Early Stages of Deleterious Phases in Super and Hyper Duplex Stainless Steel and Their Effect on Toughness

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Abstract: Duplex stainless steels combine excellent mechanical properties with good corrosion resistance. Consequently, they are in frequent use in various highly demanding applications, like Oil & Gas, chemical processing, pulp and paper, and desalination plants. Due to their high alloying contents, super and hyper duplex are susceptible to the formation of detrimental secondary phases such as chromium nitrides, chi, and sigma phase.

The presented investigation deals with the precipitation of those phases in super and hyper duplex by employing rapid isothermal heat treatments on a Gleeble 3800 thermo-mechanical simulator. The Charpy-V impact toughness was measured as a function of the sensitization time and temperature in order to characterise their effect on low temperature toughness. Both alloys suffer from severe embrittlement at the early stages of sensitization. In super duplex at 850 °C for 20 s, chromium nitrides are precipitated, a chi-phase is formed after 200 s, and small amounts of sigma after 500 s. In hyper duplex, the precipitation sequence is the same but significantly faster. In this alloy, the sigma-phase is encountered after merely 50 s and ferrite is completely consumed after 500 s.

Keywords: Super duplex stainless steel, Hyper duplex stainless steel, Isothermal heat treatment, Sigma-phase, Chi-phase, Chromium Nitride, Precipitation, Embrittlement, Impact toughness

Frühphasen schädlicher Phasen in Super- und Hyperduplex-Edelstahl und ihr Einfluss auf die Zähigkeit

Zusammenfassung: Duplex-Edelstähle verbinden hervorragende mechanische Eigenschaften mit guter Korrosionsbeständigkeit. Daher werden sie häufig in verschiedenen, sehr anspruchsvollen Anwendungen eingesetzt, wie z. B. in der Öl- und Gasindustrie, der chemischen Industrie, in der

Zellstoff- und Papierindustrie sowie in Entsalzungsanlagen. Super- und Hyperduplex sind aufgrund ihres hohen Legierungsanteils anfällig für die Bildung schädlicher Sekundärphasen wie Chromnitride, Chi- und Sigma-Phase.

Die vorgestellte Untersuchung beschäftigt sich mit der Ausfällung dieser Phasen im Super- und Hyperduplex durch den Einsatz schneller isothermer Wärmebehandlungen auf einem thermomechanischen Gleeble 3800 Simulator. Die Charpy-V Kerbschlagzähigkeit wurde als Funktion der Sensibilisierungszeit und -temperatur gemessen, um ihren Einfluss auf die Tieftemperaturzähigkeit zu charakterisieren. Beide Legierungen weisen in den frühen Phasen der Sensibilisierung eine starke Versprödung auf. Im Superduplex bei 850 °C für 20 s werden Chromnitride ausgefällt, nach 200 s bildet sich eine Chi-Phase und nach 500 s kleine Mengen Sigma. Im Hyperduplex ist die Fällungssequenz gleich, aber deutlich schneller. Bei dieser Legierung tritt die Sigma-Phase bereits nach 50 s ein und Ferrit ist nach 500 s vollständig verbraucht.

Schlüsselwörter: Superduplex-Edelstahl, Hyperduplex-Edelstahl, Isotherme Wärmebehandlung, Sigma-Phase, Chi-Phase, Chromnitrid, Fällung, Versprödung, Schlagfestigkeit

1. Introduction

Duplex stainless steels consist of balanced amounts of ferrite and austenite, resulting in high corrosion resistance and excellent mechanical properties [1]. By increasing the alloying content, super and hyper duplex were developed [2]. Both duplex steels are stronger than equally resistant austenitic stainless steels and considerably cheaper than nickel base alloys. Hence, they represent a cost effective alternative when mechanical strength and corrosion resistance are required at the same time. However, the high alloying content in super and hyper duplex may result in the precipitation of unwanted detrimental phases. The most prominent in that regard are chromium nitrides, chi- and sigma-phase. They typically form between 700–1000 °C,

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TABLE 1
Chemical composition and PREN(W) of SDSS and HDSS, in wt. %

	Si	Mn	Cr	Mo	Ni	W	Cu	N	PREN(W)
SDSS	0.25	0.50	25.35	3.58	7.48	0.53	0.57	0.23	41.7
HDSS	0.19	2.93	26.30	4.61	6.95	0.45	0.20	0.37	48.2

due to inadequate cooling or excessive reheating during fabrication, processing, or welding. These secondary phases result in severe embrittlement and reduce the corrosion resistance due to segregating alloying elements.

Proper information about the precipitation kinetics of intermetallic phases in super duplex is available in the literature [3–6], but it is limited for hyper duplex [7, 8]. However, most of the reported investigations consisted of quenching from the solution annealing temperature with subsequently reheating to a designated sensitization temperature. In many cases, this was done with a slow heat transfer from air to steel. Hence, short tempering durations include a substantial uncertainty in respect to the actual material temperature. This blurs transformation temperatures and kinetics substantially.

Since the formation of deleterious phases in super and hyper duplex occurs rapidly, a precise time-temperature control is necessary. To ensure that in the presented investigation, a Gleeble 3800 thermo-mechanical simulator with conductive heating was used to apply a proper heat treatment.

2. Experimental

Both investigated Super- (SDSS) and Hyperduplex (HDSS) were melted in an electric arc furnace, subsequently treated by argon oxygen decarburization and casted in blocks. The castings were forged on a rotary forging machine to diameters of 205 mm and 168 mm for SDSS and HDSS, respectively. The concluding solution heat treatment consisted of soaking and water quenching. SDSS was annealed at 1100 °C for 1 h and HDSS at 1120 °C for 1 h. The chemical compositions and PREN(W)-values for both investigated alloys are shown in Table 1.

Samples with 10.2 × 10.2 × 100 mm were machined from the forgings in the longitudinal direction. The sensitization treatments were carried out on a Gleeble 3800 by conductive heating. The sample arrangement can be seen in Fig. 1.

Copper jaws were used as sample holders and heat sinks, with a free span of 40 mm. The thermo-couple was centered between the jaws. According to [9], the chosen arrangement results in a near constant temperature field, expanding roughly 10 mm from the center. The heating rate from ambient to the soaking temperature was 200 K/min. The soaking temperatures for SDSS and HDSS were 1100 °C and 1120 °C, respectively, for 300 s each. Soaking was followed by rapidly quenching to the sensitization temperature (750–1000 °C), which was maintained for 20–500 s. After sensitizing, the heat treatment was concluded by rapidly quenching to room temperature in order to minimize further uncontrolled phase transformations. An exemplary presentation of an applied heat treatment can be seen in Fig. 1. Rapid quenching always refers to the maximum amount of free cooling, without further external heat input.

After applying the heat treatment, a notch was machined at the connecting sites of the thermo-couple to ensure a constant temperature in the tested volume.

The impact toughness was determined according to [10], at a temperature of –46 °C. Electrochemical etching with 4% NaOH was applied to reveal the microstructure in the tested area after impact testing. A SEM Zeiss Ultra 55 was used for further microstructural characterisation; all samples were grinded and subsequently polished with OPS.

3. Results

As shown in Fig. 2, a sensitization treatment at 1000 °C for 20 s in HDSS yields an impact toughness of 30 J. Maintaining this temperature up to 500 s does not result in a reduced toughness. By decreasing the temperature to 950 °C, no initial decline in toughness is visible after 20 s. However, an extended sensitization result in a deteriorating impact toughness, which drops to 5 J after 500 s. A further reduction in temperature to 900 or 850 °C results in 30 J after 20 s, and longer treatments cause a more pronounced drop compared to 950 °C. Maintaining 850 °C and 900 °C for 200 s or

Fig. 1: Sample arrangement in the Gleeble during heat treating and an obtained time-temperature profile for super duplex when annealing at 850 °C for 20 s

Fig. 2: Charpy-V impact toughness of HDSS at sensitization temperatures between 750 to 1000 °C for 20–500 s

Fig. 3: Charpy-V impact toughness of SDSS at sensitization temperatures between 750 to 950 °C for 20–500 s

longer reduces the toughness to 5 J. After 20 s at 800 °C, the measured toughness is 45 J. However, toughness declines when sensitizing is maintained and ultimately reaches 6 J after 500 s. At 750 °C, the impact toughness remains at approximately 30 J for durations up to 200 s. A longer sensitization results in a decrease to 20 J after 500 s. The observed decline in impact toughness between 800 to 900 °C

correlates to the logarithm of the sensitization duration, indicated by reasonably high R^2 -values.

As illustrated in Fig. 3, sensitizing SDSS at 950 °C for 200 s results in an impact toughness of 300 J, after 500 s it declines to 240 J. A reduced sensitization temperature of 900 °C results in 220 J after 20 s, which gradually declines to 10 J by extending the heat treatment up to 500 s. Further

Fig. 4: Impact toughness in SDSS and HDSS as a function of sensitization temperature with isochronal lines for 20, 50, 100 (only HDSS), 200, and 500 s of sensitization

Fig. 5: Microstructure in hyper duplex after sensitizing at 900°C for (a) 20, (b) 50, (c) 100, (d) 200, and (e) 500 s (Austenite is etched white or lightly brown, ferrite appears in a bold brown or blue)

lowering the sensitization temperature reduces toughness after 20 s; at 850°C an impact toughness of 115 J is obtained, at 800°C and 750°C it declines to 90 J. At 850°C and 800°C, the impact toughness is immediately reduced by a temperature exposure of longer than 20 s, thereby following a logarithmic trend. Whereas at 750°C no initial decline is

obtained during the first 50 s, a further temperature exposure gradually reduces the impact toughness.

Fig. 4 depicts the impact toughness of sensitized SDSS and HDSS as a function of the sensitization temperature. Isochronal lines correspond to individual tempering durations. Both alloys show a declining impact toughness with

Fig. 6: Microstructure of super duplex after sensitizing at 850 °C for (a) 20, (b) 50, (c) 200, and (d) 500 s (Austenite etches white; ferrite appears in a bold brown)

lower temperatures and longer sensitization. SDSS exhibits a more pronounced drop, mostly due to higher initial values. However, the impact toughness in HDSS is much smaller for any combination of time and temperature. Furthermore, between 800 and 950 °C, the hyper duplex shows a distinct temperature range with a very low toughness. The fastest decline occurs between 850 and 900 °C, which corresponds to the nose temperature of the hyper duplex.

During the early stages of sensitization, SDSS exhibits a low toughness below 850 °C. The lowest impact values after an extended temperature exposure is obtained at 850 °C, which corresponds to the maximum rate of embrittlement (the nose temperature).

Fig. 5a–e depicts the microstructure in HDSS at the nose temperature of 900 °C, from 20 to 500 s of sensitization. As

shown in Fig. 5a, the microstructure is free of chi or sigma after 20 s and mainly consists of ferrite and austenite. However, at some ferrite/ferrite interfaces, white fringes are detectable. Maintaining the temperature of 900 °C for 50 s, as seen in Fig. 5b, leads to small amounts of a sigma-phase near the ferrite/ferrite and ferrite/austenite interfaces. This is accompanied by a near continuous grain boundary precipitation along the ferrite/ferrite interfaces. These precipitates correspond to the chi-phase, which seems irregular and edgy, and appears to act as nucleation site for the sigma-phase. Prolonged tempering for (c) 100, (d) 200, and (e) 500 s leads to a steadily increasing phase fraction of the sigma-phase, which completely consumes ferrite after 500 s of sensitization. No indication for any transformation of austenite was found.

Fig. 6a–d shows the microstructure in SDSS at a nose temperature of 850 °C, from 20–500 s of sensitization. Similar to hyper duplex, super duplex is free of chi- and sigma-phases after 20 s, as can be seen in Fig. 6a. Occasionally, some ferrite/ferrite interfaces exhibit white fringes with black features (chromium nitrides) in their center. An extended tempering duration of 50 s, illustrated in Fig. 6b, results in a more noticeable precipitation of nitrides along the grain boundaries. However, neither chi nor sigma are detectable at this stage. After 200 s, as shown in Fig. 6c, white irregular precipitates, corresponding to the chi-phase manifested along the ferrite/ferrite interfaces, though no sigma-phase precipitated. After 500 s at 850 °C, demonstrated in Fig. 6d, small quantities of a sigma-phase eventually formed at the decorated grain boundaries, which appear to act as nucleation sites for sigma.

Fig. 7 shows a ferrite/ferrite and ferrite/austenite interface in super duplex at 850 °C after 200 s of sensitization, this corresponds to Fig. 6c. Precipitates are clearly visible

Fig. 7: Grain boundary precipitates at a ferrite/ferrite and ferrite/austenite grain boundary in super duplex at 850 °C after 200 s of sensitization

Fig. 8: Microstructure of super duplex after 50 s of sensitization at (a) 750 °C and (b) 900 °C

at both interfaces, with an overall higher amount at the ferrite/ferrite grain boundary. At this site, the precipitates appear serrated, with an alternating arrangement of two precipitate species. Both were identified by EDX as chromium nitride and chi-phase, appearing in black and white, respectively. The ferrite/austenite interface reveals a less dense occupation with precipitates, especially in regards to nitrides. Furthermore, a chi-phase appears in a smooth and rounded rather than serrated shape, compared to their appearance at the ferrite/ferrite interface.

Fig. 8a, b illustrates the microstructure in super duplex for an identical sensitization duration of 50 s, but at different temperatures. At 750 °C, as seen in Fig. 8a, fringes with chromium nitrides manifested at the ferrite/ferrite interfaces. They already cover large parts of the interface. At 900 °C, as illustrated in Fig. 8b, the microstructure is free of grain boundary precipitates and solely consists of austenite and ferrite.

4. Discussion

Regardless of the actual alloying composition, small amounts of precipitates cause severe embrittlement in super and hyper duplex stainless steels. At –46 °C even precipitate free hyper duplex hardly reaches 30 J of impact toughness and consequently falls behind super duplex, which maintains 300 J in a precipitate free condition. This difference may be caused by dissimilar ductile-to-brittle transition temperatures. Yet, due to limited information regarding the transition temperature in hyper duplex, this is up for debate. Regardless, hyper duplex exhibits a lower toughness in every tested combination of time and temperature.

Both alloys initially form chromium nitrides during the early stages of sensitization at their respective nose temperatures. Nitrides are most frequently present at the ferrite/ferrite grain boundaries. Further sensitization leads to the precipitation of the chi-phase, mainly decorating ferrite/ferrite grain boundaries and, in smaller quantities, ferrite/austenite interfaces. A longer temperature exposure results in the formation of a sigma-phase at both interfaces. This precipitation sequence is particularly well documented for super duplex, as can be seen in Fig. 6a–d. In this case, the sigma-phase is preceded by chi and chromium nitrides and is eventually formed after 500 s of sensitization. In hy-

per duplex, the precipitation at its nose temperature is considerably faster, and noticeable amounts of a sigma-phase are already present after 50 s.

Nevertheless, in both alloys, the sigma-phase is not solely responsible for a low impact toughness, especially during the early stages of sensitization. This becomes particularly obvious by comparing the high and low sensitization temperatures in the super duplex. At 900 °C and after 50 s, the microstructure is free of nitrides, and the toughness remains at 200 J. Yet, after sensitizing at 750 °C for 50 s, nitrides form, and the toughness drops to roughly 100 J. The subsequent formation of chi further reduces the toughness substantially, even before sigma precipitates. This detrimental effect of nitrides and chi is known in literature, though sigma is mostly seen as the root cause for low impact values, which is clearly not the case in the presented investigation.

These unforeseen results most likely arise from diverging heat treatment parameters between this investigation and those in literature. Firstly, most of the available literature concerns quenched and tempered material. By quenching to ambient temperature and subsequently reheating, diffusion processes may influence the precipitation sequence. Secondly, nitrides and the chi-phase form rapidly, especially at the nose temperature. Uncontrolled reheating conditions can distort early precipitation states and hide the formation of chromium nitrides and the chi-phase.

Therefore, inaccurate sensitization conditions are of particular concern for hyper duplex, with its rapid precipitation kinetics. Sigma formation occurs in under one minute of tempering, and insufficient reheating conditions would hide the detected precursor phases.

5. Conclusion

Early stages of intermetallic phases and their effect on toughness in super and hyper duplex stainless steels were investigated:

- Hyper duplex forms detrimental phases multiple times faster than super duplex, which leads to a rapid embrittlement, especially at low service temperatures.
- Minute quantities of detrimental phases result in a substantial reduction of impact toughness. No discrimina-

tion between the contributions of the individual phases was possible.

- The following precipitation sequence was observed in both alloys: chromium nitride over to chi-phase over to sigma-phase. This was shown for the peak transformation temperatures of 850°C and 900°C in super and hyper duplex, respectively.
- Chromium nitrides form especially fast at temperatures below the nose temperature and mainly cover the ferrite/ferrite interfaces.

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