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Sigma Phase Precipitation and Properties of Super-duplex Stainless Steel UNS S32750 Aged at the Nose Temperature

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Abstract: The nose temperature for σ-phase precipitation in super-duplex stainless steel (SDSS) UNS S32750 was evaluated by hardness method. Color-optical microscopy, scanning electron microscopy, energy spectrum analysis, impact and corrosion testing were carried out to investigate characteristics of microstructure and properties of the SDSS aged at the nose temperature. The experimental results indicate that the nose temperature of precipitation is 920 ℃ and aging at this temperature tiny σ phases can precipitate at phase interfaces or ferrite grain boundaries within 2 min. Prolonging aging duration the amount of σ-phase increases and a dual structure with σ and γ is obtained when aging for 120 min. The precipitation of σ-phase leads to severe deterioration in impact toughness (longitudinal/transverse direction) and corrosion resistance of SDSS.

Key words: super-duplex stainless steel; aging; σ-phase; impact toughness; corrosion resistance

1 Introduction

Super-duplex stainless steel (SDSS) has been applied widely in the marine and petrochemical industries, especially in aggressive corrosion environments such as pressure vessels and heat exchangers[1]. All these applications are attributed to its attractive combination of mechanical properties, corrosion resistance and welding performance. It is well known that SDSS is characterized by an austenite/ferrite (γ/α) dual phase structure with no other precipitates, and the best comprehensive property can be obtained when containing approximately equal amounts of the two phases. However, during hot working or welding, several microstructural changes can happen in SDSS[2]. A number of undesirable precipitates having detrimental effects on the behavior of the steel, such as sigma (σ), nitrides (Cr_2N), secondary austenite (γ_2) and chi (χ), may appear in α areas and/or at γ/α interfaces in the 600-1000 ℃ range[3, 4]. Generally, σ-phase is considered as the most harmful phase because of its rapid precipitation rate and strong influence on the toughness and corrosion resistance[5]. As for σ precipitation, most investigations were focused on isothermal aged duplex stainless steel UNS S31803. Many results have shown that σ is a brittle phase enriched Cr and Mo elements, and the surrounding Cr-depleted areas are the reason for the decrease in corrosion resistance. The formation mechanism of σ-phase is a eutectoid reaction of $\alpha\rightarrow\gamma_2+\sigma$[3-7]. SDSS has high alloying concentrations, which tends to accelerate the kinetics of precipitation of σ-phase[8]. In this paper, the influence of aging time on microstructure, toughness and corrosion properties of SDSS UNS S32750 was investigated under the nose temperature for σ precipitation.

2 Experimental

The material studied was commercial SDSS UNS S32750. Table 1 gives its chemical composition. This material was fabricated to hot rolled plates with 12 mm thickness, and solution treated at 1080 ℃ for 50 min following by water quenching. The temperature of 1080 ℃ was chosen to obtain the even microstructures with approximately equal volume fractions of austenite and ferrite phases. Solution treated specimens were subjected to aging at 750-1000 ℃ for 60 min to evaluate the nose temperature for σ-phase formation.

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Then, the aging treatments at the nose temperature for various time intervals from 2 to 120 min were carried out to investigate phase transformation behavior and its effect on the corresponding toughness and corrosion resistance.

Table 1 Composition of SDSS UNS S32750/wt%

C	Cr	Ni	Mo	Si	Mn	Cu	N	Fe
0.02	25.3	7.0	4.0	0.8	1.2	0.5	0.3	Bal.

For observation of microstructure, specimens after etched were examined by a color-optical microscope (model: Canon Powershot S70) and a scanning electron microscope (SEM, model: Leo438VP). Meanwhile, energy spectrum analysis was conducted to study the chemical composition of σ and γ_2. The volume fractions of phases in heat treated specimens were estimated by automatic image analysis computer program attached to the optical microscope. An area of 250 μm×250 μm was analyzed and each value was an average recorder of 5 observation times.

The Brinell hardness of specimens aged at different temperatures was measured by HB-3000B hardness tester under 3000 kg load for 15 s. At least 3 indentations were taken on each specimen and mean hardness values were reported. Instrumented Charpy-V impact specimens were prepared in standard form of 10 mm×10 mm×55 mm. Impact test was carried out at room temperature, using a JB-30B impact machine with maximum capacity of 650 J. Following the impact tests, the fracture mechanisms were determined by observation of the fractured surfaces using SEM.

The corrosion resistance of specimens after different heat treatments was evaluated by an FS-04 corrosion test instrument according to GB/T17897-1999. The electrolyte was 6% $FeCl_3$ and 0.05 mol/L HCl at 35 ℃, and measurements were taken after 24 h of immersion in the electrolyte. The measuring unit of pitting factor was g/m^2h. To characterize the preferential pit location, specimens with different aging and erosive time were cleaned and analyzed under SEM with backscattered electron (BSE) detecter.

3 Results and Discussion

3.1 Nose temperature evaluation

In order to determine the most sensitive temperature of σ-phase formation, specimens were aged between 750 ℃ and 1000 ℃ for 60 min. The mean hardness of the specimen exhibits a convexity curve relationship with aging temperatures, as shown in Fig.1. This is correlated with the amount of σ-phase in the microstructure. Due to its hard characteristic[4], the more the content of σ-phase is, the higher the hardness value is. From 750 to 920 ℃, σ-phase increases with aging temperatures. While, a sharp decrease in hardness after 920 ℃ can be explained by the re-dissolution of σ precipitates at higher temperatures. Therefore, the 920 ℃ is the most sensitive temperature for σ-phase precipitation, considering as the nose temperature of phase transformation.

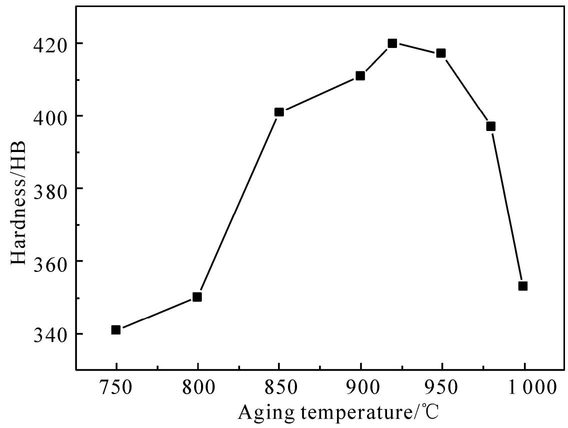

Fig.1 The relationship between aging temperature and hardness

3.2 σ-phase precipitation

Fig.2(a) is the micrograph of solution treated specimen along the longitudinal section. Austenite phases, the banded texture of elongated islands, are uniformly embedded in the ferrite matrix with no other emerging. The volume fraction of austenite phase measured by quantitative metallography is about 55%. Figs.2(b-d) show the microstructural changes during isothermal aging at 920 ℃ with aging time. It is clear that SDSS with high alloying elements is more sensitive to σ precipitation. For the specimen aged for 2 min, a huge of tiny σ particles can be found to precipitate at narrow ferrite area along the phase boundaries or grain boundaries of γ/α and α/α. These interfaces have been well known as the preferential nucleation sites for the heterogeneous precipitation of σ-phase[6]. Prolonging the aging time, both size and amount of σ-phase increase quickly and σ-phase grows into the adjacent ferrite region, and then merges it. Therefore, the ferrite phase content decreases with increasing σ-phase precipitation and an increase in austenite phase can also be found. After aging for 120 min, ferrite phase disappears and a two-phase microstructure comprised of σ and austenite is obtained. Phase content of σ-phase and ferrite as a function of aging time at 920 ℃ are plotted in Fig.3, respectively. It is clear that σ-phase indeed increases with aging time, in particularly in the period from 0 to 5 min, in which its precipitation rate is the greatest. But from 5 to 120 min, σ-phase increment tends to slow down. Aging within 120 min, σ-phase transformation would be completed, which is identical with the previous micrographs.

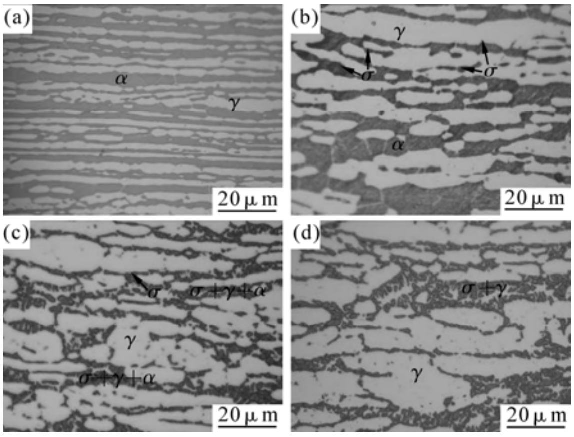

Fig.2 Optical metallograph of aged specimens at the nose temperature (920 ℃) for: (a) 0 min, (b) 2 min, (c) 30 min, (d) 120 min

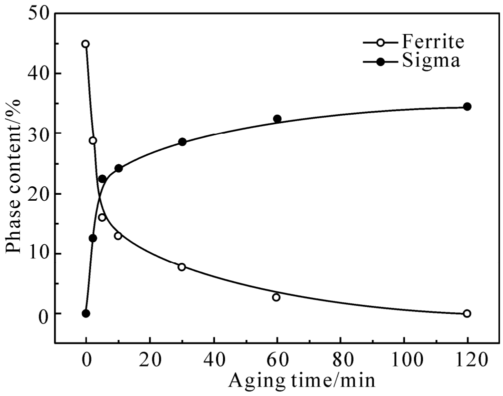

Fig.3 Phase contents of σ and ferrite in SDSS UNS S32750 aged at 920 ℃ for different aging time

Fig.4 shows the secondary electron (SE) image of scanning electron micrograph obtained from the specimen aged at 920 ℃ for 60 min. Reticular σ precipitates distribute in the original ferrite matrix and the ferrite phase in this condition has been little left. The white area is considered as σ particles and the bright contrast shows the σ-phase contains elements of high atomic number[9]. As we known that the differential distribution of the alloying elements in the ferritic and austenitic phase - the richness of Cr and Mo in ferrite leads to the preferential precipitation of σ-phase from ferrite. Meanwhile, the higher diffusion rate of alloying elements in the ferritic phase, about 100 times faster than in austenite[10], is also in favor of σ-phase growing into the ferrite. Owing to the depletion in Cr and Mo and enrichment in Ni of the ferrite close to σ-phase region accompanying with σ-phase precipitation, this ferrite becomes unstable and transforms into a new austenite which can be clearly observed under SEM, called second austenite (γ_2) to distinguish from the original austenite[9, 11]. In this experiment, the formation of σ-phase is decomposed by a ferrite phase eutectoid into σ and γ_2, which does not run counter to the previous studies[6,9, 11].

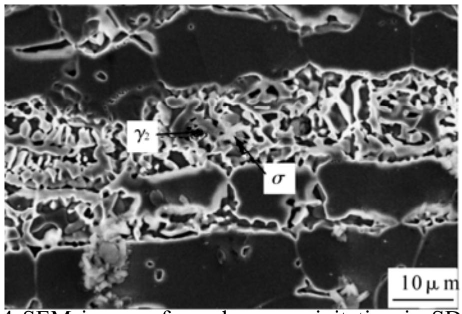

Fig.4 SEM image of σ-phase precipitation in SDSS UNS S32750 aged at 920 ℃ for 60 min

3.3 Impact toughness

Charpy impact toughness of aged specimens with longitudinal and transverse direction was determined at room temperature. The results are shown in Fig.5. It can be seen that both directions toughness decrease with aging time. A drastic drop in toughness occurs within the aging time of only 5 min with the impact energy decreasing from the solubilized 260 J to 28 J. This severe deterioration in toughness is attributed to the precipitation brittle phase- σ. It is also found that the impact energy of transverse direction is lower than that of longitudinal direction within 10 min, which may be due to cracks are prone to run through ferrite phase over long distances.

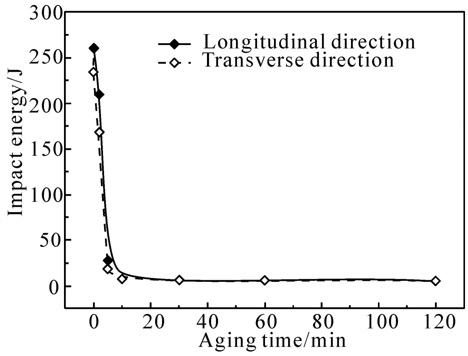

Fig.5 Impact energy as function of aging time at 920 ℃

Fig.6 shows microfracturegraphs after impact testing for different heat treated specimens. A typical ductile failure mode can be seen in Fig.6 (a) with solution treated. However, the fracture surface aged for 10 min provides evidence to indicate that small quasi-cleavage facets are distributed uniformly and tearing ridges around the periphery of the facets can be seen clearly, as shown in Fig.6 (b). Due to the TCP structure of σ-phase, little deformations in this condition may cause transcrystalline, finely structured brittle fractures of σ-phase particles[7]. Therefore, the optimum heat treatments and quick cooling at sensitive temperatures of σ precipitation must be taken to avoid its effect on the toughness of this steel.

3.4 Corrosion resistance

Fig.7 shows the influence of aging time on corrosion rate of the SDSS. The corrosion rate increases rapidly with aging time and the increment rate within 5 min is the fastest. Therefore, the corrosion resistance of the steel deteriorates severely. The surface appearance of corroded specimen aged for 5 min (immersed for 1 h) is shown in Fig.8(a), using the BSE mode. Pits with diameter of 3 μm initiate close to the σ particles. After longer aging and immersing duration, a high density of pits around σ-phase was found in Fig.8(b). This can be explained by different chemical composition in the two phases, namely the pitting resistance equivalent number (PREN) of the two phases. It is confirmed that the higher the value of PREN is, the better the pitting corrosion resistance can be[12, 13]. Energy spectrum analyses on σ and γ_2 are listed in Table 2. Due to the depletion of Cr and Mo, the corrosion resistant elements, in the new formed austenite (γ_2) accompanied with σ-phase precipitation, this austenite has the low PREN value, exhibiting poor corrosion resistance. So a corroded reticulation forms in the γ_2 region with increasing aging time, providing a path for the corrosive environment to penetrate from the outer surface to inside of the specimens[13]. The increase in amounts of σ and γ_2 results in the loss of resistance on corrosion.

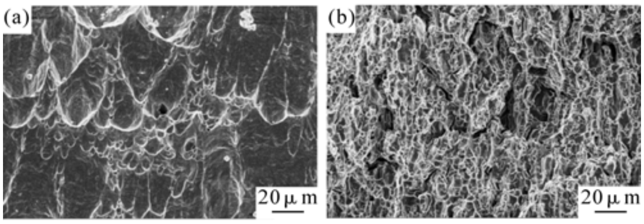

Fig.6 Fracture after impact testing (longitudinal direction): (a) solution treated, (b) aged at 920 ℃ for 10 min

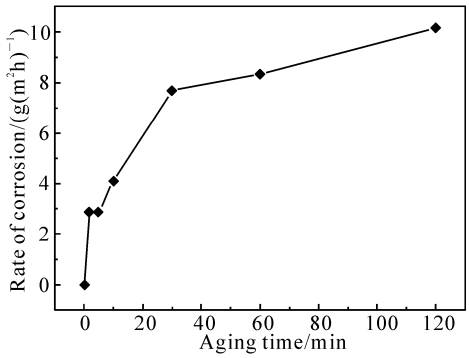

Fig.7 Corrosion rate as function of aging time at 920 ℃

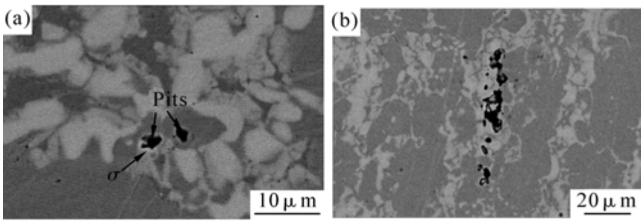

Fig.8 Surface appearance of corroded specimens, BSE images: (a) Aged at 920 ℃ for 5 min (immersed for 1 h), (b) Aged at 920 ℃ for 60 min (immersed for 6 h)

Table 2 Energy spectrum analysis of σ and γ_2 in the specimen aged at 920 ℃ for 5 min

Phase	Composition/%				
	Cr	Mo	Ni	Si	Fe
σ	27.62	7.86	5.43	1.47	57.62
γ_2	24.0	2.9	10.07	1.05	61.99

4 Conclusions

In this work, 920 ℃ is determined as the nose temperature for σ-phase formation in SDSS UNS S32750 and aging above this temperature the σ-phase seems to be re-dissolved. When aging at 920 ℃, the following conclusions are obtained:

a) σ-phase, with rather fast formation rate, precipitates at phase interfaces or ferrite grain boundaries within 2 min. With increasing aging time σ-phase coarsens and grows into ferrite phase. The ferrite phase is decomposed into σ and γ_2.

b) The impact toughness decreases obviously with aging time owing to the forming and growing of σ-phase and there is a drastic decrease within 5 min. Compared with the impact energy of longitudinal direction, transverse direction presents lower toughness at any aging time.

c) Increasing aging time the corrosion resistance reduces. The main reason for this is that a new austenite (γ_2) depleted Cr and Mo forms surrounding the σ-phase.

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