of mass reduction in metal materials during corrosion solution immersion, as is calculated from Equation (3):

$$V^{-} = \frac{W_0 - W_1}{S \times t} \tag{3}$$

where V^- is the corrosion weight loss rate; W_0 is the initial mass of sample; W_1 is the mass after corrosion products removed; *S* is the surface area of sample exposed in corrosive solution; and *t* is corrosion time. It can be inferred from Figure 6 that the corrosion weight loss rate of state I is about three times higher than that of state R, which means the pitting corrosion resistance of state I is much lower than state R in the same conditions.





The negligible corrosion pits in state R are observed distributing spherically on the surface of samples (Figure 7a). As indicated by the red arrow in Figure 7c, the pits are open-type with an inner diameter less than the orifice diameter. Corrosion cracks emerge around the pits (yellow circle in Figure 7c), which indicates that the "bifurcation" expansion forms along a specific interface, for instance, grain boundaries or phase boundaries. In state I, the number of the corrosion pits increase (Figure 7d). There are evident peeling marks on the surface (Figure 7e). The morphologies of pits change from open-type to narrow-type, presenting a tiny outlet with a large cavity structure (Figure 7f). Corrosion develops to the inner areas of the sample, indicating that the dissolution rate inside the pits is greater than that of the surface. Similar to state R, a "bifurcation" corrosion gap still appears around the pits.



Figure 7. SEM morphologies of the corrosion samples in state R (a-c) and state I (d-f).

A thermal scanning electron microscope (CSLM) was used to observe 3D morphologies of the typical corrosion pits in state R (Figure 8a–c) and state I (Figure 8d–f). It is more

intuitive to prove that both the area and depth of the corrosion pits in state I exceed those in state R. Local surface bulging at the edge is concluded to be the common accumulation of corrosion products. The overall surface in state R exhibits as relatively smooth, with the products invisible, which indicates that the corrosion is more uniform. We randomly measured the depths of pits in R and I (Figure 8g) and averaged the depths as 4.12 μ m and 59.71 μ m, respectively (Figure 8h). Therefore, the average pit depth in state I is about 15 times larger than state R.



Figure 8. Three-dimensional morphologies of the corrosion pits in state R (**a**–**c**) and state I (**d**–**f**) and depth of corrosion pits (**g**,**h**).

Analyzing metallographs of state R, the corrosion pits mostly initiate at α grain boundaries (Figure 9a) and α/γ phase boundaries (Figure 9b), part of which arrange neatly along phase boundaries and spread into α (as shown in the yellow circle). In state I, the initiation sites of the corrosion pits remain the same. Nevertheless, the pits formed at α/γ phase boundaries expand or even cover γ entirely (as shown in the red circle). In addition, rosary-liked pits are found initiated around IA that have precipitated at α grain boundaries (Figure 9d), while the IA itself is hardly eroded. It is also observed in Figure 9d that no pits arise around the IA in the internal α grains. Therefore, the occurrence of corrosion pits is also related to the location of IA.



Figure 9. Optical morphologies of the corrosion pits in state R (a,b) and state I (c,d).

4. Discussion

IA precipitates at ferrite (α) grain boundaries or the interior of α grains in the cooling process from hot-rolled temperatures and enriches in N element. The existence of IA significantly deteriorates the pitting corrosion resistance of DSS. Therefore, the formation mechanism of IA and its behavior during the corrosion procedure will be discussed.

4.1. Precipitation Mechanism of Isolated Austenite

As a metastable structure, the precipitation of IA has two indispensable conditions: solution temperature and cooling rates, which are analyzed in detail below, respectively.

4.1.1. Solution Temperature

The composition of N element in α and austenite (γ) of S32750 DSS at different solution temperatures was calculated by Thermal-calc software (TCFE12 database, Thermal-calc 2016b, Thermo-Calc Software Company, Stockholm, Sweden). The results in Table 3 indicate that N highly concentrates in γ , and the distribution coefficient in two phases (element ratio of α/γ) is as low as 0.1. N increases gradually in α with the increase in temperature, while higher N content leads to a greater nucleation driving force. During the subsequent rapid cooling, IA precipitates due to the supersaturation of N.

Table 3. N contents in α and γ under different temperatures in S32750 (mass. %).

Temperature/°C	1200	1150	1100
α	0.049	0.034	0.023
γ	0.221	0.237	0.247
Distribution coefficient (α/γ)	0.22	0.14	0.09

4.1.2. Cooling Rates

The influence of cooling rates on the formation mechanism of isolated austenite can be discussed from the perspective of diffusion kinetics. In DSS, α and γ both belong to the cubic crystal system. Assuming that the internal atoms jump randomly, the atomic random walk model in a cubic crystal system is

$$\overline{R_n^2} = 6Dt \tag{4}$$

where R_n^2 is the average square of the distance between final position and original position after the atom jumping for n times; 6 refers to the six directions of atoms in space (meaningly upper, lower, anterior, posterior, left and right); *D* is the diffusion coefficient; and *t* is the atomic diffusion time. The relationship between diffusion coefficient *D* and temperature *T* follows the Arrhenius Formula (Equation (5))

$$D = D_0 \exp(-\frac{Q}{RT}) \tag{5}$$

where D_0 is the frequency factor; Q is diffusion activation energy; and R is the molar gas constant. Combining Equations (4) and (5), we can predict diffusion distance (r) of the atom at a certain temperature and time, as is expressed in Equation (6).

$$r = \sqrt{\overline{R_n^2}} = \sqrt{6tD_0 \exp(-\frac{Q}{RT})}$$
(6)

The COMSOL software (COMSOL 6.0, COMSOL AB, Stockholm, Sweden) was used to simulate the time cost during cooling with the results listed in Table 4. Table 5 is the D_0 and Q of N, Cr, Ni, and Mo in S32750 DSS. Combined with Table 4 and Equation (6), diffusion distance of the elements above in the process of water cooling from 1200 °C, 1150 °C or 1100 °C to room temperature were calculated, respectively, as shown in Table 6.

Table 4. Time cost during water cooling from 1200 °C, 115 °C and 1100 °C (s).

Temperature/°C	1200	1150	1100		
Time/s	10	9.60	8.80		

Table 5. D_0 and Q of different elements in S32750 duplex stainless steel.

Elements	Ν		Cr		Мо		Ni	
Base metal	α-Fe	γ-Fe	α-Fe	γ-Fe	α-Fe	γ-Fe	α-Fe	γ-Fe
$\frac{D_0/\mathrm{cm}^2 \cdot \mathrm{s}^{-1}}{Q/\mathrm{KJ} \cdot \mathrm{mol}^{-1}}$	0.0078 79.10	0.2 151.00	8.52 250.80	10.80 291.80	1.30 229.00	0.036 240.00	9.9 259.20	3 314.00

Table 6. Diffusion distance of elements during water cooling from 1200 °C, 1150 °C and 1100 °C (μm).

Temperature/°C	1200	1150	1100	1200	1150	1100	1200	1150	1100	1200	1150	1100
Elements		Ν			Cr			Ni			Mo	
γ	36.4	28.7	21.8	0.85	0.55	0.34	0.18	0.11	0.07	0.41	0.28	0.19
α	135.4	118.4	100.4	4.04	2.76	1.80	3.09	2.09	1.34	3.84	2.71	1.82

Parts of γ transform into α during its high-temperature solution state, which results in an approximate 1:1 balance between α and γ being destroyed in the original structure. Accompanied by the migration of atoms, γ reprecipitates from α in the subsequent cooling process. The calculation results demonstrate that the diffusion distances of Cr, Mo and Ni in α are all less than 5 μ m; that is, these three elements distribute uniformly at the initial stage of cooling. As a long-range diffusion element [12], N migrates farther than other elements. The reduction in temperature promotes N atoms diffusing from α to γ . For the N atoms near the α/γ phase boundaries, enough time is provided to diffuse into γ , following the decrease in N partially with no isolated austenite precipitates. However, N atoms at the center of α remain invariant, attributed to the inadequate time transiting into γ . When the temperature reduces below 1100 °C, the N content exceeds its solubility in α and then precipitates in the form of IA, which concentrates N locally. In addition, the grain boundary of α is a favorable nucleating position for IA due to its high-density dislocation [13]. The tiny-sized γ precipitates in diffusion type tend to conform with the K-S orientation relationship with α [14]. Investigating the solution treatment of state R, it can be speculated that the metastable IA formed during the hot-rolled procedure can be fully homogenized by reheating to 1150 °C. The supersaturated N in α diffuses into γ thoroughly with furnace cooling from 1150 °C to 1100 °C, which lowers the element segregation and inhibits the precipitation of IA. For state I, the hot-rolled microstructure is kept at 1100 °C for 1 h. The solution temperature is not enough to provide diffusion driving force to homogenize the segregation elements in IA, which results in quantities of IA being retained in state I.

In general, the precipitation of isolated austenite is the combination of "solution temperature and cooling rates". As a metastable structure, IA has the enrichment effect on N element.

4.2. Element Gradient and Pitting Corrosion Resistance

The work function detected by SKP was converted into Kelvin surface potential to indicate the difficulty level of electron escaping. The energy applied by the excitation electron rises in conditions of PREN proliferation, which results in a reduction in potential. The accumulation of corrosion products leads to the enhancement of local surface potential [15]. It is speculated that the uniform corrosion mainly occurred in this period on account of no obvious cathode or anode area appearing in state R and state I after corroding for 12 h (Figure 4). As for 24 h, the surface potential shifts positively as the potential difference enlarges. Typical cathodic and polar regions are found, which proves the generation of local corrosion and trends to develop into corrosion pits. The phenomena above performed particularly obviously in state I. Combined with the SEM (Figure 7), CSLM (Figure 8) and OM (Figure 9) observations of corrosion pits in states R and I, we summarized that compared with state R, local corrosion is more severe in state I, with corrosion products accumulating and the pits initiated more frequently. The pitting corrosion resistance significantly induces in state I. Analyzing the microscopic data, the influence of phase ratio and the precipitated phases on pitting corrosion resistance can be disregarded. Combined with the changes in microstructure, two major factors, including the concentration of N in IA, and the increased initiation of corrosion pits, are expected to reduce pitting resistance. A detailed discussion will be provided in the following sections.

4.2.1. Element Contents

Element contents exhibit a remarkable effect on pitting corrosion resistance. As listed in Table 1, IA reduces the PREN value of original austenite in state I, and α shows the lowest PREN value. The pitting resistance of DSS depends on the minimum PREN phase; thus, α is preferentially corroded. The locally etched original austenite in state I also proved the reduced PREN value of γ_I . IA causes the segregation of N and the corresponding poverty of N in the surrounding area. The element gradient between α /IA further increases accordingly. In general, the element dilution area performs weak corrosion resistance, which tends to form galvanic corrosion. Therefore, local corrosion is more severe than average corrosion. Current density also turns higher due to the variation in element gradient and promotes the aggravation of pitting corrosion [16]. An active–passive cell formed inside and outside the corrosion pits and local corrosion spreads around. The increased micro-current density in the vicinity of IA accelerates anodic dissolution rates inside the pits, which continuously leads to deeper expansion and keeps the surface of pits small [17]. Finally, we summarize the sequence of pitting corrosion resistance of duplex stainless steel in the presence of IA: α – γ –IA.

4.2.2. Specific Interfaces

Corrosion pits mainly generate at α grain boundaries or α/γ phase boundaries in state R (Figure 9). As the defect region of crystal, phase boundaries have a discontinuous composition with greater local differences and quantities of active positions. Defects are more likely to appear in these regions, which are also the main positions for pitting

nucleation [18]. Although α grain boundaries have corrosion pits observed, they show relatively better stability compared with α/γ phase boundaries. The Cl⁻ are adsorbed at phase boundaries and rupture the surface, and following, the corrosion cracks act as new active adsorption points and expand along the unstable phase boundaries or grain boundaries, as circled in yellow in Figure 7.

For the corrosion process involving isolated austenite, several pits are founded at the α /IA interfaces. Compared with the IA precipitated from interior α , IA distributed intermittently at α grain boundaries increases the unstable interface between IA and α in a unit area, which intensifies the galvanic corrosion effect, providing favorable positions for corrosion pits.

5. Conclusions

The current work presents a comprehensive study on the formation mechanism of isolated austenite (IA) and its influence on pitting corrosion resistance of S32750 DSS. The main findings are:

- (1) Isolated austenite can be considered to be the product of an uneven diffusion of elements during rapid cooling from high temperatures, which mainly nucleates at ferrite grain boundaries or as intragranular ferrite grains, and presents a K-S orientation relationship with ferrite. N element segregates in IA.
- (2) With the precipitation of IA, the element concentration gradient is partially enhanced, leading to more frequent local corrosion. Pitting corrosion resistance significantly induces with the pitting depth increases by nearly 15 times. IA precipitated at ferrite grain boundaries furthers the deterioration of the pitting corrosion resistance.
- (3) The element redistribution phenomenon brought about by IA diminishes the PREN value of original austenite; thereby, the precedence order of pitting corrosion in DSS is: ferrite–austenite–IA.

Author Contributions: Conceptualization, X.W. and Z.S.; methodology, X.W., H.F. and W.Z.; validation, J.H.; formal analysis, X.W. and Z.B.; investigation, X.W. and Y.Z.; writing—original draft preparation, X.W.; writing—review and editing, J.H. and Z.S.; visualization, X.W.; supervision, Z.S.; project administration, Z.S. and H.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Wu, X.H.; Song, Z.G.; Liu, L.Z.; He, J.G.; Zheng, L. Effect of secondary austenite on fatigue behavior of S32750 super duplex stainless steel. *Mater. Lett.* 2022, 332, 132487. [CrossRef]
- Cojocaru, E.M.; Raducanu, D.; Nocivin, A.; Cinca, I.; Vintila, A.N.; Serban, N.; Angelescu, M.L.; Cojocaru, V.D. Influence of aging treatment on microstructure and tensile properties of a hot deformed UNS S32750 super duplex stainless steel (SDSS) alloy. *Metals* 2020, 10, 353. [CrossRef]
- 3. Li, J.; Shen, W.; Lin, P.; Wang, F.; Yang, Z. Effect of solution treatment temperature on microstructural evolution, precipitation behavior, and comprehensive properties in UNS S32750 super duplex stainless steel. *Metals* **2020**, *10*, 1481. [CrossRef]
- Gennari, C.; Lago, M.; Bögre, B.; Meszaros, I.; Calliari, I.; Pezzato, L. Microstructural and corrosion properties of cold rolled laser welded UNS S32750 duplex stainless steel. *Metals* 2018, 8, 1074. [CrossRef]
- Helbert, V.S.; Nazarov, A.; Vucko, F.; Rioual, S.; Thierry, D. Hydrogen effect on the passivation and crevice corrosion initiation of AISI 304 using scanning kelvin probe. *Corros. Sci.* 2021, 182, 109225. [CrossRef]
- Nazarov, A.; Vucko, F.; Thierry, D. Scanning kelvin probe for detection of the hydrogen induced by atmospheric corrosion of ultra-high strength steel. *Electrochim. Acta* 2016, 216, 130–139. [CrossRef]
- Wu, X.H.; Song, Z.G.; Wang, B.S.; Wu, M.H.; Nai, Q.L.; Yao, L.; Feng, H.; Zheng, W.J. Morphologies of secondary austenite in 2507 duplex stainless steel after heat treatment. *J. Iron Steel Res. Int.* 2022, 29, 994–1003. [CrossRef]
- Haghdadi, N.; Cizek, P.; Hodgson, P.D.; Tari, V.; Rohrer, G.S.; Beladi, H. Effect of ferrite-to-austenite phase transformation path on the interface crystallographic character distributions in a duplex stainless steel. *Acta Mater.* 2017, 145, 196–209. [CrossRef]

- 9. Du, J.; Zhang, W.Z.; Dai, F.Z.; Shi, Z.Z. Caution regarding ambiguities in similar expressions of orientation relationships. *J. Appl. Crystallogr.* **2016**, *49*, 40–46. [CrossRef]
- Tan, H.; Jiang, Y.; Deng, B.; Tao, S.; Xu, J.; Li, J. Effect of annealing temperature on the pitting corrosion resistance of super duplex stainless steel UNS S32750. *Mater. Charact.* 2009, 60, 1049–1054. [CrossRef]
- 11. An, L.C.; Cao, J.; Wu, L.C.; Mao, H.H.; Yang, Y.T. Effects of Mo and Mn on pitting behavior of duplex stainless steel. *J. Iron Steel Res. Int.* **2016**, 23, 1333–1341. [CrossRef]
- 12. Ramirez, A.J.; Lippold, J.C.; Brandi, S.D. The relationship between chromium nitride and secondary austenite precipitation in duplex stainless steels. *Metall. Mater. Trans. A* 2003, 34, 1575–1597. [CrossRef]
- Jeon, S.H.; Kim, H.J.; Park, Y.S. Effects of inclusions on the precipitation of chi phases and intergranular corrosion resistance of hyper duplex stainless steel. *Corros. Sci.* 2014, 87, 1–5. [CrossRef]
- 14. Chen, C.Y.; Yen, H.W.; Yang, J.R. Sympathetic nucleation of austenite in a Fe–22Cr–5Ni duplex stainless steel. *Scr. Mater.* **2007**, *56*, 673–676. [CrossRef]
- Shubina Helbert, V.; Nazarov, A.; Vucko, F.; Larché, N.; Thierry, D. Effect of Cathodic Polarisation Switch-Off on the Passivity and Stability to Crevice Corrosion of AISI 304L Stainless Steel. *Materials* 2021, 14, 2921. [CrossRef] [PubMed]
- Ma, C.Y.; Zhou, L.; Zhang, R.X.; Li, D.G.; Shu, F.Y.; Song, X.G.; Zhao, Y.Q. Enhancement in mechanical properties and corrosion resistance of 2507 duplex stainless steel via friction stir processing. *J. Mater. Res. Technol.* 2020, *9*, 8296–8305. [CrossRef]
- 17. Tarantseva, K.R. Models and methods of forecasting pitting corrosion. Prot. Met. Phys. Chem. Surf. 2010, 46, 139–147. [CrossRef]
- 18. Guo, L.Q.; Bai, Y.; Xu, B.Z.; Pan, W.; Li, J.X.; Qiao, L.J. Effect of hydrogen on pitting susceptibility of 2507 duplex stainless steel. *Corros. Sci.* 2013, 70, 140–144. [CrossRef]