

Thermodynamic modeling of chromium nitride precipitation in duplex stainless steels and weld metals

Sten Wessman

`sten.wessman@hv.se`

Swerim AB <https://orcid.org/0000-0001-5110-449X>

Elin M. Westin

voestalpine Böhler Welding Austria GmbH

Staffan Hertzman

Swerim AB

Research Article

Keywords: Duplex Stainless Steel, Welding, Heat-Affected Zone (HAZ), Grain Coarsening, Cr₂N, Precipitation, Computational Thermodynamics, DICTRA

Posted Date: September 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10840631/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Thermodynamic modeling of chromium nitride precipitation in duplex stainless steels and weld metals

Sten Wessman^{1,2,*}, Elin M. Westin³, Staffan Hertzman¹

¹ Swerim AB, Box 7047, 16407 Kista, Sweden

² Department of Engineering Science, University West, 46186 Trollhättan, Sweden

³ voestalpine Böhler Welding Austria GmbH, Böhler-Welding-Str. 1, 8605 Kapfenberg, Austria

* Corresponding author: sten.wessman@hv.se

Abstract

Duplex stainless steels (DSSs), containing roughly equal amounts of ferrite and austenite, offer an attractive combination of high strength and good corrosion resistance. The kinetics and factors controlling how fully ferritic material at temperatures near the solidus regains the desired 50/50 duplex microstructure around 1100 °C have previously been explored. The most important factor is nitrogen, present in the alloy, weld filler and shielding gas. Other important factors are ferrite grain size and cooling rate, both influencing the time available for austenite formation at temperatures >1000 °C, where kinetics remain favorable. Undesired intermetallic phases may form if the cooling rate is too slow, whereas rapid cooling rates and large ferrite grains promote chromium nitride precipitation. This study uses computational thermodynamics and the diffusion module DICTRA within Thermo-Calc to investigate how austenite formation influences nitride precipitation. The work focuses on the lean duplex grade LDX 2101, super duplex 2507, and 2509 weld metal filler. The simulations explore the influence of nitrogen content, grain size, and cooling rate on nitride precipitation. Furthermore, the commonly applied linear cooling rate in simulations is compared with non-linear conditions to evaluate their influence on nitride precipitation. Finally, the methodology developed in this work was applied to experimental data from a published study. Good agreement was obtained using the critical austenite spacing required for nitride precipitation as the comparison criterion. The simulations also reproduced the formation of nitride-free zones adjacent to austenite, indicating that high peak temperatures are required for these to form.

Keywords: Duplex Stainless Steel, Welding, Heat-Affected Zone (HAZ), Grain Coarsening, Cr₂N, Precipitation, Computational Thermodynamics, DICTRA

1. Introduction

Duplex stainless steels (DSSs) are ferritic-austenitic alloys designed to contain approximately equal proportions of the two phases. Owing to this balanced microstructure, they combine high mechanical strength with excellent corrosion resistance, making them well suited for aggressive service environments. Since their industrial introduction in the early twentieth century [1], DSSs have become established materials in applications where conventional stainless steels may be inadequate. Compared with fully ferritic or fully austenitic grades, duplex alloys provide superior resistance to stress corrosion cracking [2], and localized corrosion phenomena such as pitting and crevice corrosion [3]. In addition, their yield strength is significantly higher than that of common austenitic stainless steels [4]. Another advantage is the reduced nickel requirement, which lowers alloying costs.

Depending on alloy composition and performance level, DSSs are commonly divided into lean, standard, super, and hyper duplex categories. Lean duplex grades are based on a reduced nickel concept, where manganese and nitrogen are used to partly compensate for the lower nickel content. Manganese is particularly important because it increases nitrogen solubility in the alloy [5]. For applications involving highly corrosive conditions, super and hyper duplex steels have been developed with elevated chromium, molybdenum, and nitrogen contents, providing enhanced corrosion resistance and strength compared with standard duplex grades [6,7].

During solidification, DSSs first form ferrite, and immediately below the solidus temperature the microstructure is fully ferritic over a limited temperature interval. Austenite subsequently precipitates during cooling in the solid state, and the final phase balance is strongly influenced by alloy chemistry and thermal history. In rolled

plate, an approximately equal ferrite-to-austenite ratio is generally targeted, whereas weld metals are typically accepted within a ferrite range of about 30–70 vol.-% or 35–65 vol.-% [8,9]. Earlier duplex stainless steels suffered from poor austenite reformation in the high-temperature heat-affected zone (HT-HAZ) after welding, which restricted their weldability [10]. The introduction of nitrogen alloying represented a major improvement because nitrogen is a highly effective austenite stabilizer with rapid diffusivity in steel [11]. Besides accelerating austenite formation, nitrogen contributes to solid-solution strengthening and improves resistance to localized corrosion [12]. Nitrogen can also delay the formation of detrimental intermetallic phases in stainless steels, although this effect is less pronounced in duplex grades, where its dominant role is to promote austenite formation and shift the phase balance accordingly [13].

Despite these benefits, nitrogen additions are associated with the risk of chromium nitride precipitation within the ferritic phase. Such precipitates may reduce both corrosion resistance and toughness [14,15]. In highly alloyed duplex grades, the elevated chromium and molybdenum levels further increase susceptibility to intermetallic phase formation, which can severely deteriorate material performance. Consequently, cooling conditions after welding or heat treatment become critical. Slow cooling promotes intermetallic precipitation, whereas excessively rapid cooling may suppress austenite formation and instead favor nitride formation in ferrite.

The development of computational thermodynamics, often referred to as CALPHAD (Calculation of Phase Diagrams) [16], has provided powerful possibilities for analyzing such phase transformations. Commercial software packages such as Thermo-Calc [17], used in the present study, enable simulation of thermodynamic and kinetic phenomena based on assessed databases describing phase equilibria and diffusion behavior in multicomponent alloy systems.

Several previous investigations have applied computational thermodynamics to austenite formation in duplex stainless steels. Wessman and Selleby [18] studied the kinetics of austenite formation during cooling and reviewed different modelling approaches applicable to this transformation. Similar methodologies were later employed by Westin and Wessman [19], who identified limitations in the predictive capability of the simulations, particularly regarding the influence of nitrogen and cooling rate. Their results confirmed the beneficial effect of nitrogen on austenite formation but indicated an overestimation of austenite fractions at high nitrogen contents together with an underestimation of cooling-rate effects. Related modelling work on austenite formation in austenitic stainless steels has also been reported by Valiente Bermejo and Wessman [20], although the transformation mechanisms in those alloys differ significantly from those in DSSs.

The present study was motivated primarily by the findings reported by Wessman et al. [21], with particular emphasis on achieving a deeper understanding of the coupled interactions between ferrite, austenite formation, and chromium nitride precipitation during cooling.

2. The precipitation of nitrides in duplex stainless steels and welds

The present work focuses specifically on chromium nitrides in DSSs, whereas other nitride-forming systems, such as titanium or niobium nitrides, are outside the scope of the study. The precipitation of chromium nitrides in DSSs is primarily associated with the combined effects of high chromium and nitrogen contents together with the decreasing solubility of nitrogen in ferrite during cooling. An important aspect is that nitrogen diffusion in ferrite controls the process kinetics. Nitrogen is an interstitial element with very high diffusivity compared with substitutional elements such as chromium, which diffuse considerably more slowly. Since DSSs solidify with ferrite as the primary phase [22], the subsequent precipitation of nitrides strongly depends on the extent to which austenite has formed during cooling and thereby accommodated nitrogen from the ferrite.

Previous work [21] demonstrated that sufficient austenite formation effectively suppresses nitride precipitation during cooling to lower temperatures, largely independent of cooling rate. However, this relationship is also influenced by ferrite grain size. In coarse ferrite grains, nitrides may form even at comparatively low cooling rates, whereas finer ferrite grains reduce the tendency for precipitation. Metallographic observations often reveal nitrides as dark regions or “clouds” within larger ferrite areas. Another characteristic feature is the so-called nitride-free zone adjacent to austenite regions. This phenomenon is explained by the rapid diffusion of nitrogen towards nearby austenite during cooling, which locally depletes the ferrite of nitrogen before nitrides can precipitate. Typically, the nitrogen concentration in austenite is approximately one order of magnitude higher than in ferrite, with the partitioning between the phases being strongly dependent on temperature. The nitrides discussed in the present work are commonly described as quenched-in nitrides, emphasizing that rapid cooling is required to retain the supersaturation conditions necessary for precipitation. Their formation is generally undesirable because chromium nitrides deteriorate both corrosion resistance and mechanical properties [23],[24]. In multipass welding, repeated thermal cycles introduce additional complexity through the possible formation of secondary austenite associated with

chromium nitride precipitation [25],[26]. Although secondary austenite formation is not considered in the present study, it remains an important phenomenon in DSS welding.

The modelling concepts applied in the present study are most readily interpreted in the context of optical metallography. However, because chromium nitrides precipitate on the nanoscale, detailed characterization requires scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Extensive experimental work has therefore been devoted to understanding the nucleation and growth behavior of nitrides in DSSs. To the knowledge of the authors, no successful *in-situ* studies of nitride precipitation in DSSs have yet been reported, although attempts have been made [27]. Most investigations have instead relied on dilatometry-based thermal simulations in which small specimens are subjected to controlled thermal cycles, often using hollow geometries to achieve sufficiently rapid cooling rates. In addition to metallographic characterization, nitride precipitation can be quantified using selective chemical extraction methods that isolate chromium nitride particles from the matrix for subsequent gravimetric and microstructural analysis [28,29].

Pettersson et al. [30] investigated nitride precipitation in cylindrical 2507 DSS specimens with dimensions $\varnothing 4 \times 8$ mm. The samples were heated to 1250 °C and subsequently cooled at rates between 20 and 100 °C/s in order to promote nitride formation. The characterization included light optical microscopy (LOM), ferrite fraction measurements, and quantification of both the fraction and width of nitride-containing ferrite regions. Detailed microstructural analysis was carried out using SEM and TEM combined with electron energy loss spectroscopy (EELS), EDS and EELS measurements were performed in STEM mode. Liao [31] performed Gleeble simulations using peak temperatures of 1350 °C followed by cooling rates between 20 and 150 °C/s. Nitride precipitation has also attracted increasing attention in the context of additive manufacturing of DSSs. Guo et al. [32] investigated selective laser melting (SLM) of 2205 duplex stainless steel powder, where cooling rates on the order of 10^5 – 10^6 °C/s were reported. Such extreme cooling conditions illustrate the substantial challenges associated with excessive ferrite contents and nitride precipitation in additively manufactured DSS components [33].

Although the present work solely considers the precipitation of Cr₂N in ferrite, it is important to recognize that cubic CrN may also form [34]. This subject has been discussed by both Liao [31] and Pettersson et al. [30], who proposed that metastable CrN acts as a precursor to the thermodynamically more stable Cr₂N phase. CrN has a cubic crystal structure and is often denoted FCC#2, representing a chromium-rich variant related to the FCC austenitic matrix phase FCC#1. In contrast, Cr₂N exhibits a hexagonal HCP crystal structure. Owing to the structural similarity between CrN and the surrounding matrix, nucleation of CrN is expected to occur more readily than nucleation of Cr₂N. High-resolution TEM observations have shown CrN precipitates forming as thin films, whereas Cr₂N typically appears as rod-shaped precipitates.

3. Simulation set-up

3.1 Materials

The simulations performed in the present work were based on the DSS grades LDX 2101 (EN 1.4162, UNS S32101) and 2507 (EN 1.4410, UNS S32750), together with the matching super duplex filler metal 2509 (25 9 4 N L, abbreviated 2594). The filler alloy contains a higher nickel concentration than the corresponding base material in order to facilitate austenite formation and improve weldability. The chemical compositions applied in the calculations are summarized in Table 1. To reduce computational complexity and simulation time, simplified nominal compositions containing only the principal alloying elements were employed. The same compositional approach has previously been used in earlier modelling studies by Westin and Wessman [19] and Wessman et al. [21].

Table 1 Nominal and simplified chemical compositions used in the simulations, wt.-%

Alloy	Mn	Cr	Ni	Mo	N	Fe
LDX 2101	5.0	21.0	1.5	0.3	0.22	Balance
2507	0.8	25.0	7.0	4.0	0.27	Balance
2509	0.8	25.0	9.5	4.0	0.25	Balance

3.2 General simulation basis

All thermodynamic calculations were carried out using Thermo-Calc version 2025a [17] together with the TCFE13 thermodynamic database for steels and stainless steels. Diffusion-controlled transformations were simulated using the DICTRA module [35] in combination with the MOBFE8 mobility database.

The homogenization approach available in DICTRA was selected for the present work because it enables treatment of dispersed precipitates within a matrix phase and is therefore suitable for describing nitride precipitation

in ferrite [36]. In the simulations, austenite growth was represented as a moving phase boundary, while chromium nitrides were treated as dispersed particles within the ferritic matrix. A schematic illustration of the simulation concept is shown in Fig. 1.

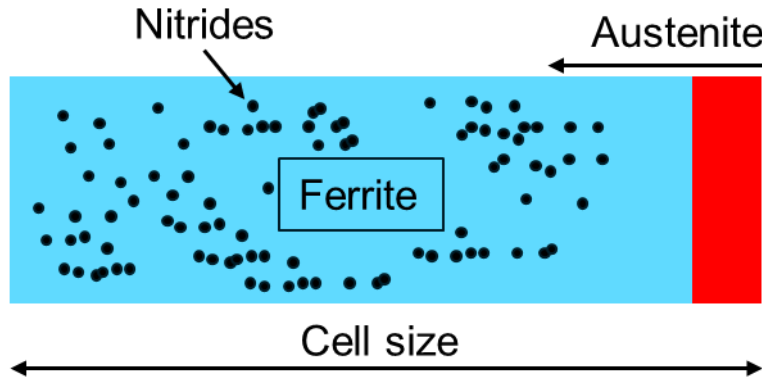


Fig. 1 Schematic illustration of the DICTRA homogenization model [36] used in the present study. Austenite grows from the ferritic matrix, while chromium nitrides are represented as dispersed precipitates within ferrite.

For DICTRA simulations, the geometry and corresponding diffusion length must be specified through a cell size parameter defined at the beginning of each calculation. Different cell sizes were employed depending on the investigated case. From a metallurgical perspective, the selected cell size may be interpreted either as ferrite grain size or, in duplex base materials, as the characteristic spacing between neighboring austenite regions [37]. The geometries represented in Fig. 1 correspond to one-half of the simulated domain, with the center of the ferrite region located at the left-hand side.

In DICTRA, phase nucleation is not treated explicitly. Instead, precipitation occurs when a sufficient thermodynamic driving force is reached. The default driving force criterion in DICTRA corresponds to $10^{-5} \cdot R \cdot T$ J/mol, where R denotes the gas constant and T the absolute temperature. While this approach is relatively straightforward for modelling austenite formation, the description of chromium nitride precipitation proved more challenging and required extensive evaluation during the development of the present work.

3.3 Modelling of austenite formation and nitride precipitation

The modelling strategy adopted for austenite formation was based on the moving phase boundary approach [18,38]. The present simulations follow the same general methodology as reported in later studies [19,21]. Thermal cycles were primarily represented by constant cooling rates between 1400 and 800 °C, assuming that the ferrite-to-austenite transformation is essentially completed by 800 °C. Although actual welding thermal cycles are considerably more complex, constant cooling-rate simulations provide a practical and reproducible framework for evaluating the influence of individual parameters.

The cooling rates most extensively used in the present study were 20, 75, and 400 °C/s, corresponding to the same conditions considered in earlier investigations [19,21]. These cooling conditions may approximately be related to air cooling, intermediate cooling, and rapid water quenching, respectively.

A major objective of the present work was to extend previous simulations of austenite formation to also include precipitation of Cr_2N nitrides using the DICTRA homogenization model [21]. In this configuration, ferrite acts as the matrix phase, austenite forms through a moving interface, and nitrides precipitate as dispersed particles within the ferrite. The simulated arrangement was selected to resemble experimentally observed microstructures in both duplex base materials, HT-HAZ, and weld metals. In practice, nitride precipitation is frequently concentrated within larger ferrite regions, primarily in the HT-HAZ and duplex weld metals with low amounts of Widmanstätten austenite. The modelling approach therefore also aimed to capture the development of the characteristic nitride-free region adjacent to austenite.

3.4 Metallographic verification

To place the simulation results in an experimental context, the work of Pettersson et al. [30] was used for validation. The material investigated was a 2507 super duplex stainless steel, and the heat treatments were performed in a dilatometer using cylindrical specimens with dimensions $\text{Ø}4 \times 8$ mm. Two different microstructures were studied: the as-delivered material and a coarse-grained condition produced by heat treatment at 1100 °C for two weeks [39].

The experimental conditions reported by Pettersson et al. [28] were reproduced by simulation, including heat treatments at 1100 and 1250 °C with holding times of 10 and 60 s, followed by cooling rates of 20, 50, and 100 °C/s. The metallographic characterization included measurements of ferrite fraction, austenite spacing, the fraction of nitride-containing ferrite (NCF), and the width of NCF regions. The NCF fraction was determined as the ratio of points counted within nitride-containing ferrite to the total number of ferrite points. The NCF width was obtained from austenite spacing measurements by considering only ferrite regions containing visible nitrides.

4. Results

4.1 Nitrogen alloying to avoid nitrides

The heading of this section reflects the seemingly contradictory observation that increasing the nitrogen content may reduce the tendency for chromium nitride precipitation. This concept originates from the work by Blom [40], who investigated the influence of shielding gas composition on the microstructure of 2205 duplex stainless steel welds. In that study, the addition of approximately 5 % nitrogen to the shielding gas increased nitrogen absorption in the weld metal, promoted austenite formation, and thereby strongly reduced the precipitation of chromium nitrides. Blom concluded that the improved phase balance enhanced toughness, ductility, and corrosion resistance without the need for over-alloyed filler metals. Consequently, the somewhat paradoxical conclusion was drawn that chromium nitride precipitation in DSS welds can be suppressed by increasing the nitrogen content.

To investigate this phenomenon, simulations were performed using the LDX 2101 composition listed in Table 1. The nominal nitrogen concentration of 0.22 wt.-% was systematically varied between 0 and 0.30 wt.-%. Two cooling conditions were considered: 75 °C/s using cell sizes of 20, 30, 40, and 50 µm, and 400 °C/s using cell sizes of 10, 15, and 20 µm.

The results obtained at 75 °C/s are presented in Fig. 2, which shows the solidus temperature together with the calculated onset temperatures for austenite formation and chromium nitride precipitation for cell sizes of 40 and 50 µm as a function of nitrogen content. Corresponding results for 400 °C/s are shown in Fig. 3 for cell sizes of 15 and 20 µm. Under the investigated conditions, no nitride precipitation was predicted for cell sizes of 20 and 30 µm at 75 °C/s, nor for the 10 µm cell size at 400 °C/s.

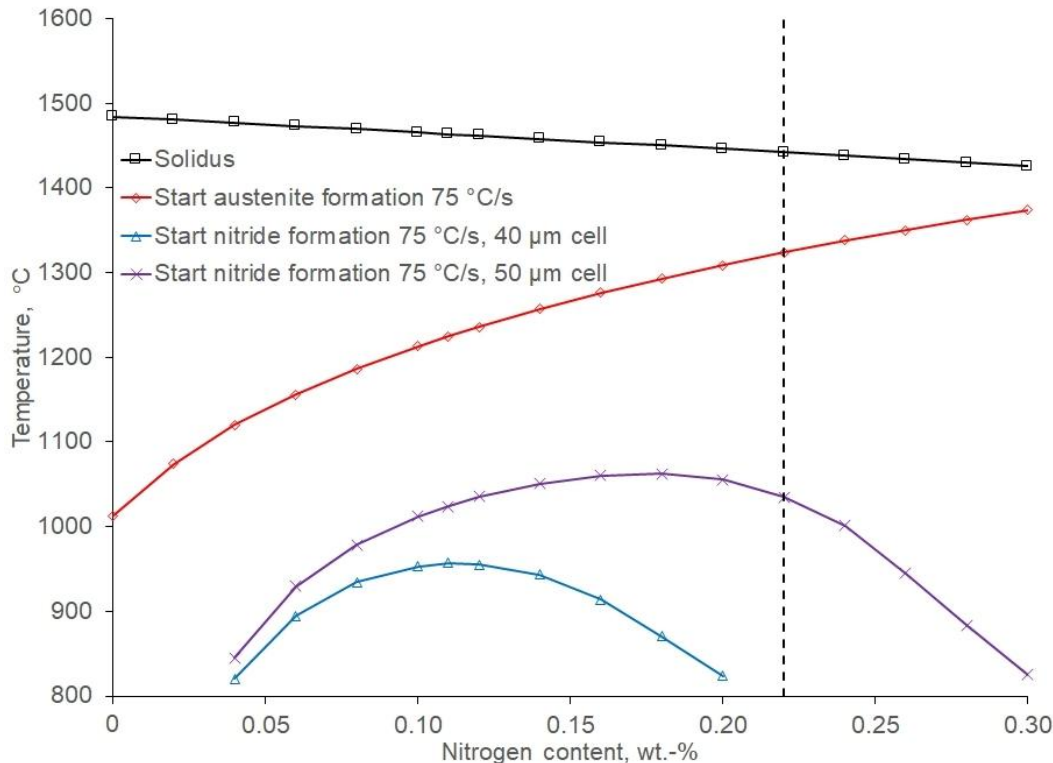


Fig. 2 LDX 2101 cooled at 75 °C/s: calculated solidus temperature together with onset temperatures for austenite formation and chromium nitride precipitation as a function of nitrogen content for cell sizes of 40 and 50 µm. No nitrides were predicted for 20 and 30 µm cell sizes. The nominal nitrogen content of LDX 2101 is 0.22 wt.-%.

Both increasing cell size and increasing cooling rate promoted nitride formation. Larger cell sizes expanded the nitrogen concentration range within which nitrides formed and increased the nitride precipitation start temperature. A clear effect of cooling rate was also observed. At the higher cooling rate of 400 °C/s, nitride precipitation was initiated already at a cell size of 15 µm, whereas a substantially larger cell size of approximately 40 µm was required at 75 °C/s.

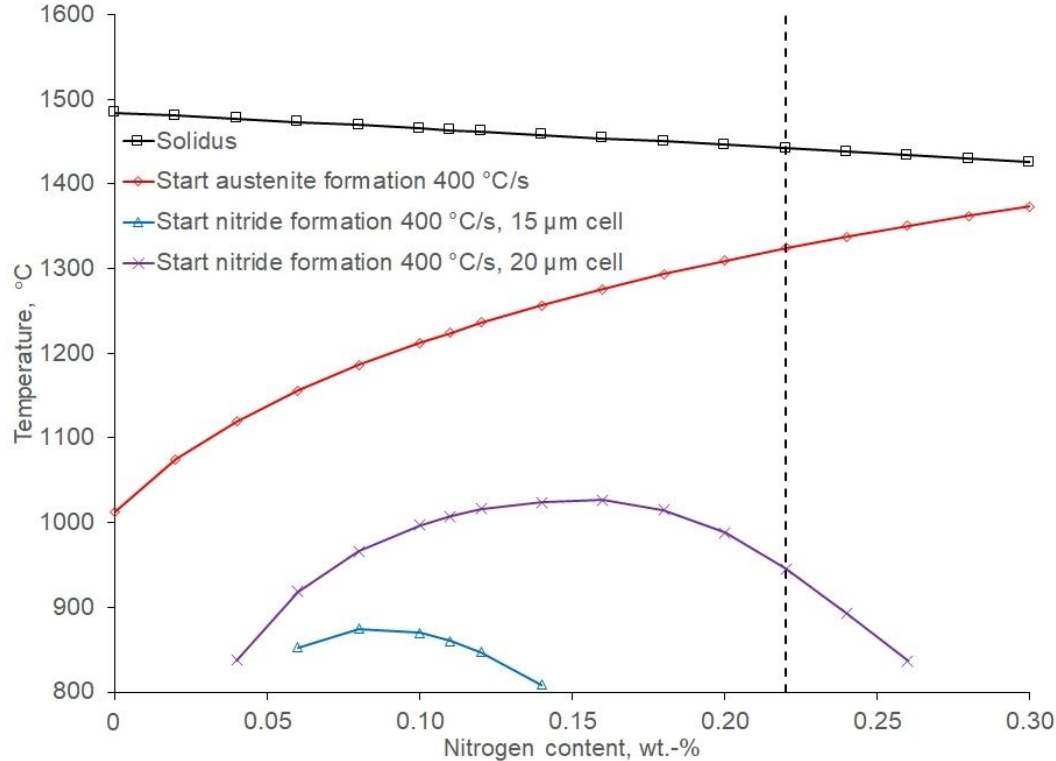


Fig. 3 LDX 2101 cooled at 400 °C/s: calculated solidus temperature together with onset temperatures for austenite formation and chromium nitride precipitation as a function of nitrogen content for cell sizes of 15 and 20 µm. No nitrides were predicted for the 10 µm cell size. The nominal nitrogen content of LDX 2101 is 0.22 wt.-%.

4.2 Influence of cooling rate on nitride formation

Additional simulations were carried out for LDX 2101 to investigate the combined influence of cooling rate, nitrogen content, and cell size on ferrite formation and nitride precipitation. Two nitrogen contents were considered: the nominal alloy composition containing 0.22 wt.-% N and a reduced content of 0.11 wt.-% N, corresponding to a hypothetical 50 % loss of nitrogen. Cell sizes of 10, 15, and 20 µm were simulated in combination with cooling rates ranging from 10 to 10 000 °C/s.

The ferrite fractions calculated at 800 °C are presented in Fig. 4 as a function of cooling rate. As expected, increasing cooling rate resulted in higher retained ferrite fractions because the time available for austenite formation decreased. The ferrite fraction also increased with increasing cell size and with decreasing nitrogen content. At the highest cooling rates, all simulated conditions resulted in ferrite fractions exceeding 80 vol.-%. The effect of nitrogen content was particularly pronounced at lower cooling rates. After reducing the nitrogen level to 0.11 wt.-%, none of the investigated conditions produced ferrite fractions below 70 vol.-%.

The corresponding nitride fractions at 800 °C are shown in Fig. 5. The start of nitride formation in Fig. 4 is reflected in the kink in the curves. Lower nitrogen contents reduced the critical cooling rate required for nitride precipitation to occur, and larger cell sizes further increased the susceptibility to precipitation. However, once nitrides formed, the total nitride fraction was generally higher for the nominal nitrogen level of 0.22 wt.-%. This behavior illustrates the dual role of nitrogen in DSSs. Although higher nitrogen promotes austenite formation and thereby suppresses nitride precipitation under many conditions, excess nitrogen remaining in ferrite at rapid cooling rates may instead increase the driving force for nitride formation.

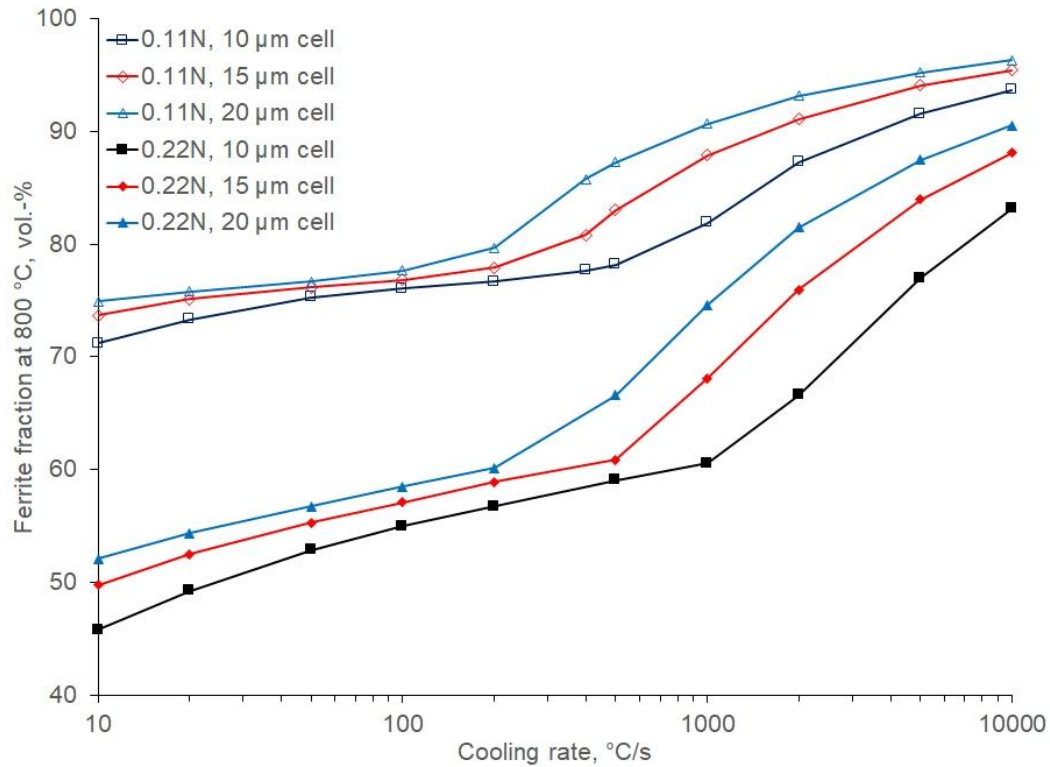


Fig. 4 LDX 2101: Ferrite fraction at 800 °C as a function of cooling rate for nitrogen contents of 0.11 and 0.22 wt.-% and cell sizes of 10, 15, and 20 μm.

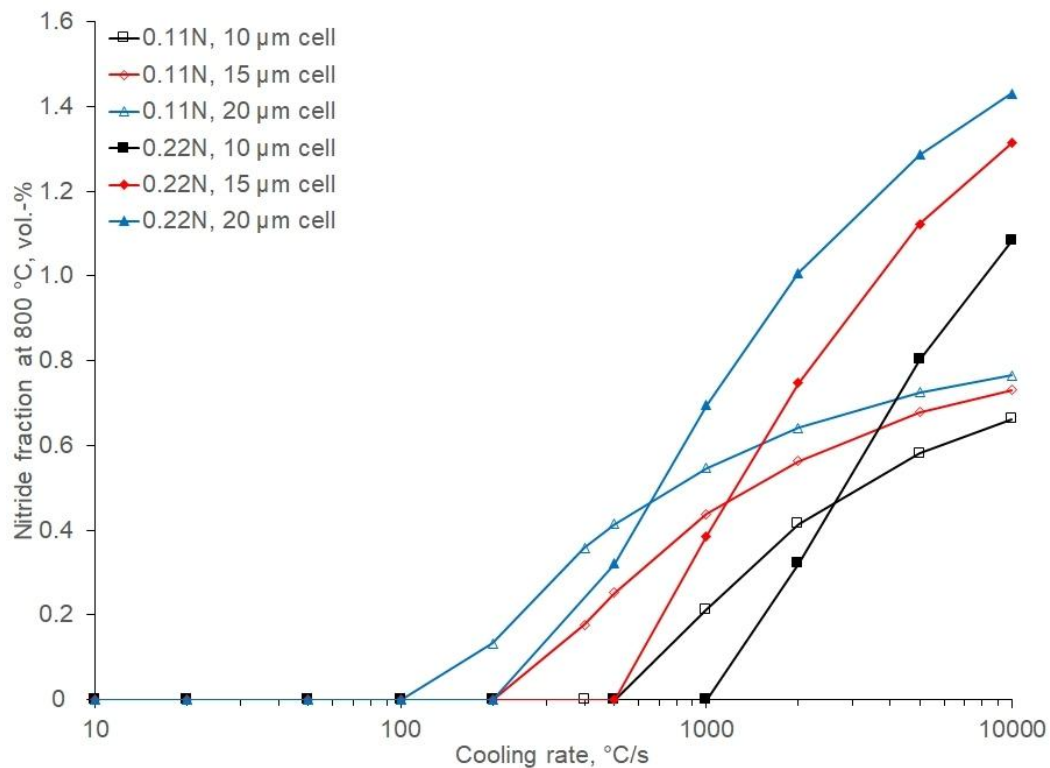


Fig. 5 LDX 2101: Nitride fraction at 800 °C as a function of cooling rate for nitrogen contents of 0.11 and 0.22 wt.-% and cell sizes of 10, 15, and 20 μm.

4.3 Influence of the cooling rate temperature-time sequence: LDX 2101

An objection to the validity of the results presented in [21] was that they were obtained using a constant linear cooling rate from 1400 to 800 °C. This criticism is justified, since actual welding thermal cycles are inherently non-linear and may differ substantially from an idealized linear cooling profile. However, the use of a linear cooling rate remains a reasonable first approximation when experimental thermal cycle data are unavailable.

To explore the influence of different cooling sequences, LDX 2101 with a cell size of 50 µm was selected. This relatively large cell size was chosen to promote nitride precipitation and thereby facilitate comparison between the different thermal cycles. The linear cooling rate of 75 °C/s was used as the reference condition, corresponding to a cooling time of 8 s between 1400 and 800 °C.

Three fast-slow and three slow-fast cooling sequences were evaluated, together with a quasi-logarithmic cooling profile based on 16 temperature-time points. The temperature-time points were selected to generate a cooling curve resembling those typically recorded during welding using thermocouples and data acquisition systems, while maintaining the boundary conditions of 1400 °C at the start of cooling and 800 °C after 8 s.

The cooling sequences investigated and the corresponding ferrite and nitride fractions at the end of the simulations are presented in Table 2. A graphical representation of the cooling sequences is shown in Fig. 6, the evolution of ferrite fraction as a function of temperature in Fig. 7, and the final nitride fractions in Fig. 8.

Table 2 LDX 2101, 50 µm cell size: Temperature-time sequences and simulation results.

Cooling rate	Sequence 1	Sequence 2	Ferrite 800 °C, vol.-%	Cr ₂ N at 800 °C, vol.-%
Linear	1400–800 °C, 8 s		65.9	0.29
1. 400 °C/s 2. 53 °C/s	1400–1200 °C 0.5 s	1200–800 °C 7.5 s	60.8	0.13
1. 400 °C/s 2. 41 °C/s	1400–1100 °C 0.75 s	1100–800 °C 7.25 s	72.0	0.66
1. 400 °C/s 2. 29 °C/s	1400–1000 °C 1 s	1000–800 °C 7 s	79.0	0.96
1. 29 °C/s 2. 400 °C/s	1400–1200 °C 7 s	1200–800 °C 1 s	74.5	0.59
1. 41 °C/s 2. 400 °C/s	1400–1100 °C 7.25 s	1100–800 °C 0.75 s	68.6	0.35
1. 53 °C/s 2. 400 °C/s	1400–1000 °C 7.5 s	1000–800 °C 0.5 s	65.2	0.23
Quasi logged	1400–800 °C, 8 s		76.1	0.81

The nitride fractions shown in Fig. 8 are directly related to the ferrite fractions presented in Fig. 7, which in turn are governed by the temperature-time sequences illustrated in Fig. 6. Although all cooling sequences represent an 8 s cooling interval from 1400 °C to 800 °C, significant differences in the resulting nitride fractions are observed owing to differences in ferrite evolution during cooling. Since nitride precipitation is controlled by the amount of ferrite present, the ferrite evolution shown in Fig. 7 provides the primary basis for interpreting the results.

The reduction in ferrite fraction, corresponding to the formation of nitrogen-consuming austenite, proceeds rapidly at high temperatures but becomes progressively slower as the temperature decreases, as demonstrated by the TTT diagrams presented in the previous study [21]. At elevated temperatures, however, the equilibrium fraction of austenite remains relatively low, limiting its formation by thermodynamic constraints. According to the simulations, austenite formation in this alloy begins at approximately 1325 °C. Consequently, austenite formation is primarily thermodynamically limited at high temperatures, whereas at lower high temperatures, whereas at lower temperatures the transformation becomes increasingly controlled by diffusion kinetics. The extent of austenite formation during cooling determines the amount of nitrogen remaining in ferrite and thereby the tendency for nitride precipitation. Although nitride precipitation is likely unavoidable for a cell size as large as 50 µm, the results demonstrate that certain cooling sequences are more favorable than others. In particular, the quasi-logarithmic cooling profile resulted in comparatively high nitride fractions, indicating that this cooling sequence is less beneficial for suppressing nitride formation.

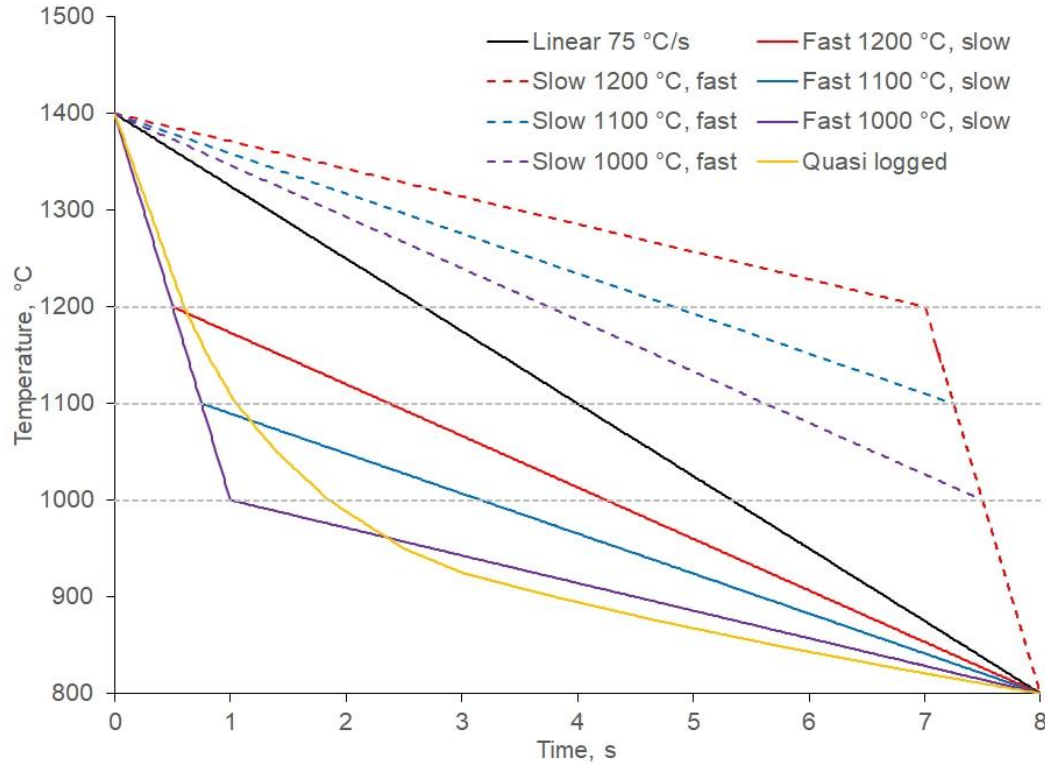


Fig. 6 LDX 2101: Cooling sequences showing temperature as a function of time. All sequences correspond to an average cooling rate of 75 °C/s, starting at 1400 °C and ending at 800 °C after 8 s.

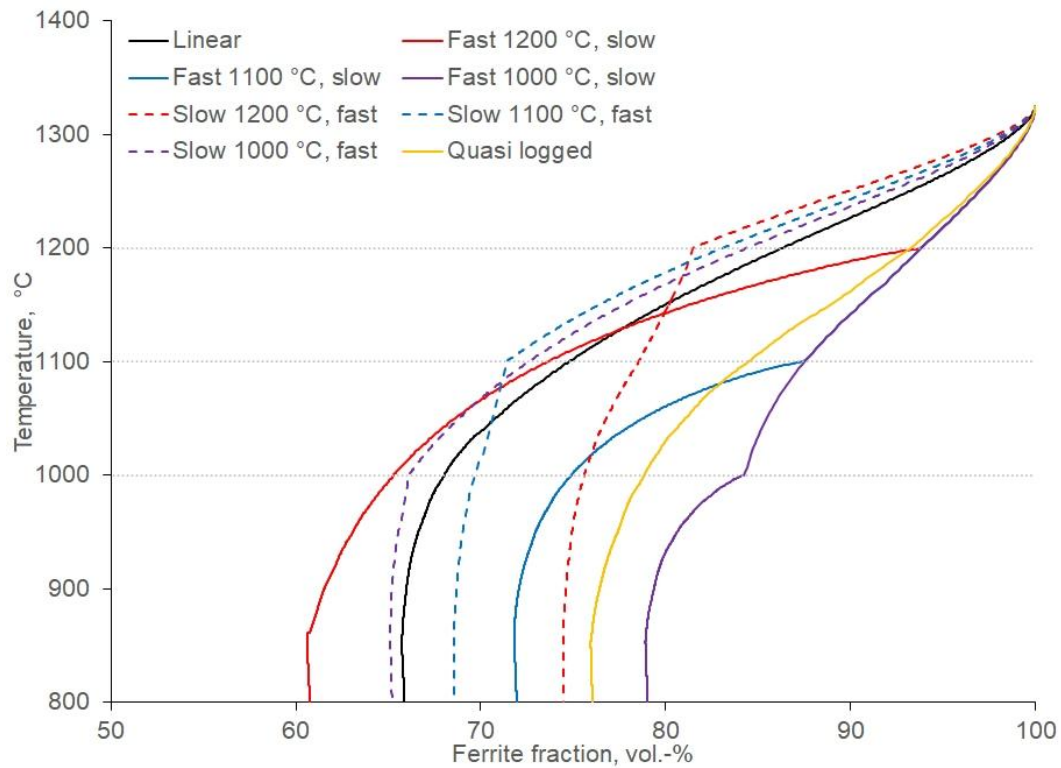


Fig. 7 LDX 2101: Ferrite fraction as a function of temperature for the different cooling sequences between 1400 and 800 °C.

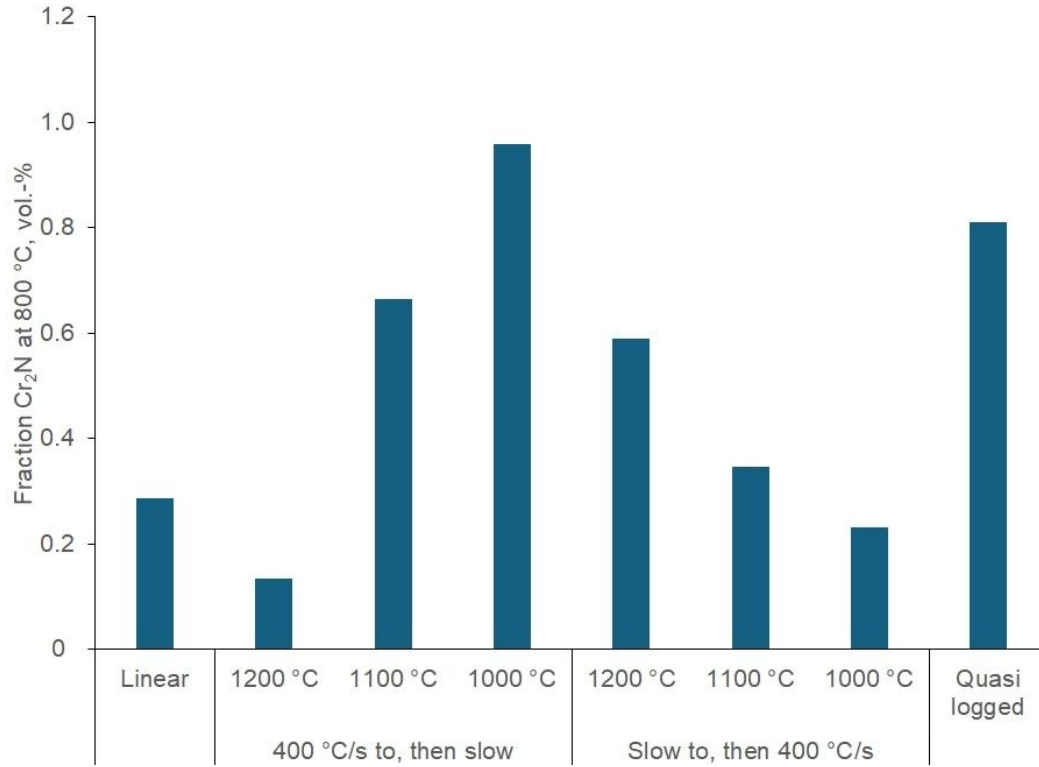


Fig. 8 LDX 2101: Nitride fraction at 800 °C, corresponding to the end of the simulations, for the different cooling sequences.

4.4 Influence of the cooling rate temperature-time sequence: 2509

A similar analysis to that described in Section 4.3 was performed for 2509 weld metal. Fast-slow and slow-fast cooling sequences were evaluated with transition temperatures of 1200, 1100, and 1000 °C, followed by the corresponding complementary cooling rate down to 800 °C. All thermal cycles were completed within 8 s, corresponding to a nominal cooling rate of 75 °C/s. The quasi-logarithmic cooling sequence was omitted from this analysis because it represented a constructed reference profile rather than a systematic variation of cooling conditions.

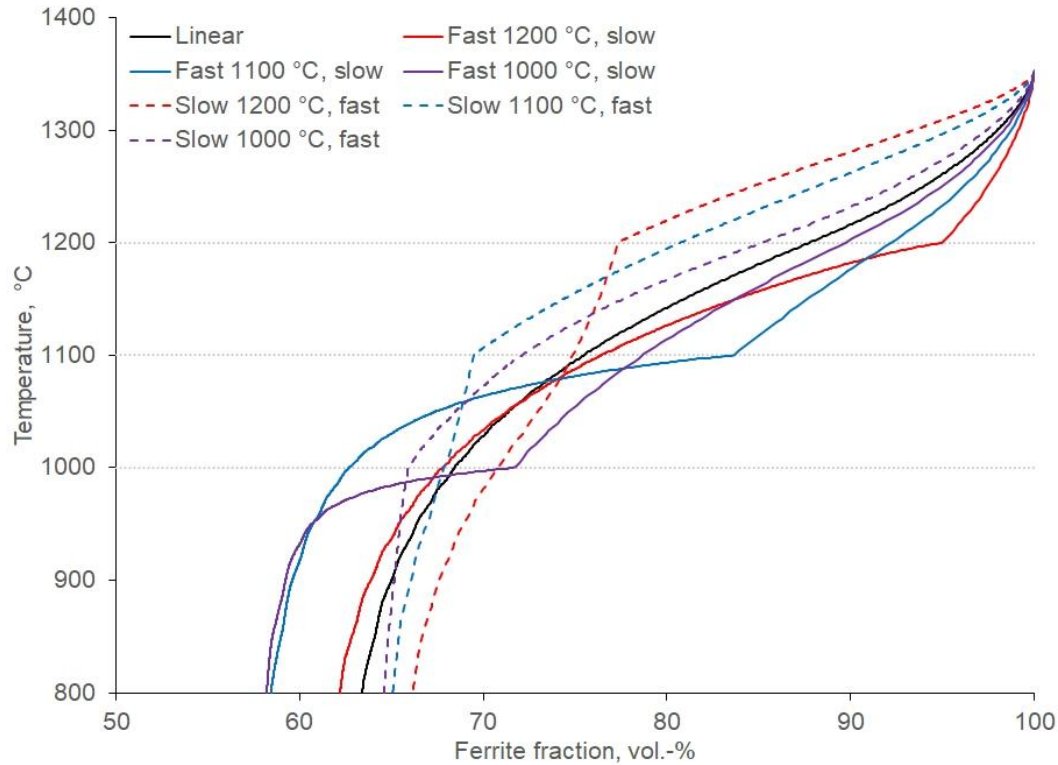
The objective of these simulations was to determine, with a resolution of 0.1 μm , the maximum cell size that could be achieved without nitride precipitation prior to reaching 800 °C. The resulting ferrite fractions at the end of the simulations (800 °C) and the corresponding critical cell sizes required to avoid nitride precipitation are presented in Table 3. The evolution of ferrite fraction as a function of temperature for the investigated cooling sequences is shown in Fig. 9.

Similar to the results obtained for LDX 2101, the results for 2509 presented in Table 3 and Fig. 9 illustrate the difficulty of forming sufficient austenite during the limited cooling interval of 8 s between 1400 and 800 °C to suppress nitride precipitation completely. Whereas the LDX 2101 simulations quantified the amount of nitride precipitation for a given cell size, the present analysis instead identifies the maximum allowable cell size for each cooling sequence that avoids nitride formation.

The two materials differ in that LDX 2101 represents a base material, whereas 2509 is a weld metal containing a substantially higher Ni content to promote austenite reformation. Nevertheless, the influence of the cooling sequence remains significant, with the maximum nitride-free cell size varying by a factor of approximately 2.8 between the most favorable condition (51.1 μm) and the least favorable condition (18.4 μm). This behavior can again be explained by the interplay between thermodynamic limitations at high temperatures and kinetic limitations at lower temperatures governing austenite formation. From a practical perspective, these results demonstrate that optimization of the cooling cycle, or equivalently the welding heat input, can substantially reduce the susceptibility to nitride precipitation. It should also be noted that austenite formation in 2509 begins at approximately 1353 °C, providing a slight thermodynamic advantage compared with LDX 2101.

Table 3 2509: Temperature-time sequences and simulation results for conditions without nitride precipitation.

	Sequence 1	Sequence 2	Ferrite at 800 °C, vol.-%	Cell size, μm
Linear	1400–800 °C, 8 s		63.4	44.6
1. 400 °C/s 2. 53 °C/s	1400–1200 °C 0.5 s	1200–800 °C 7.5 s	62.2	51.1
1. 400 °C/s 2. 41 °C/s	1400–1100 °C 0.75 s	1100–800 °C 7.25 s	58.4	31.9
1. 400 °C/s 2. 29 °C/s	1400–1000 °C 1 s	1000–800 °C 7 s	58.2	23.6
1. 29 °C/s 2. 400 °C/s	1400–1200 °C 7 s	1200–800 °C 1 s	66.2	18.4
1. 41 °C/s 2. 400 °C/s	1400–1100 °C 7.25 s	1100–800 °C 0.75 s	65.1	24.4
1. 53 °C/s 2. 400 °C/s	1400–1000 °C 7.5 s	1000–800 °C 0.5 s	64.6	40.2

**Fig. 9** 2509: Ferrite fraction as a function of temperature for different cooling sequences between 1400 and 800 °C.

4.5 Sigma phase and nitride formation

In the preceding study by Wessman et al. [21], two-step simulation procedures were used to evaluate the influence of nitrogen content and ferrite cell size on sigma phase precipitation in 2509 weld metal. In the present work, the same simulation conditions were revisited with emphasis placed on the onset of chromium nitride precipitation.

The investigated compositions were based on the nominal 2509 alloy listed in Table 1, while the nitrogen content was varied between 0.15, 0.25, and 0.50 wt.-% for a fixed cell size of 25 μm . In addition, cell sizes of 15, 20, and 25 μm were investigated at the nominal nitrogen concentration of 0.25 wt.-%. The previous sigma phase calculations were represented as time–temperature–transformation (TTT) diagrams showing the time required to form 1 vol.-% sigma phase. In the present study, the calculated onset of chromium nitride precipitation was superimposed

on these diagrams, Consequently, the figures combine TTT information for sigma phase formation with continuous cooling temperature (CCT) information for nitride precipitation.

The results are shown in Fig. 10 for varying nitrogen contents and in Fig. 11 for varying cell sizes. For the fixed 25 μm cell size, chromium nitride precipitation occurred during rapid cooling within approximately the first 1–3 s, whereas sigma phase formation was predicted only after considerably longer times, typically in the range of 25–40 s depending on nitrogen content. These results clearly illustrate the well-known processing challenge associated with DSSs cooling must be sufficiently rapid to suppress sigma phase formation, but not so rapid that extensive nitride precipitation occurs.

At the nominal nitrogen content of 0.25 wt.-%, increasing cell size increased the tendency for nitride precipitation while simultaneously reducing susceptibility to sigma phase formation. The results therefore indicate that ferrite geometry and diffusion distance strongly influence the balance between these competing precipitation phenomena.

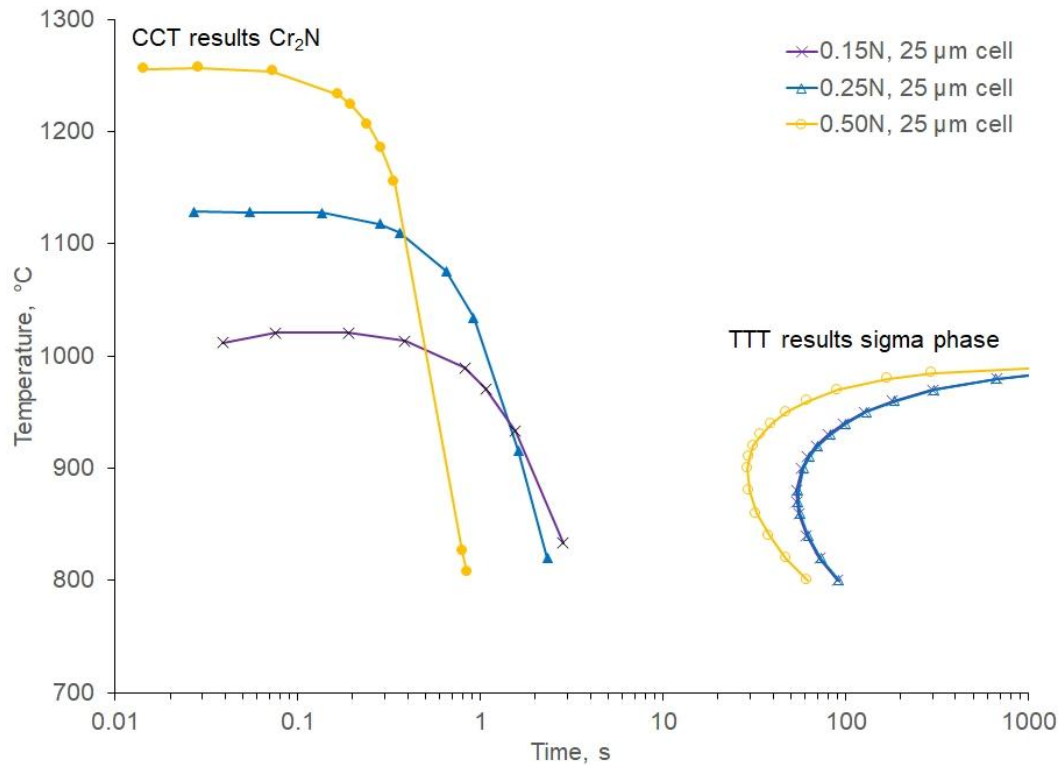


Fig. 10 2509: Combined TTT/CCT diagram showing the formation of 1 vol.-% sigma phase from ref. [21] together with the calculated onset of chromium nitride precipitation for nitrogen contents of 0.15, 0.25 and 0.50 wt.-%.

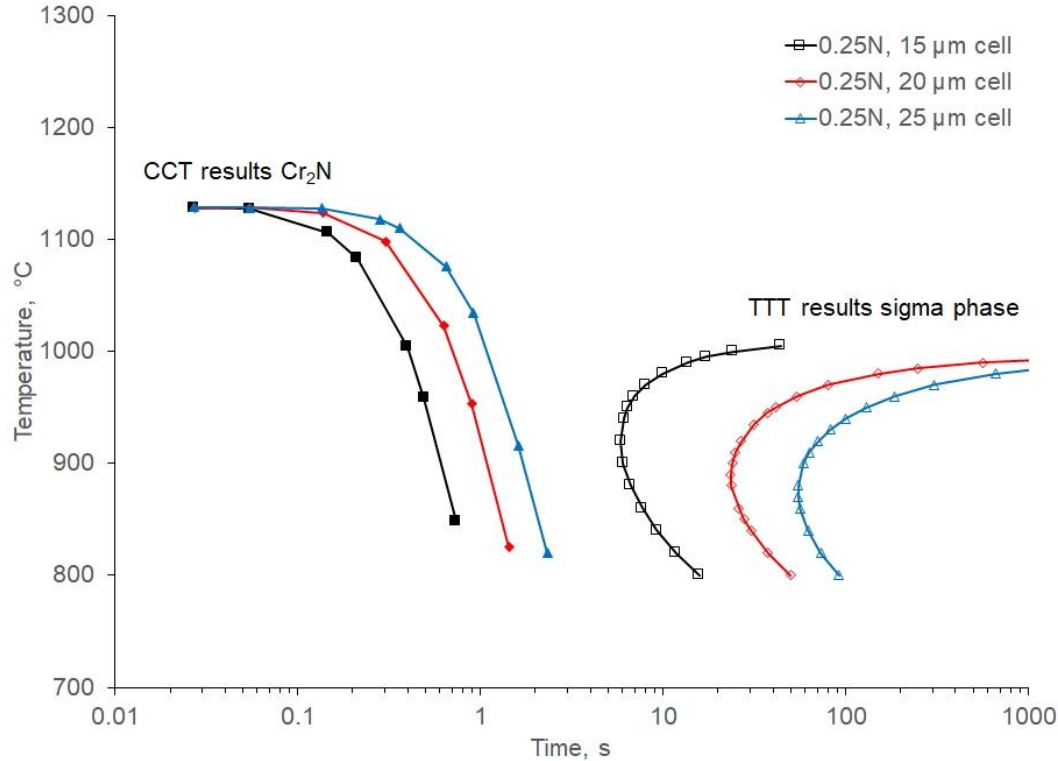


Fig. 11 2509: Combined TTT/CCT diagram for formation of 1 vol.-% sigma phase from ref. [21] with calculated onset of nitride precipitation added for cell sizes of 15, 20, and 25 μm at 0.25 wt.-% nitrogen.

4.6 HAZ dilatometry heat treatments and simulations

Experimental results from the dilatometry study of Pettersson et al. [30] on 2507 super DSS were used to validate the simulations performed in the present work. Table 4 summarizes the results for specimens D1–3 with a fine microstructure and specimen D4 representing the coarse microstructure obtained by long-term heat treatment. The measured ferrite fraction, austenite spacing, and nitride-containing ferrite (NCF), expressed as both area fraction and width, are included.

A simplified alloy composition of Fe-0.83Mn-24.84Cr-6.90Ni-3.80Mo-0.28N, corresponding to the chemical composition in Table I from Ref. [30], was used in the simulations. Since the experimental material was initially delivered with an approximately equal ferrite-austenite balance and subjected to heat treatments up to 1250 °C, where the microstructure remains duplex, two different simulation approaches were employed.

The first approach assumed a fully ferritic starting condition at 1400 °C using the nominal alloy composition. The second approach represented the experimentally relevant duplex starting condition. An equilibrium calculation was first performed to determine the ferrite and austenite compositions corresponding to a 50/50 phase balance. The resulting phase compositions were Fe-0.76Mn-26.27Cr-5.40Ni-4.65Mo-0.077N for ferrite and Fe-0.90Mn-23.41Cr-8.39Ni-2.96Mo-0.483N for austenite.

For the fully ferritic simulations, the material was held at 1250 °C for 5 min prior to cooling at 100 °C/s. The extended holding time was used to obtain a more homogeneous distribution of alloying elements. For the duplex simulations, the thermal cycle more closely followed the experimental procedure, consisting of heating from 800 to 1250 °C at 100 °C/s, holding for 60 s at 1250 °C, and cooling to 800 °C at 100 °C/s.

Since the experimental results are reported in terms of austenite spacing, the corresponding simulation values were estimated as twice the cell size multiplied by the ferrite fraction at the end of the simulation (800 °C). Experimental NCF widths for the fine and coarse microstructures, 18.7 and 40.1 μm respectively, are compared with simulation results from both modelling approaches in Fig. 12.

The simulation approaches predict a critical austenite spacing of 36 and 42 μm , respectively for complete nitride precipitation throughout the ferrite. This agrees reasonably well with the experimental observations for specimen D4 with a coarse microstructure, where essentially all ferrite regions contained nitrides. The fully ferritic simulations produced ferrite fractions between 61 and 70 vol.-%, with larger ferrite fractions corresponding to larger

austenite spacings. In contrast, the duplex simulations yielded ferrite fractions close to 58 vol.-% for all conditions, in better agreement with the experimental measurements presented in Table 4.

Direct comparison between the experimentally measured NCF fractions and widths and the simulated nitride fractions of approximately 0.2–0.6% (Fig. 12) is not straightforward. The nanometer-sized nitride particle clusters predicted by the simulations cannot readily be translated into area fractions obtained by conventional metallographic image analysis, making quantitative comparison difficult.

Table 4 Experimental results from the dilatometry study of Pettersson et al. [30], including ferrite fraction, austenite spacing, and nitride-containing ferrite (NCF) expressed as both fraction and width.

Specimen	Heat treatments	Ferrite, %	Austenite spacing, μm	NCF, %	NCF, μm
D1, fine	1250 °C/10 s + 20 °C/s	51	7.7 ± 0.8	16	23.8 ± 4.6
D2, fine	1250 °C/10 s + 50 °C/s	49	7.5 ± 0.6	22	22.7 ± 3.2
D3, fine	1250 °C/10 s + 100 °C/s	52	7.2 ± 0.6	36	18.7 ± 1.9
D4, coarse	1250 °C/60 s + 100 °C/s	56	40.1 ± 2.3	100	40.1 ± 2.3

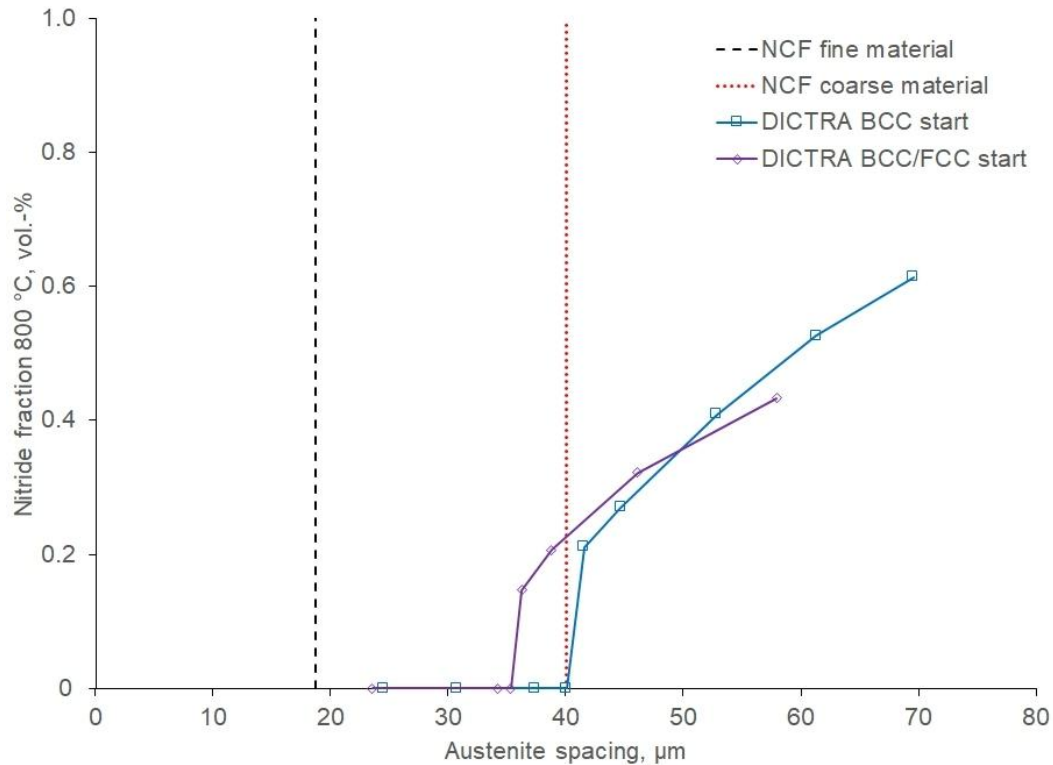


Fig. 12 2507: Nitride fraction versus austenite spacing. Experimental results from ref. [30] represented by the width of nitride-containing ferrite (NCF) regions for fine and coarse microstructures together with simulation results obtained using fully ferritic and duplex starting conditions.

Additional simulations were performed to reproduce the heat treatment consisting of 1250 °C for 10 s followed by cooling at 20, 50, or 100 °C/s. These calculations employed the duplex starting condition and followed the thermal cycle of heating to 1250 °C at 100 °C/s, holding for 10 s, and subsequently cooling to 800 °C at the prescribed cooling rate. The simulations showed that nitride precipitation at 20 °C/s requires an austenite spacing exceeding approximately 80 μm , whereas corresponding critical spacings of approximately 51 and 36 μm were predicted for cooling rates of 50 and 100 °C/s, respectively. The experimental metallographic observations presented in Table 4 are in reasonable agreement with these predictions, although direct quantitative comparison between simulations and metallographic measurements remains challenging.

Although mentioned qualitatively by Pettersson et al. [30], the width of the nitride-free zones adjacent to austenite was not quantified. To investigate the conditions required for the formation of such zones, additional

simulations were performed using a fixed cell size of 50 μm . Thermal cycles consisted of heating from 800 °C to peak temperatures between 1000 and 1400 °C, holding for 10 s, and subsequently cooling to 800 °C at 100 °C/s. It should be noted that liquid formation was not included in the simulations, although limited incipient melting is expected at 1400 °C.

The evolution of the ferrite fraction during these thermal cycles is shown in Fig. 13, while the final nitride distributions are presented in Fig. 14. A pronounced increase in ferrite fraction was observed for peak temperatures above approximately 1300 °C. The corresponding nitride distributions indicate that such high ferrite fractions are necessary for the development of a distinct nitride-free zone adjacent to austenite. At lower peak temperatures, nitrides were present throughout the ferrite, and no clear depletion zone was predicted.

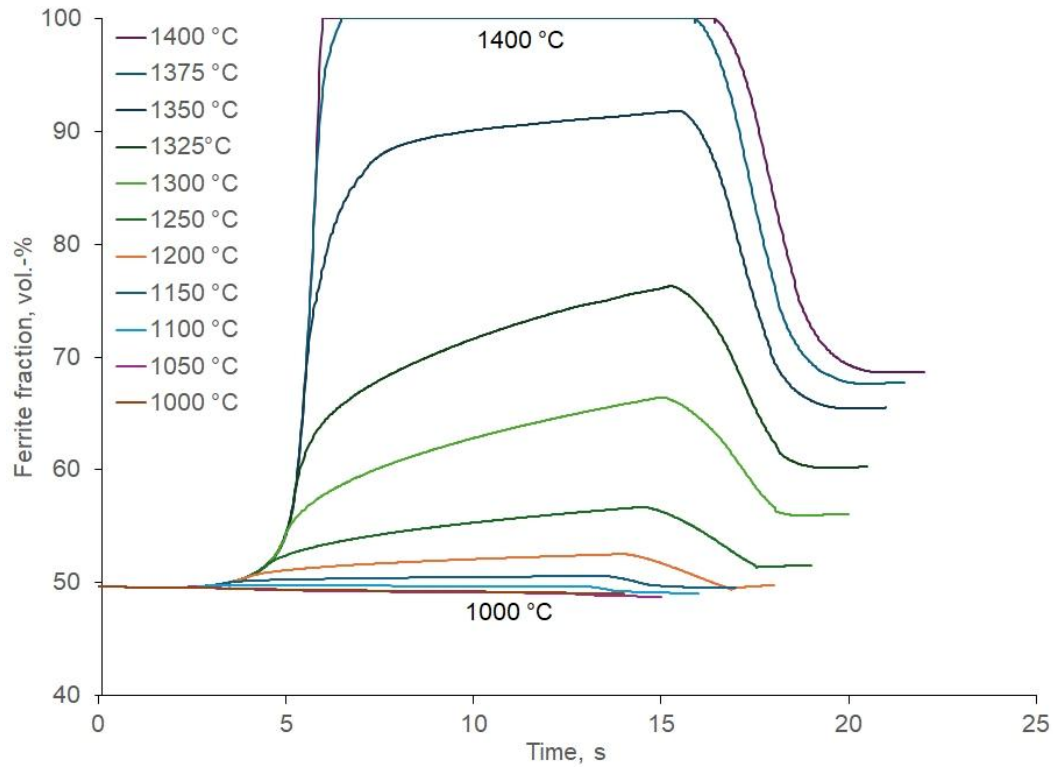


Fig. 13 2507: Ferrite fraction as a function of time for simulations involving heating from 800 °C to the indicated peak temperatures, holding for 10 s, followed by cooling to 800 °C.

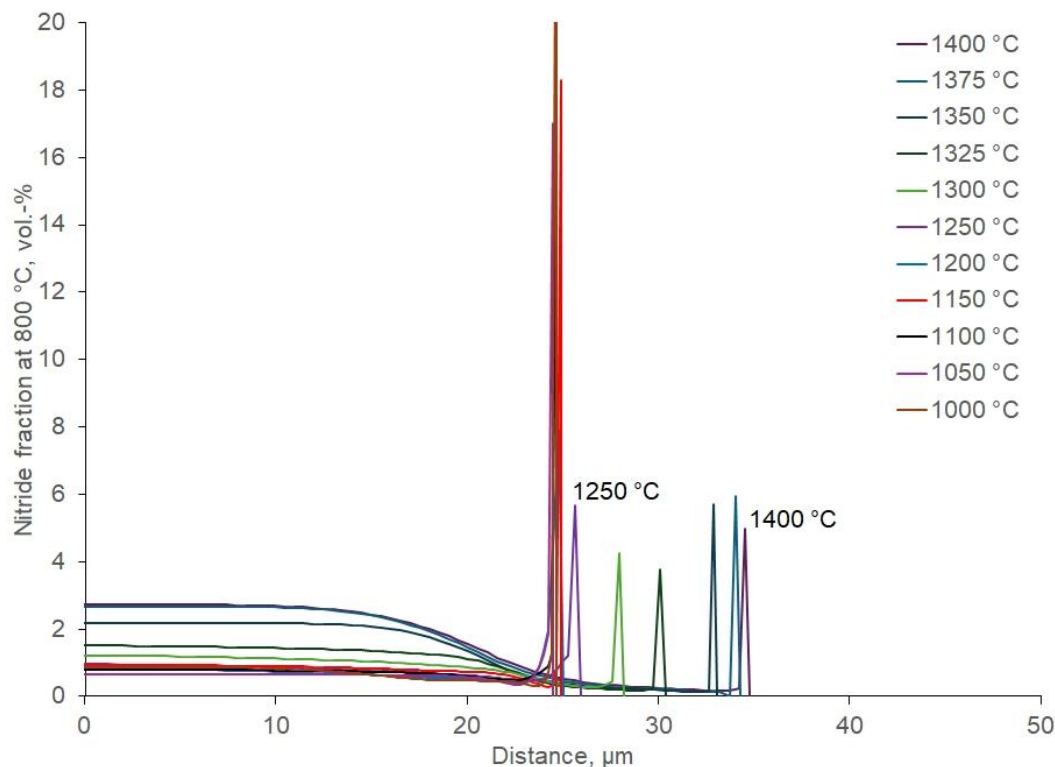


Fig. 14 2507: Nitride fraction at the end of the simulation (800 °C) as a function of position within the computational cell. Ferrite is located on the left side of each profile, while the regions to the right are fully austenitic.

Interestingly, all simulations predicted a local maximum in nitride content at the ferrite–austenite interface. However, this feature was represented by only a single computational node. Whether this interfacial peak represents a physically meaningful phenomenon or merely a numerical artefact of the simulation remains uncertain and warrants further investigation.

5. Discussion

5.1 Role of nitrogen in nitride precipitation

Nitrogen is the key parameter governing chromium nitride precipitation in DSSs. At first sight, the conclusion by Blom [40] that nitrides can be avoided by increasing the nitrogen content appears contradictory. However, the present simulations support this interpretation when the interaction between nitrogen, ferrite fraction, and austenite formation is considered in detail.

For the quenched-in nitrides investigated in the present work, the decisive parameter is not simply the nominal alloy nitrogen content but rather the nitrogen concentration remaining in the ferrite grain center during cooling. Under sufficiently rapid cooling conditions, diffusion of substitutional alloying elements becomes limited, and the ferrite grain center largely retains the nominal alloy composition. Nitrogen represents the important exception because of its high diffusivity. The redistribution of nitrogen during austenite formation is related to para-equilibrium concepts [41], although the present work instead focuses on identifying a critical nitrogen concentration in the ferrite center above which nitride precipitation is initiated.

This behavior is illustrated in Fig. 15 for LDX 2101 cooled at 75 °C/s. The results indicate a critical ferrite-center nitrogen concentration of approximately 0.03 wt.-%, above which chromium nitride precipitation occurs. A clear correspondence can be observed between the trends in Fig. 15 and the nitride precipitation behavior shown previously in Fig. 2. However, in the latter case, no nitrides were predicted for cell sizes of 20 and 30 μm. For the more highly alloyed 2509, the corresponding critical center nitrogen concentration was approximately 0.062 wt.-%, reflecting differences in alloy chemistry and nitrogen solubility.

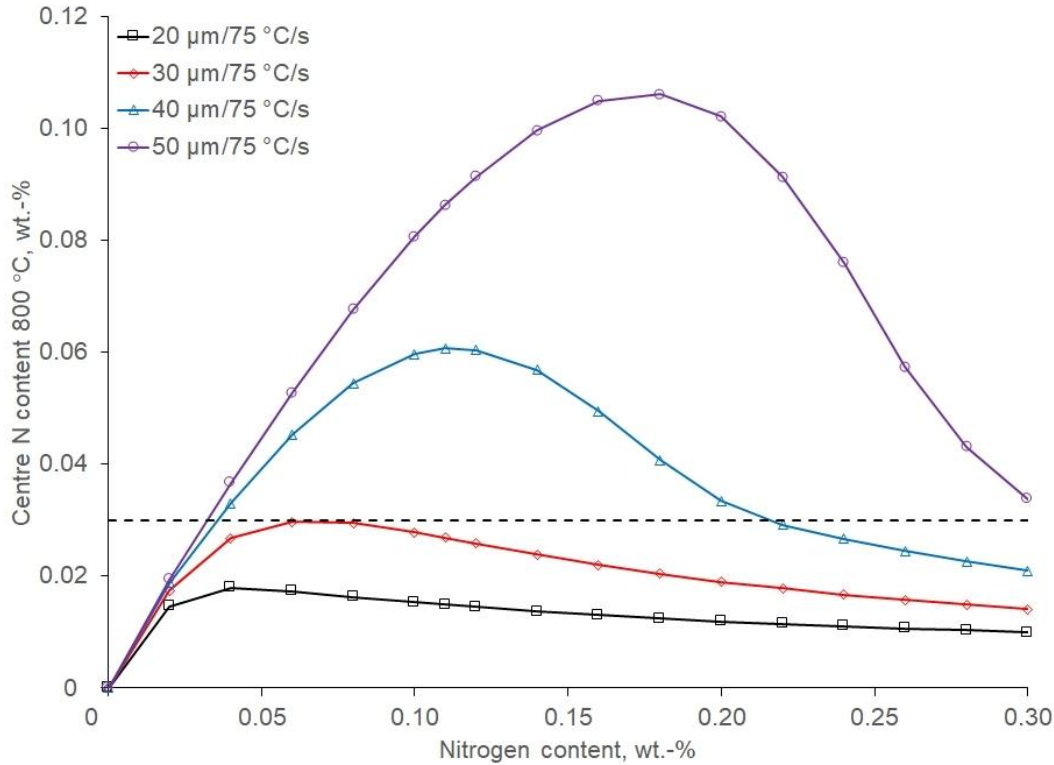


Fig. 15 LDX 2101 cooled at 75 °C/s: calculated nitrogen concentration in the ferrite center as a function of alloy nitrogen content for cell sizes of 20, 30, 40, and 50 μm. The dotted line indicates the critical ferrite-center nitrogen concentration of 0.03 wt.-% associated with nitride precipitation.

A more experimentally accessible parameter is the ferrite fraction, which closely follows the ferrite-center nitrogen content. For LDX 2101 containing 0.11 wt.-% N, the critical ferrite fraction associated with nitride formation was approximately 79.4 vol.-%, whereas the corresponding value for LDX 2101 containing 0.22 wt.-% N was 61.1 vol.-%. For 2509, the critical ferrite fraction was approximately 63.4 vol.-%. These results emphasize that nitride precipitation is governed not only by the nominal alloy nitrogen content, but also by the extent to which nitrogen can redistribute from ferrite into austenite during cooling.

An interesting feature of the simulations is that the maximum nitrogen concentration in the ferrite center shifts towards lower nominal alloy nitrogen contents with decreasing cell size. A corresponding shift is also observed for the nitride precipitation start temperatures in Fig. 2 and Fig. 3. This behavior is likely related to the shorter diffusion distances in smaller ferrite regions, which allow nitrogen redistribution towards austenite to occur more efficiently during cooling. Consequently, the ferrite center reaches its critical nitrogen concentration at lower nominal alloy nitrogen levels than in larger ferrite regions.

5.2 Influence of grain size and cooling rate

Initially, the intention was to discuss grain size and cooling rate separately. However, the simulation results demonstrate that these parameters are fundamentally interconnected in relation to chromium nitride precipitation. A high cooling rate requires a correspondingly small ferrite grain or cell size in order to avoid nitrides, whereas larger ferrite regions require slower cooling conditions.

Within the DICTRA framework, the geometry is represented by the cell size parameter. To simplify the calculations, only one-half of the geometry is simulated, using symmetry conditions to mirror the remaining half. The cell size must be defined at the start of the calculation and remains constant throughout the simulation. Consequently, grain growth during cooling cannot be directly incorporated. As in earlier work [21], this limitation was instead addressed through systematic variation of the cell size parameter.

In metallurgical terms, the DICTRA cell size may be interpreted either as half the spacing between neighboring austenite regions in duplex base materials or as the characteristic ferrite grain dimension in HAZs and weld metals. The simulations clearly demonstrate that this parameter strongly influences nitride precipitation behavior. The results for 2509 shown in Fig. 16 illustrate that smaller ferrite regions tolerate substantially higher cooling rates

without nitride precipitation than larger regions. Conversely, increasing ferrite grain size reduces the maximum cooling rate that can be applied without nitride formation.

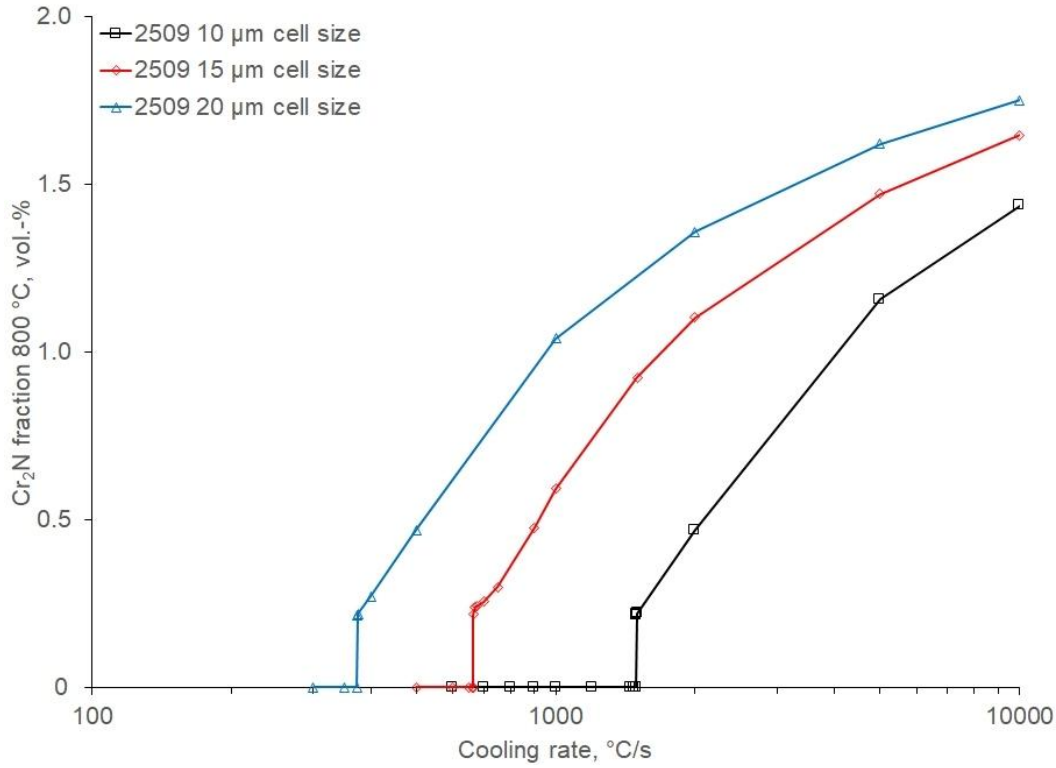


Fig. 16 2509: calculated nitride fraction at 800 °C as a function of cooling rate for cell sizes of 10, 15, and 20 μm.

It is noteworthy that the critical ferrite fraction associated with nitride-free conditions remained essentially constant for all investigated cell sizes in 2509, approximately 63.4 vol.-%, corresponding to a ferrite-center nitrogen concentration of 0.062 wt.-%. This observation further supports the interpretation that the ferrite-center nitrogen content governs nitride precipitation.

The combined influence of cell size and cooling rate is summarized in Fig. 17, where the nitride-free conditions for LDX 2101 and 2509 are plotted as cell size versus cooling rate. The results indicate a clear relationship between these parameters, which may be approximated by:

$$Cell\ size = \frac{Constant}{\sqrt{Cooling\ rate}}$$

Using SI units, the proportionality constants obtained from the simulations were approximately $1.81 \cdot 10^{-4} (K/s)^{1/2}$ for LDX 2101 containing 0.11 wt.-% N, $3.55 \cdot 10^{-4} (K/s)^{1/2}$ for LDX 2101 containing 0.22 wt.-% N, and $3.86 \cdot 10^{-4} m \cdot (K/s)^{1/2}$ for 2509.

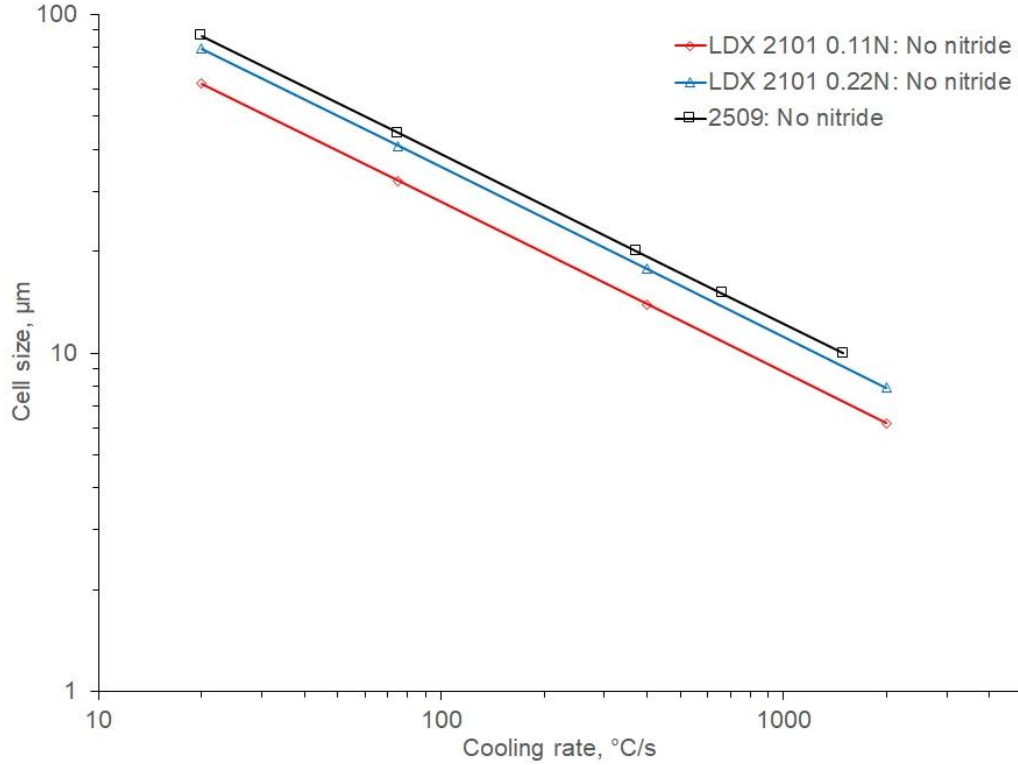


Fig. 17 LDX 2101 and 2509: calculated combinations of cell size and cooling rate resulting in nitride-free conditions.

Since nitrogen diffusion is expected to dominate the process, these results were compared with nitrogen diffusion coefficients calculated by DICTRA for ferrite at 800 °C. The tracer diffusion coefficients were approximately $4.78 \cdot 10^{-11} \text{ m}^2/\text{s}$ for LDX 2101 containing 0.11 wt.-% N, $4.68 \cdot 10^{-11} \text{ m}^2/\text{s}$ for LDX 2101 containing 0.22 wt.-% N, and $2.85 \cdot 10^{-4} \text{ m}^2/\text{s}$ for 2509. The proportionality constant in Fig. 17, may therefore be qualitatively associated with a diffusion-controlled process described by:

$$\text{Constant} = f \left(\sqrt{D_N^{BCC}}, \sqrt{T}, \frac{1}{V(BCC)} \right)$$

where D is the diffusion coefficient for nitrogen in ferrite, T temperature and V the volume fraction of ferrite.

A quantitative description of the relationship remains challenging because the process is inherently dynamic. During cooling, both the ferrite fraction and the nitrogen diffusion coefficient vary continuously with temperature, resulting in a complex coupling between phase transformation and diffusion kinetics. Although the observed relationships are physically plausible and consistent with diffusion-controlled behavior, additional work is required to establish a more rigorous description of the coupled transformation and diffusion processes. Furthermore, the present analysis is based on the assumption of linear cooling, whereas actual welding thermal cycles are inherently non-linear. The influence of realistic temperature–time histories therefore requires further investigation before the proposed relationship can be generalized to practical welding conditions.

5.3 The influence of the cooling sequence

In DSS welding, heat input and cooling conditions must be carefully controlled to balance two competing requirements. Cooling must be sufficiently rapid to suppress the formation of detrimental intermetallic phases such as sigma phase, while excessively rapid cooling may limit austenite formation and thereby promote chromium nitride precipitation. This balance is reflected in welding recommendations, where both excessively high and excessively low heat inputs are generally avoided. A similar compromise is often applied in laboratory heat-treatment studies, where small-sized specimens are removed from the furnace and allowed a short period of air cooling (~10 s) before water quenching rather than being quenched immediately.

A systematic study was carried out to evaluate how deviations from a linear cooling rate of 75 °C/s between 1400 and 800 °C (8 s total cooling time) influence nitride precipitation. The motivation was to determine whether the distribution of cooling time over the temperature interval is as important as the average cooling rate itself. Temperatures of 1200, 1100, and 1000 °C were selected as intermediate breakpoints, and a cooling rate of 400 °C/s was used as the fast-cooling condition. Consequently, three fast-slow and three slow-fast cooling sequences were investigated, with transitions at 1200, 1100, and 1000 °C, respectively. In all cases, the total cooling time from 1400 to 800 °C was maintained at 8 s.

The results for LDX 2101 with a cell size of 50 µm indicate that the most favorable cooling sequence is rapid cooling to 1200 °C followed by slower cooling to 800 °C. The second-best alternative was slow cooling to 1000 °C followed by rapid cooling. The least favorable conditions were rapid cooling to 1000 °C followed by slow cooling and the quasi-logged cooling sequence.

The results can be understood by considering the relationship between austenite formation and nitride stability. In LDX 2101, austenite formation begins at approximately 1323 °C, whereas chromium nitrides become thermodynamically stable below approximately 1180 °C in the absence of austenite. Since only 8 s are available for cooling from 1400 to 800 °C, efficient austenite formation before entering the nitride stability range becomes critical. At lower temperatures, austenite growth is increasingly sluggish, resulting in higher nitrogen concentrations remaining in the ferrite and thereby increasing the tendency for nitride precipitation. However, at higher temperatures, although austenite growth kinetics are favorable, the equilibrium austenite fraction is relatively low. The optimum cooling sequence therefore represents a balance between thermodynamic driving force and transformation kinetics.

Additional insight is obtained from the previous TTT simulations for LDX 2101, which predicted the time required to reach 30 vol.-% austenite as 7.3 s at 1200 °C, 0.08 s at 1100 °C, and 0.06 s at 1000 °C. Similarly, the CCT simulations for a 10 µm cell size predicted 30 vol.-% austenite at approximately 1104 °C during cooling at 400 °C/s. Examination of Fig. 7 shows that the fast 1200 °C/slow cooling sequence produces substantially greater austenite growth than the other cooling schedules. For cooling sequences involving slower cooling below 1100 or 1000 °C, the austenite formation rate becomes too low to effectively reduce the nitrogen concentration in the ferrite center. Likewise, for the slow-fast cooling sequences, the transformation behavior is similar up to the breakpoint temperature, after which progressively less austenite forms during the rapid-cooling stage as the breakpoint temperature decreases.

The quasi-logged cooling sequence was included to approximate the thermal cycles commonly observed during practical welding operations, where cooling is initially rapid and subsequently slows. Although this profile may appear more realistic than a linear cooling rate, the simulations indicate that it is less effective in suppressing nitride precipitation. This observation further illustrates why chromium nitrides are often difficult to avoid in practical welding applications.

The corresponding study for 2509 weld metal employed the same fast-slow and slow-fast cooling sequences but with the more ambitious objective of determining the critical cell size required to avoid nitride precipitation with an accuracy of ± 0.1 µm. Once again, rapid cooling to 1200 °C followed by slower cooling produced the most favorable result, corresponding to the largest cell size that remained free from nitrides. The second-best condition was linear cooling, closely followed by slow cooling to 1000 °C and subsequent rapid cooling. The least favorable condition was slow cooling to 1200 °C followed by rapid cooling.

The overall trends were consistent with those observed for LDX 2101. For cooling sequences involving an initial rapid-cooling stage, higher breakpoint temperatures were beneficial, whereas lower breakpoint temperatures were preferred when the initial cooling stage was slow. The ferrite fractions predicted at 800 °C did not exhibit a clear systematic trend, which is likely related to the fact that the simulations were performed using different critical cell sizes. Despite the substantial compositional differences between LDX 2101 and 2509, the similarities in behavior suggest that the governing mechanisms are largely the same. In 2509, austenite formation begins at approximately 1351 °C, while chromium nitrides become stable below approximately 1205 °C in the absence of austenite.

5.4 Nitrides in relation to sigma phase formation

A central aspect of DSS processing is the need to balance the risks of sigma phase formation and chromium nitride precipitation. In industrial practice, DSS components must be cooled sufficiently rapidly to suppress sigma phase formation, while excessively rapid cooling may instead promote nitrides.

The combined CCT/TTT diagrams presented in Fig. 10 and Fig. 11 provide a direct comparison between these two precipitation phenomena. The results indicate that the available processing window for precipitation-free microstructures remains relatively constant. Conditions favoring rapid nitride precipitation also tend to favor rapid sigma phase formation, whereas reduced susceptibility to one precipitation reaction is generally accompanied by reduced susceptibility to the other.

The simulations therefore support the established metallurgical practice for DSSs: cooling should be sufficiently rapid to avoid intermetallic phase formation, but not so rapid that nitrogen becomes trapped in ferrite and promotes chromium nitride precipitation. No evidence was found suggesting that alloy modifications alone could fundamentally eliminate this balance between competing precipitation mechanisms.

5.5 Ferrite grain center and phase boundary effects

The simulations indicate that nitride precipitation is initiated when the ferrite-center nitrogen concentration exceeds approximately 0.03 wt.-% for LDX 2101 and 0.062 wt.-% for 2509. Under rapid cooling conditions or for large ferrite regions, the ferrite grain center largely retains the nominal alloy composition for substitutional alloying elements, while nitrogen remains the principal variable because of its significantly higher diffusivity.

The present results therefore suggest that quenched-in nitride precipitation is primarily controlled by the local nitrogen concentration in the ferrite center. However, precipitation at grain boundaries represents a considerably more complex problem. During austenite growth, ferrite-stabilizing elements such as chromium and molybdenum are rejected into the adjacent ferrite, whereas austenite-stabilizing elements such as nickel and nitrogen partition into the growing austenite. As a consequence, ferrite adjacent to austenite may become enriched in chromium while simultaneously depleted in nitrogen.

This local chemistry creates favorable conditions for nitride formation with respect to chromium availability but unfavorable conditions with respect to nitrogen concentration. The situation is further complicated by observations reported in the literature indicating that the chromium concentration in grain boundary ferrite may, under some conditions, be lower than in the adjacent austenite [42]. Such behavior was not observed for nickel and molybdenum. Additional experimental and modelling work is therefore required to fully understand the mechanisms governing phase boundary nitride precipitation in duplex stainless steels.

5.6 The nitride-free zone

The simulations involving a 10 s holding time at peak temperatures ranging from 1000 to 1400 °C, followed by cooling at 100 °C/s, indicated that elevated peak temperatures are required for the development of a nitride-free zone. Analysis of the ferrite fraction during the thermal cycle showed that a significant increase in the maximum ferrite fraction occurs only for peak temperatures of approximately 1250 °C and above.

This increase in ferrite fraction is interpreted as producing ferrite with a substantially higher dissolved nitrogen content prior to cooling. This interpretation is further supported by the increased nitrogen concentration at the center of the ferrite at the end of the simulations. In addition, the higher peak temperatures result in increased ferrite fractions and larger austenite spacings at the end of the thermal cycle, both of which promote nitride precipitation and the development of a partially nitride-free region adjacent to the ferrite–austenite interface.

A more detailed examination of the simulation results for a peak temperature of 1350 °C confirms that a nitride-free zone is initially formed during cooling but progressively disappears as the transformation proceeds. The nitride distribution in the cell is shown in Fig. 18, while the positions of the ferrite–austenite interface and the ferrite–nitride boundary are presented in Fig. 19. The results indicate that the ferrite–austenite interface becomes essentially stationary already at approximately 1050 °C, whereas the ferrite–nitride interface continues to migrate until it ultimately disappears.

Nitride-free zones are frequently reported in the literature, where the evidence is commonly based on optical metallography. The present simulations, however, suggest the existence of a nitride-depleted zone rather than a completely nitride-free zone. Whether this reflects the actual microstructure, with residual nitrides remaining below the detection limit of conventional metallography, or instead represents a limitation of the present simulation approach remains to be established. Nevertheless, the simulations consistently indicate that elevated peak temperatures exceeding approximately 1250 °C are required for the development of such nitride-free or nitride-depleted regions.

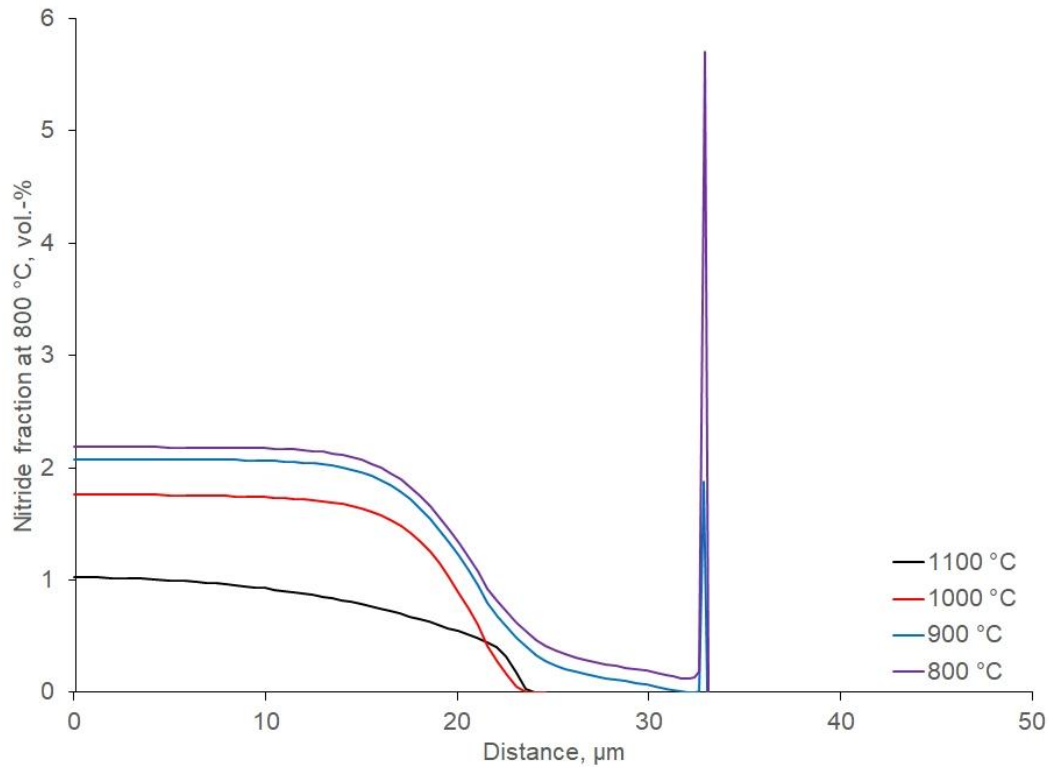


Fig. 18 2507: Dilatometer simulation with a peak temperature of 1350 °C: Nitride distributions within the computational cell during cooling at 1100, 1000, 900, and 800 °C (end of simulation).

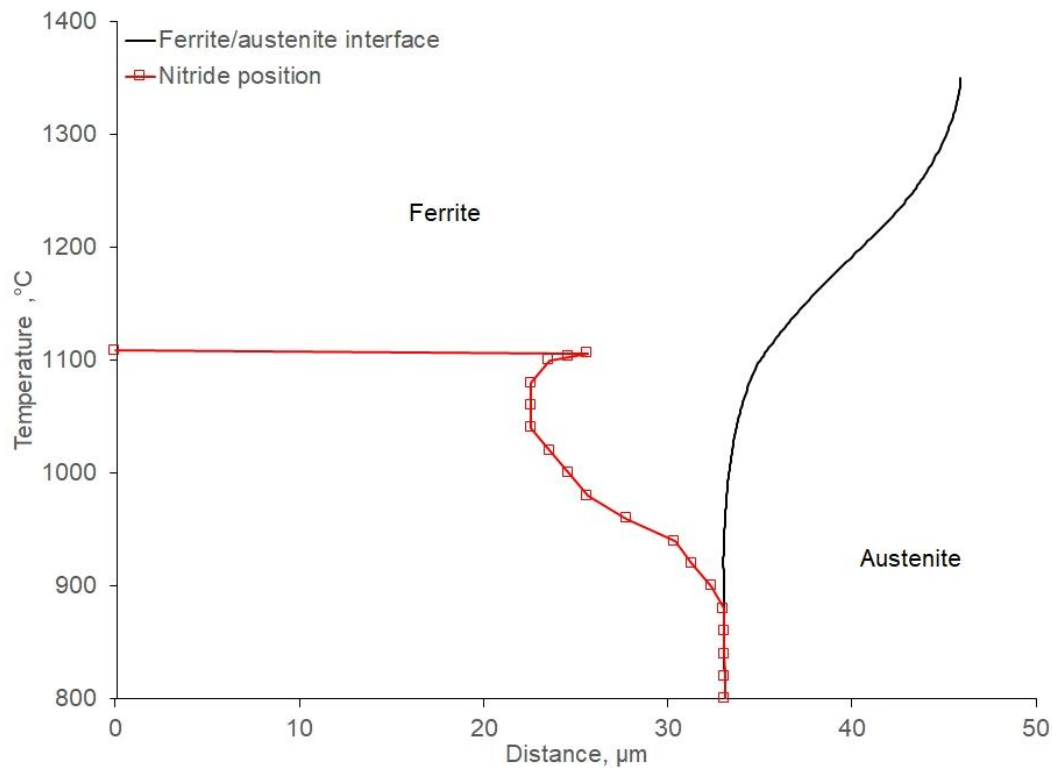


Fig. 19 2507: Dilatometer simulation with a peak temperature of 1350 °C: Positions of the ferrite–austenite interface and the ferrite–nitride boundary as a function of distance during cooling.

5.7 Simulation set-up and numerical considerations

The simulations presented in the present work were based on a number of interconnected thermodynamic, kinetic, and numerical parameters. The principal components of the DICTRA set-up were:

- the TCFe13 thermodynamic database for Fe-based alloys
- the MOBFE8 mobility database for Fe-based alloys
- the alloying elements Fe, Mn, Cr, Ni, Mo, and N
- the ferrite (BCC_A2), austenite (FCC_A1), and Cr₂N (HCP_A3#2) phases
- thermal cycles between 1400 and 800 °C at different cooling rates
- a one-dimensional planar ferrite cell geometry with specified cell size and numerical grid
- introduction of austenite as a moving precipitating phase boundary
- treatment of Cr₂N as a dispersed precipitate phase within ferrite
- the nominal ferrite composition listed in Table 1
- specified simulation times together with numerical time-step parameters

Beyond these principal parameters, DICTRA also contains a large number of numerical solver settings that may significantly influence convergence behavior and computational stability.

In total, approximately >500 DICTRA simulations were performed in the present work. Computational times varied substantially, from approximately two days for rapidly converging cases to several weeks for the most computationally demanding calculations. Some simulations had to be terminated before completion because of numerical instability or impractically long computation times.

The occurrence of occasional numerical inconsistencies also became evident during work. For example, among the 63 simulations used to generate Fig. 4 and Fig. 5, nine calculations had to be repeated because nitrides appeared in conditions where precipitation was not expected. Repeated calculations subsequently showed no nitride formation. Similarly, one of the 78 simulations associated with Table 3 produced an apparent outlier result involving unexpected nitride precipitation.

These observations indicate that systematic simulation strategies are essential in order to identify numerical artefacts and distinguish them from physically meaningful trends. The deviations are most likely related to a combination of database limitations, convergence behavior, and numerical aspects of the DICTRA calculations.

6. Conclusions

This study used computational thermodynamics and the diffusion module DICTRA within Thermo-Calc to investigate the relationship between austenite formation and chromium nitride precipitation in the lean duplex stainless steel (DSS) LDX 2101, the super duplex 2507 and weld metal 2509. The main conclusions are as follows:

Role of nitrogen in nitride precipitation

Increasing the nitrogen content reduced the tendency for chromium nitride precipitation. The simulations therefore support the nitrogen paradox, namely that increasing the nitrogen content can reduce nitride formation. Conversely, nitrogen loss promotes nitride precipitation. Lower nitrogen contents also delayed austenite formation, increased the temperature range over which the microstructure remained fully ferritic, and promoted ferrite grain growth at temperatures relevant to the HT-HAZ. These effects collectively increased the susceptibility to nitride precipitation during cooling.

Influence of grain size and cooling rate

The simulations demonstrated a strong relationship between ferrite cell size, cooling rate, and nitride precipitation. Larger ferrite cell sizes and reduced nitrogen contents both increased the tendency for nitride formation. For both LDX 2101 and 2509, the critical combination of cell size and cooling rate required to avoid nitrides could be predicted with good accuracy. Regression analysis indicated that the critical cell size is proportional to the inverse square root of cooling rate, suggesting that nitride precipitation is fundamentally governed by nitrogen diffusion in ferrite. Although the results apply to the specific alloys and thermal cycles investigated, the demonstrated predictive capability represents an important step towards quantitative assessment of nitride precipitation in DSSs.

Influence of non-linear cooling sequences

The influence of non-linear cooling sequences was investigated by comparing different fast–slow and slow–fast cooling schedules having the same average cooling rate between 1400 and 800 °C. The results showed that the distribution of cooling time over the temperature range significantly affects nitride precipitation. For both alloys, the

most favorable condition was rapid cooling to approximately 1200 °C followed by slower cooling, whereas the opposite sequence promoted nitride formation. The results indicate that sufficient time for austenite formation below approximately 1200 °C is important for reducing the nitrogen concentration in ferrite and thereby suppressing nitride precipitation. Consequently, average cooling rate alone is insufficient to fully describe nitride formation behavior.

Experimental validation

The methodology was validated against the dilatometry experiments of Pettersson et al. [30] on 2507 super DSS. Good agreement was obtained when the critical austenite spacing required for nitride precipitation was used as the comparison criterion. The simulations also reproduced the formation of nitride-free zones adjacent to austenite and indicated that their development requires elevated ferrite fractions associated with high peak temperatures.

Acknowledgement

Sten Wessman gratefully acknowledges the support from Swerim AB and University West.

Author contribution

S. Wessman performed the Thermo-Calc and DICTRA simulations and wrote the paper in collaboration with E. M. Westin and S. Hertzman. All authors have read and approved of the final version of the manuscript.

Conflicts of Interest The authors declare no conflicts of interest.

Funding No funding was obtained for this study.

Data availability

The majority of the work presented in this publication was conducted using the diffusion module within Thermo-Calc, also known as DICTRA. Simulations were performed in console mode using macro files, which can be made available upon reasonable request. Additionally, the results from the simulations are available on request.

References

- [1] Olsson J, Liljas M (1994) 60 Years of Duplex Stainless Steel Applications. Proc. NACE Corrosion 94' Baltimore, MD, United States, AMPP, Paper No. C1994-94395, 12pp. <https://doi.org/10.5006/C1994-94395>
- [2] Jargelius RFA, Blom R, Hertzman S, Linder J (1991) Chloride Induced Stress Corrosion Cracking of Duplex Stainless Steels in Concentrated Chloride Environments. Proc. Duplex Stainless Steels '91. Beaune, France, Les editions de physique, 1:211-220
- [3] Bernhardsson S (1991) The Corrosion Resistance of Duplex Stainless Steels. Proc. Duplex Stainless Steels '91. Beaune, France, Les editions de physique, 1:185-210
- [4] Nordberg H (1993) Mechanical Properties of Austenitic and Duplex Stainless Steels. Proc. 1st European Stainless Steel Conference. Processes and Materials Innovation Stainless Steel. Florence, Italy, 2:217-229
- [5] Wessman S, Hertzman S, Pettersson R, Lagneborg R, Liljas M (2008) On the Effect of Nickel Substitution in Duplex Stainless Steels. Mat Sci Tech 24(3):348-355. <https://doi.org/10.1179/174328408X276116>
- [6] Nilsson J-O (1992) Overview super duplex stainless steels. Mat Sci Tech 8(8):685-699. <https://doi.org/10.1179/mst.1992.8.8.68>
- [7] Göransson K, Nyman ML, Holmquist M, Gomes E (2007) Sandvik SAF 2707 HD (UNS S32707): A hyper-duplex stainless steel for severe chloride containing environments. Rev Metall 104(9):411–417. <https://doi.org/10.1051/metal:2007207>
- [8] NACE MR 0175/ISO 15156-3 (2020) Petroleum and Natural Gas Industries – Materials for Use in H₂S-containing Environments in Oil and Gas Production – Part 3: Cracking-Resistant CRAs (Corrosion Resistant Alloys) and Other Alloys, 71pp.
- [9] Norsok Standard M-630 (2020) Material data sheets for piping, Revision 4, Standards Norway, Lysaker, Norway, 228pp.
- [10] Liljas M (1995) The welding metallurgy of duplex stainless steels. Proc. Duplex Stainless Steels '94, Glasgow, UK, TWI, 2(Paper KV):15pp
- [11] Hertzman S, Ferreira PJ, Brolund B (1997) An experimental and theoretical study of heat-affected zone austenite reformation in three duplex stainless steels. Metall Mater Trans A 28(2):277–285. <https://doi.org/10.1007/s11661-997-0130-6>
- [12] Streicher MA (1956) Pitting corrosion of 18 Cr - 8 Ni stainless steel. J Electrochem Soc 103(7):375-390.

<https://doi.org/10.1149/1.2430359>

- [13] Hertzman S, Pettersson R, Frisk K, Jerwin T (2000) The relation between alloy composition and kinetics of intermetallic phase formation, Proc. 6th World Duplex Conference, Venice, Italy, AIM, 347-354
- [14] Cao HL, Hertzman S (1991) The relationship between impact properties and welding simulated microstructures in three duplex stainless steels. Proc. Duplex Stainless Steels '91. Beaune, France, Les editions de physique, 1:363-372
- [15] Jargelius-Pettersson RFA (1996) Sensitization behaviour and corrosion resistance of austenitic stainless steels alloyed with nitrogen and manganese. ISIJ Int 36(7):818-824. <https://doi.org/10.2355/isijinternational.36.818>
- [16] Kaufman L, Ågren J (2014) CALPHAD, first and second generation – Birth of the materials genome. Scripta Mat 70(1):3-6. <https://doi.org/10.1016/j.scriptamat.2012.12.003>
- [17] Sundman B, Jansson B, Andersson J-O (1985) The Thermo-Calc databank system. CALPHAD 9(2):153-190. [https://doi.org/10.1016/0364-5916\(85\)90021-5](https://doi.org/10.1016/0364-5916(85)90021-5)
- [18] Wessman S, Selleby M (2014) Evaluation of austenite reformation in duplex stainless steel weld metal using computational thermodynamics. Weld World 58(2):217-224. <https://doi.org/10.1007/s40194-013-0104-9>
- [19] Westin EM, Wessman S (2024) Characteristics of high-temperature heat-affected zones in duplex stainless steels, Weld World 68(8):1981-1997. <https://doi.org/10.1007/s40194-024-01715-7>
- [20] Valiente Bermejo MA, Wessman S (2019) Computational thermodynamics in ferrite content prediction of austenitic stainless steel weldments. Weld World 63(5):627–635. <https://doi.org/10.1007/s40194-018-00685-x>
- [21] Wessman S, Westin EM, Hertzman S (2026) On the precipitation of secondary phases in duplex stainless steels and welds. Weld World XX(X):XXXX–XXXX. <https://doi.org/10.1007/s40194-026-02365-7>
- [22] Pettersson N, Wessman S, Hertzman S, Studer S (2017) High-temperature phase equilibria of duplex stainless steels assessed with a novel in situ neutron scattering approach. Met Mat Trans 48A(4):1562–1571. <https://doi.org/10.1007/s11661-016-3953-1>
- [23] Cao HL, Hertzman S (1991) The relationship between impact properties and welding simulated microstructures in three duplex stainless steels. Proc. Duplex Stainless Steels '91. Beaune, France, Les editions de physique, 1:363-372.
- [24] Jargelius-Pettersson RFA (1996) Sensitization behaviour and corrosion resistance of austenitic stainless steels alloyed with nitrogen and manganese. ISIJ Int 36(7):818-824. <https://doi.org/10.2355/isijinternational.36.818>
- [25] Nilsson J-O, Karlsson L, Andersson J-O (1995) Secondary austenite formation and its relation to pitting corrosion in duplex stainless steel weld metal. Mat Sci Tech. 11(3):276-283. <https://doi.org/10.1179/mst.1995.11.3.276>
- [26] Ramirez AJ, Lippold JC, Brandi SD (2003) The relationship between chromium nitride and secondary austenite precipitation in duplex stainless steels. Met Mat Trans 34A(8):1575-1597. <https://doi.org/10.1007/s11661-003-0304-9>
- [27] Avoidance of detrimental nitrides in duplex stainless steels, national project Sweden, Vinnova Sweden's Innovation Agency project no. 2016-02822.
- [28] Burke KE (1975) Chemical extraction of refractory inclusions from iron-and nickel-base alloys. Metallography 8(6):473–488. [https://doi.org/10.1016/0026-0800\(75\)90023-3](https://doi.org/10.1016/0026-0800(75)90023-3)
- [29] Westin EM, Riffel KC, Jonsson JY, Bos MM, Ramirez AJ, Goulas C (2026) Enhancing microstructural analysis: Best practices for preparing duplex stainless steel welds and additive manufacturing deposits. Weld World 70(XX):XXXX–XXXX. <https://doi.org/10.1007/s40194-025-02286-x>
- [30] Pettersson N, Pettersson RFA, Wessman S (2015) Precipitation of chromium nitrides in the super duplex stainless steel 2507. Met. and Mat. Trans. 46A(3):1062–1072. <https://doi.org/10.1007/s11661-014-2718-y>
- [31] Liao J (2001) Nitride precipitation in weld HAZs of a duplex stainless steel. ISIJ Int 41(9):1033–1041. <https://doi.org/10.2355/isijinternational.41.460>
- [32] Guo J, Zhang Y, Li X, Wang Y (2025) On the formation mechanism of Cr nitrides in an additively manufactured duplex stainless steel. Mater Charact 227:115261. <https://doi.org/10.1016/j.matchar.2025.115261>
- [33] Hooper PA (2018) Melt pool temperature and cooling rates in laser powder bed fusion. Add Man 22(8):248-559. <https://doi.org/10.1016/j.addma.2018.05.032>
- [34] Hertzman S, Roberts W, Lindenmo M (1986) Microstructure and properties of nitrogen alloyed duplex stainless steel after welding treatments. Proc. Duplex Stainless Steel, The Hague, The Netherlands, NIL, pp 257–267
- [35] Andersson J-O, Höglund L, Jönsson B, Ågren J (1990) Fundamentals and application of ternary diffusion, C.R. Purdy (Editor), Pergamon Press, NY, USA 153-163
- [36] Larsson H, Engström A (2006) A homogenization approach to diffusion simulations applied to a $\alpha + \gamma$ Fe-Cr-Ni diffusion couples. Acta Mater 54(9):2431-2439. <https://doi.org/10.1016/j.actamat.2006.01.020>
- [37] Recommended Practice DNV-RP-F112 (2019) Design of Duplex Stainless Steel Subsea Equipment Exposed to Cathodic Protection, DNV, 44pp.

- [38] Andersson J-O, Helander T, Höglund L, Shi P, Sundman B (2002) Thermo-Calc & DICTRA, Computational Tools for Materials Science. *Calphad* 26(2):273-312.
[https://doi.org/10.1016/S0364-5916\(02\)00037-8](https://doi.org/10.1016/S0364-5916(02)00037-8)
- [39] Wessman S, Wilson A, Hertzman S, Pettersson R (2013) An Experimental and theoretical evaluation of coarsening of ferrite and austenite in duplex stainless steel microstructure. *Steel Res Int* 84(11):1126–1137.
<https://doi.org/10.1002/srin.201200323>
- [40] Blom K-J (1987) Improving properties of weld joints in duplex stainless steel by welding with shielding gas contacting nitrogen. *Proc. Stainless Steels '87*, York, UK, 123–125.
- [41] Hillert M, Ågren J (2004) On the definitions of paraequilibrium and orthoequilibrium. *Scripta Mat* 50(5):697–699. <https://doi.org/10.1016/j.scriptamat.2003.11.020>
- [42] Wessman S (2022) On the use of computational thermodynamics for predicting the precipitation and growth of secondary phases in duplex stainless steels. Poster, 49th International Conference on Computer Coupling of Phase Diagrams and Thermochemistry, Stockholm, Sweden, May 22-27.