Non-isothermal Dissolution Modelling of Sigma Phase in Duplex Stainless Steels

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Abstract In this work, the non-isothermal dissolution kinetics of the sigma phase in duplex stainless steels has been studied and modelled. A semi-empirical model is proposed to describe the kinetics of sigma phase precipitation/dissolution during continuous heating starting from the isothermal transformation kinetics. The proposed model, which presumes validity of the additivity rule, is validated by means of experimental investigations. A good agreement is found between experimental and analytical results.

KEY WORDS: Kinetics; Non-isothermal dissolution; Modelling; Semi-empirical models; Sigma phase; Duplex stainless steels

List of Symbols

c	Impingement exponent for the precipitation reaction
C	Kinetic constant
c_d	Impingement exponent for the dissolution reaction
D_{eff}	Diffusion coefficient
d_{grain}	Ferrite grain size
D_i^0	Frequency factor for the diffusion of element i in the ferrite matrix
f	Shape factor
G_r	Growth rate
k	Function of growth rate
K	Constant
l_c	Critical length
n	Time exponent for the precipitation reaction
N_0	Total number of active nucleation sites per unit volume
n_d	Time exponent for the dissolution reaction

Q_d	Activation energy for the dissolution reaction
Q_{eff}	Activation energy for diffusion
Q_i	Activation energy for the diffusion of element i in the ferrite matrix
R	Ideal gas constant
t	Time
t'	Fictitious time
T	Temperature
T^*	Temperature at which the maximum growth rate is reached
T_{eq}	Equilibrium temperature (solvus)
$V_{\delta\sigma}$	Volume fraction of σ phase transformed at time t during precipitation
V_{σ}^e	Equilibrium amount of σ phase
V_{σ}^i	Volume fraction of σ phase before dissolution
$V_{\sigma\delta}$	Volume fraction of σ phase at time t during dissolution
V_0	Volume fraction of σ phase before heating
x_0	Fixed volume proportion of sigma phase
x_i	Mole fraction of element i
ΔG_m	Molar driving force for growth
ΔT	Undercooling
τ	Time required for the precipitation of a fixed volume proportion of sigma phase

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ω	Kinetic constant for the dissolution reaction
ω_0	Pre-exponential factor

1 Introduction

Sigma phase is a Cr- and Mo-rich intermetallic phase, which can arise after relatively long holding time at temperatures ranging from 923 to 1223 K as well as after cooling from high temperatures. Its presence, even in small volume fractions, dramatically decreases the toughness of duplex stainless steels (DSS). This phenomenon was observed in welding joints both by El Koussy *et al.* [1] and by Chen *et al.* [2]. Ahn and Kang [3] studied a series of DSS 2205 compositions and claimed that the steels containing 25 vol.% sigma phase in the microstructure had an impact energy of 32 J, being 288 J lower than precipitation-free specimens.

Moreover, σ phase might decrease corrosion properties because of Mo and Cr depletion in the surrounding regions. Due to the presence of the ferrite, in which the diffusion rate is faster than that in austenite [4], the kinetics of sigma phase precipitation and dissolution is found significantly faster in DSS than in austenitic stainless steels. This means that sigma phase may already form in heat treatment or welding operation if the cooling rate is not insufficiently high. In the same way, the time required for sigma particle dissolution may be very short [5]. In order to obtain sound weld, solution heat treatments were carried out [6] with well-calibrated time–temperature parameters [7, 8].

In the case of DSS, the precipitation of sigma phase can be complete in a few hours and consume all the ferrite (δ) in the microstructure [9]. In this case, precipitation can be represented by a eutectoid-type reaction of $\delta \rightarrow \gamma^* + \sigma$, where γ^* is a chromium- and molybdenum-depleted austenite in contrast to a non-transformed austenite (γ).

Precipitation starts at the δ/γ interface and moves into ferrite grains until the ferrite is almost exhausted. Up to 1073 K, the eutectoid morphology is nearly lamellar, resulting from σ and austenite cooperative growth, whereas around 1173 K, the σ phase precipitates with a massive morphology, leading to a microstructure called divorced eutectoid [10]. Conversely, the nucleation of σ phase along ferrite/ferrite grain boundaries suggests that a direct reaction $\delta \rightarrow \sigma$ can also occur.

In order to optimize welding operations and heat treatments of DSS, it is very important to model the kinetics of dissolution and precipitation of the sigma phase. Most of the published literature is focused on the study of the precipitation kinetics mainly based on the well-known Johnson–Mehl–Avrami–Kolmogorov (JMAK) model [11–13]. Sieurin and

Sandström [14] modelled the σ phase precipitation in DSS 2205 during isothermal heat treatment and continuous cooling from high temperatures, assuming that Mo controls the transformation in the ferrite matrix and also that only equilibrium contents of Mo in the ferrite and σ phase are needed for calculations. It is worth mentioning that a very high nucleation rate was calculated so that σ precipitation was considered to be controlled by the growth. Similarly, Li *et al.* [15] verified that nucleation is so easy when conditions of nucleation site saturation were applied in many of the cases considered.

Another important consideration is that most of the non-isothermal precipitation models of sigma phase are based on the use of the rule of “additivity” [4]. Ferro and Bonollo [16] applied the “additivity rule” to model sigma phase precipitation in duplex and superduplex stainless steels. Such a model was then improved by using a modified JMAK equation [17]. Kim *et al.* [18] applied the “additivity rule” to calculate the continuous-cooling transformation (CCT) diagrams in cast duplex stainless steels. They started from the work of Scheil [19], who suggested the “additivity rule”, which assumes that all nucleation takes place at the early stage of the reaction. This assumption is generally made in situations involving continuous cooling, where heterogeneous nucleation occurs, and is often referred to, as mentioned above, as site saturation. Nucleation effects are negligible under this condition so that growth is the predominant mechanism for a reaction. Kim *et al.* [18] considered the Avrami exponent taken from experimentally determined time–temperature–transformation (TTT) diagrams as a function of temperature and calculated the corresponding CCT diagrams through a modified Avrami equation. A similar procedure was used by Wilson and Nilsson [4], and in both cases, a good agreement was found between experimental and predicted results. However, some theoretical doubts about the applicability of the “additivity rule” under such conditions arise. As a matter of fact, there have been several attempts to define the conditions under which the “additivity rule” is valid [20–23]. In summary, all these works commonly assume that a condition for the rule of additivity to be valid is that the transformation rate is a state function independent of the thermal path by which it reached the state [24]. That is to say, the transformation rate depends only on temperature and volume fraction. However, Lusk and Jou [25] showed that when the Avrami exponent depends on temperature, it is no longer guaranteed that the rule of additivity is valid, even though several authors continue to use it in such condition.

While secondary-phase precipitation in stainless steels has been studied extensively by means of experimental, analytical and numerical methods, much less attention has

been paid to the microstructure evolution during heating. This is a critical point when considering that many heat treatments start with material homogenization and that any undissolved precipitates or chemical non-uniformity in the parent phase greatly affect both the material properties at room temperature and the subsequent precipitation process during cooling [26]. An experimental work on this topic was carried out by Wong *et al.* [27]. They studied the dissolution of sigma phase in DSS by differential thermal analysis (DTA) and scanning electron microscopy (SEM). The DTA measurements showed that the onset temperature (T_s) and peak temperature (T_p) for σ dissolution strongly depend on the initial distribution and morphology of the σ phase. It was demonstrated that such behaviour was related to the coarsening effect induced by long ageing time or high ageing temperature on the σ phase grains. When all ferrite is transformed to σ phase, the redissolution of σ phase requires nucleation of ferrite at the σ/γ boundary; thus, the larger the σ grains, the higher the onset temperature for σ phase redissolution. However, in that work, a model which describes the kinetics of σ phase redissolution was not developed. In a recent work [28], a semi-empirical dissolution model was proposed in which the Wang *et al.* [29] equation was generalized by an impingement factor of the form y^{c+1} and an Arrhenius-type equation for the kinetic parameter k . The model was applied to the analysis of the isothermal σ phase dissolution in a DSS. On the basis of the apparent activation energy value obtained (202 kJ mol^{-1}), it was suggested that σ phase dissolution kinetics is controlled by Cr grain boundary diffusion. However, no model for the non-isothermal σ phase dissolution in DSS has been reported in the literature.

In this work, a semi-empirical model is proposed to describe the kinetics of non-isothermal σ particles dissolution in DSS based on the “additivity rule”. A computer program was written in MATLAB® code which calculates the evolution of sigma particle precipitation/dissolution during continuous heating, and experimental tests were carried out to verify the accuracy of the foreseen results. A very good agreement was found between the analytical and experimental results.

2 Mathematical Model

During continuous heating, starting from room temperature with a specific heating rate, a σ phase precipitation may occur before the solution temperature is reached. Thus, any non-isothermal dissolution model has to take into account this prior precipitate volume fraction increment induced by continuous heating.

The proposed model is based on the rule of additivity, which uses information coming from isothermal

precipitation and dissolution transformations. A generalization of a previous equation published in Ref. [16] is proposed which takes into account the impingement phenomenon during precipitation. On the other hand, the isothermal dissolution model published in a recent work [28] is used when the temperature is greater than the equilibrium (solvus) temperature.

2.1 Isothermal σ Phase Precipitation Model

The proposed model is based on the Lee and Kim's [30, 31] equation, which, in its general representation, takes the form:

$$x = \frac{V_{\delta\sigma}}{V_{\sigma}^e} = \begin{cases} 1 - (cX^n + 1)^{-1/c} & \text{for } c \neq 0 \\ 1 - \exp(-X^n) & \text{for } c = 0 \end{cases} \quad (1)$$

where $V_{\delta\sigma}$ is the volume fraction of σ phase transformed at time t ; V_{σ}^e is the equilibrium amount of σ phase; $X = kt$, where t is the time and k is a constant which takes into account the effects associated with nucleation and growth and usually evaluated empirically for each temperature [32]; c is the so-called impingement exponent [30, 31] used to correct some effects such as a depletion of the solute content in the untransformed matrix due to competitive growth of the fraction products, a direct collision of two advancing reaction products, or an exhaustion of nucleation sites; and finally, n is the time exponent which varies according to the controlling phenomenon of the phase transformation [33]. The exponent n can change if the nucleation rate is constant or nucleation site saturation has been achieved. It means that it can vary during the transformations itself [34] and/or, in the general case, according to the temperature [35]. Furthermore, n may depend on the precipitate shape [15]. It is worth mentioning that Eq. (1) is a generalization of the JMAK classical equation ($c = 0$). For conditions where nucleation site saturation has been reached, the following approximation is proposed by Li *et al.* [15]:

$$k = f^n l_c^{\frac{3-n}{n}} N_0^{\frac{1}{n}} G_r, \quad (2)$$

where N_0 is the total number of active nucleation sites per unit volume, G_r is the growth rate (m s^{-1}), f is a shape factor, and l_c is a critical dimension (m). As suggested by Li *et al.* [15] in the case of σ phase precipitation, a value for l_c of 50 nm is assumed, while f is set equal to 1 [15].

For the successful calculation of time–temperature–transformation (TTT) diagram, both the nucleation and growth rate have to be carefully calculated. The nucleation rate depends on Gibbs energy barrier to nucleation, enthalpy and molar Gibbs energy driving force of transformation, matrix/nucleus interfacial energy, wetting angle and so on. Despite that, the σ phase nucleation rate was

calculated by different authors [3, 36] who found so high values that conditions of nucleation site saturation could be applied. For this reason, in this work, Eq. (2) is considered valid for the TTT diagram calculation and it is reformulated in order to reduce the unknown terms into constants which can be calibrated by experimental tests.

As a matter of fact, if cubic grain geometry is assumed, N_0 is given by:

$$N_0 = \frac{2}{d_{\text{grain}}^3}, \quad (3)$$

where d_{grain} is the ferrite grain size. In deriving Eq. (3), it is assumed that the nucleation is limited to the grain corners and that each nucleus grows into four neighbouring ferrite grains [14].

Furthermore, the growth rate of a precipitate can be

$$D_0 = \sum_i x_i D_i^0 \quad Q_{\text{eff}} = \sum_i x_i Q_i. \quad (6)$$

In Eq. (6), x_i is the mole fraction of element i in the precipitate and D_i^0 and Q_i are the frequency factor and activation energy for the diffusion of element i in the ferrite matrix, respectively. Finally, for small undercooling (ΔT), ΔG_m can be considered proportional to the undercooling [33]. Thus,

$$\Delta G_m = C(T_{\text{eq}} - T)/T_{\text{eq}}, \quad (7)$$

where T_{eq} is the equilibrium (solvus) temperature and C is a kinetic constant.

By substituting Eqs. (2)–(7) into (1), the volume fraction of σ phase at temperature T and time t is given by:

$$x = \begin{cases} 1 - \left(c f l_c^{3-n} \frac{2}{d_{\text{grain}}^3} \left(\frac{CKD_0 T_{\text{eq}} - T}{RT_{\text{eq}}} \exp(-Q_{\text{eff}}/RT) \right)^n t^n + 1 \right)^{-1/c} & \text{for } c \neq 0 \\ 1 - \exp \left(-f l_c^{3-n} \frac{2}{d_{\text{grain}}^3} \left(\frac{CKD_0 T_{\text{eq}} - T}{RT_{\text{eq}}} \exp(-Q_{\text{eff}}/RT) \right)^n t^n \right) & \text{for } c = 0 \end{cases}. \quad (8)$$

calculated using the following equation [15]:

$$G_r = KD_{\text{eff}} \left(\frac{\Delta G_m}{RT} \right), \quad (4)$$

where K is a constant, R is the ideal gas constant, ΔG_m is the molar driving force and

$$D_{\text{eff}} = D_0 \exp(-Q_{\text{eff}}/RT), \quad (5)$$

where

From Eq. (2), it can be observed that the shape of the C-curve is controlled by the growth rate. In particular, setting the derivative of Eq. (4) to zero, the following relation is obtained:

$$Q_{\text{eff}} = R \frac{T^* T_{\text{eq}}}{T_{\text{eq}} - T^*}, \quad (9)$$

where T^* corresponds to the temperature at which the maximum growth rate is reached (temperature at the nose of the C-curve). Finally, the TTT diagram is given by Eq. (10):

$$\tau = \begin{cases} \frac{1}{f^{1/n} l_c^{3-n} \left(\frac{2}{d_{\text{grain}}^3} \right)^{1/n} CKD_0 \frac{T_{\text{eq}} - T}{RT_{\text{eq}}} \exp(-Q_{\text{eff}}/RT)} \left[\frac{(1 - x_0)^{-c} - 1}{c} \right]^{1/n} & \text{for } c \neq 0 \\ \left(- \frac{\ln(1 - x_0)}{f l_c^{3-n} \frac{2}{d_{\text{grain}}^3} (CKD_0)^n \left(\frac{T_{\text{eq}} - T}{RT_{\text{eq}}} \exp(-Q_{\text{eff}}/RT) \right)^n} \right)^{1/n} & \text{for } c = 0 \end{cases}, \quad (10)$$

where τ is the time required for the precipitation of a fixed volume proportion (x_0) of sigma phase.

In Eq. (10), T_{eq} , Q_{eff} and D_0 are functions of the steel's chemical composition and temperature. In the literature, they are obtained starting from thermodynamics calculations and a self-consistent diffusion database. As an alternative, if such parameters are considered, in first approximation, constant with temperature, a calibration of Eq. (10) can be carried out starting from experimental observations. Once that Q_{eff} is calculated from empirical determination of T^* and T_{eq} (Eq. 9), the time exponent (n), the impingement exponent (c) and the constant (M),

$$M = CKD_0, \quad (11)$$

are empirically evaluated from the comparison with experimental data as described in Ref. [16].

2.2 Isothermal σ Phase Dissolution Model

The isothermal dissolution of sigma phase is modelled by using the following equation [28]:

$$x = \frac{V_{\sigma\delta}}{V_{\sigma}^i} \left[\frac{[(1 + c_d(\omega t)^{n_d})^{-1/c_d}] \text{ for } c_d \neq 0,}{\exp[(-\omega t)^{n_d}] \text{ for } c_d = 0}, \quad (12)$$

where $V_{\sigma\delta}$ is the volume fraction of σ phase at time t , V_{σ}^i is the volume fraction of σ phase prior to the dissolution process, c_d is the impingement exponent for the dissolution reaction, and ω and n_d are constants of the dissolution reaction. In particular, the parameter ω has the following form:

$$\omega = \omega_0 \exp(-Q_d/RT), \quad (13)$$

where ω_0 is the pre-exponential factor and Q_d is the activation energy for the dissolution reaction.

2.3 Non-isothermal σ Phase Dissolution Model

During heating, the initial amount of σ phase (V_0) may increase due to the precipitation of additional intermetallic phase in the range between 973 and 1173 K [4, 16, 37]. After the solvus temperature (T_{eq}) is reached, σ phase dissolution can occur. The temperature at which the dissolution starts depends on the heating rate and initial distribution and morphology of the σ phase [27].

The heating curve is approximated by a staircase curve using a constant temperature increment ΔT and a corresponding time increment Δt_i as shown in Fig. 1.

During the sigma phase precipitation [$T(t_i) < T_{eq}$], the contribution to the transformation is calculated by transferring the volume fraction transformed during previous steps $V_{\sigma\delta,i-1}$ to a fictitious time t'_{i-1} according to Eq. (14) ($V_{\sigma\delta,i-1} = V_0$ and $t'_{i-1} = 0$ for the first step):

Fig. 1 Schematic description of heating curve and its staircase curve approximation

$$t'_{i-1} = \begin{cases} \frac{1}{k} \left[\frac{\left(1 - \frac{V_{\sigma\delta,i-1}}{V_{\sigma}^e}\right) - 1}{c} \right]^{1/n} & \text{for } c \neq 0 \\ \frac{1}{k} \left[-\ln \left(1 - \frac{V_{\sigma\delta,i-1}}{V_{\sigma}^e}\right) \right]^{1/n} & \text{for } c = 0 \end{cases} \quad (14)$$

The fictitious time is simply the time to achieve a specific fraction of transformation and is used here to describe the position on the isothermal evolution curve at the start of a temperature step as schematically shown in Fig. 2a.

The transformed fraction $V_{\sigma\delta,i}$ after the step is calculated by using Eq. (15) where Δt_i is the staircase time increment:

$$V_{\sigma\delta,i} = \begin{cases} V_{\sigma}^e \left\{ 1 - [ck_i^n (t'_{i-1} + \Delta t_i)^n + 1] \right\}^{-1/c} & \text{for } c \neq 0 \\ V_{\sigma}^e \left\{ 1 - \exp[-k_i^n (t'_{i-1} + \Delta t_i)^n] \right\} & \text{for } c = 0 \end{cases} \quad (15)$$

After the equilibrium temperature (T_{eq}) is reached, the amount of particles formed ($V_{\sigma\delta,max}$) begins to dissolve. In this case, the fictitious time is calculated by means of Eq. (16):

$$t'_{i-1} = \begin{cases} \frac{1}{\omega i} \left[\frac{\left(\frac{V_{\sigma\delta,i-1}}{V_{\sigma}^i}\right)^{-c_d} - 1}{c_d} \right]^{1/n_d} & \text{for } c_d \neq 0 \\ \frac{1}{\omega i} \left[-\ln \left(\frac{V_{\sigma\delta,i-1}}{V_{\sigma}^i}\right) \right]^{1/n_d} & \text{for } c_d = 0 \end{cases}, \quad (16)$$

where V_{σ}^i is the amount of sigma phase at the end of precipitation ($V_{\sigma}^i = V_{\sigma\delta,max}$). The remaining fraction $V_{\sigma\delta,i}$ after the step is calculated by using Eq. (17) (Fig. 2b):

$$V_{\sigma\delta,i} = \begin{cases} V_{\sigma}^i \left\{ 1 + c_d [\omega_i (t'_{i-1} + \Delta t_i)^{n_d}] \right\}^{-1/c_d} & \text{for } c_d \neq 0 \\ V_{\sigma}^i \exp[-\omega_i (t'_{i-1} + \Delta t_i)^{n_d}] & \text{for } c_d = 0 \end{cases} \quad (17)$$

Fig. 2 Computation of the new precipitate formed **a** and dissolved **b**

Figure 3 shows a simplified flow chart of the routine written in MATLAB[®] code for the computation of sigma phase precipitation and dissolution during continuous heating according to Fig. 2. Both for kinetics reasons (diffusion of elements is a thermally activated phenomenon) and for the variation of temperature during time, it was supposed that a significant precipitation starts above 773 K.

In this work, a temperature increment ΔT of 1 K and a corresponding time increment Δt are used.

3 Experimental Validation

3.1 Experimental Procedure

Non-isothermal dissolution experiments were made on 2205 DSS whose chemical composition is summarized in Table 1.

In the as-received conditions, the material showed a high proportion of primary phases (γ -austenite/ δ -ferrite = 49/51), an equivalent circular grain diameter of $8.9 \pm 4.1 \mu\text{m}$ and no evidence of secondary phases (Fig. 4).

Isothermal precipitation and dissolution heat treatments were first performed in order to calibrate the model. In the case of ageing heat treatment, discs of 15 mm diameter and 4 mm thickness were isothermally aged in a laboratory furnace at 1123 K for holding time of 30, 60, 90, 200 and 10,080 min. For ageing periods less than 60 min, a liquid aluminium bath was used to guarantee rapid heating to the ageing temperature and water quenching was used to interrupt the heat treatments.

Fig. 3 Simplified flow chart for the computer program (V_0 : the amount of sigma phase before heating)

Table 1 Chemical composition (wt%) of the 2205-type DSS analysed

C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Co	V	W	Nb	Fe
0.029	0.84	0.34	0.017	0.0067	22.56	5.32	2.9	0.099	0.035	0.072	0.02	0.015	Bal.

Fig. 4 Micrograph of DSS in as-received conditions (dark phase ferrite; white phase austenite)

The isothermal dissolution heat treatment was carried out according to Ref. [28]. Prior to dissolution, samples were aged at 1123 K with a holding time of 72 h.

In the interest of analysing the effect of initial sigma phase content on the kinetics of non-isothermal dissolution, the samples were first aged at 1123 K for two different holding times in order to obtain different initial σ phase volume fractions, whose values were found to be 10.8 vol.% (2 h) and 24.0 vol.% (72 h), respectively. Finally, in order to simulate an industrial solution heat treatment of a large component, the laboratory non-isothermal solution treatment was carried out by placing two discs on a chalk mould with the aim to reduce the rate of heating within the furnace (Fig. 5). In the centre of one of the two samples, a thermocouple was inserted to monitor the temperature trend; the second disc was used for the metallographic analysis after interruption of the heating to a predetermined time by quenching. The test was repeated for different holding times, ensuring that the temperature trend was always the same in each test. Figure 5 shows the temperature obtained and a scheme of the experimental procedure.

All samples were electrolytically etched [20 ml hydrochloric acid (37%), 1 g $K_2S_2O_5$, 80 ml H_2O] before being examined by optical microscopy. The Leica QWIN image analysis code was adopted to calculate the σ phase content as a function of the test conditions. The average

amount of σ phase and the related standard deviation were calculated by working on 25 fields. In order to avoid possible errors due to OM and etching procedure as specified in Refs. [37, 38], both the etching and the image analysis parameters were accurately calibrated by means of SEM micrographs.

3.2 Results and Discussion

From experimental results found in the literature about σ phase precipitation/dissolution [16, 28, 39], the time exponent (as well as the impingement exponent) was found almost constant with temperature so that the conditions for the validity of the additivity rule are assumed as a first approximation to be well verified [25].

Magnabosco [39] studied the equilibrium fraction of sigma phase in DSS by means of long-term ageing heat treatments and found a value almost constant with temperature and equal to approximately 55%. Despite this, he suggested that equilibrium was not yet reached at the studied temperature even considering the long-term ageing heat treatments applied (1032 h). Long-term ageing heat treatments were also carried out by Wong *et al.* [27] who, on the other hand, suggested the σ phase equilibrium is reached after 168 h at 973 K. It is interesting to note that theoretical results obtained by means of Thermo-Calc[®] software and the TC-Fe% database provide much lower values of σ phase equilibrium fraction (as a function of temperature), compared to the experimental values found in the literature [2, 28]. Similarly, Nilsson *et al.* [35] observed that Thermo-Calc[®] is unable to predict details such as the dissolution temperature of σ phase and absolute volume percentages of occurring phases. They found that the formation of σ phase at 973 K after 72 h of ageing reflects equilibrium with the surrounding ferrite rather than global equilibrium. In this work, V_σ° was set constant [16] and equal to 27.8 ± 0.5 vol.%, which is the value measured after a holding time of 504 h at 1123 K. After this heat treatment, the precipitation of sigma phase was complete and consumed all the ferrite (δ) microstructure.

Taking advantage of previous works and supposing that sigma phase precipitation is controlled by Cr grain boundary diffusion [39], the impingement exponent (c) and activation energy (Q_{eff}) values were set equal to 0 [16, 28] and 202 kJ mol^{-1} [28], respectively. In this way, the only parameters that have to be calculated by experiments are

Fig. 5 Temperature during the non-isothermal σ phase dissolution tests and chalk mould (with samples) used for the experiments

M (Eq. 11) and n . These last two parameters were obtained by means of the “Avrami plot” as found in the literature [26, 40].

The results of the precipitation model (Eq. 8) are shown in Fig. 6. The value of the time exponent (n) was 1.6, while the impingement exponent was verified to be equal to 0 as found in previous works. Finally, it is worth mentioning that the best correlation with experimental data (Fig. 6) was obtained by adjusting the value of Q_{eff} to 205 kJ mol⁻¹. According to Eq. (9) and $T^* = 1123$ K, the value of T_{eq} was found to be 1176.5 K.

The isothermal evolution of σ phase volume fraction at 1273 K is shown in Fig. 7. Surprisingly, experimental results were found to be well described by the same kinetic parameters of the precipitation process ($c_d = 0$, $n_d = 1.6$; Eq. 12).

Fig. 6 σ phase evolution during ageing heat treatment at 1123 K: comparison between experimental (points) and analytical results ($n = 1.6$, $c = 0$, $T_{\text{eq}} = 1176.5$ K, $T^* = 1123$ K, $d_{\text{grain}} = 10$ μm , $M = 42 \times 10^6$ J m mol⁻¹ s⁻¹)

The microstructures of the samples at the beginning of the non-isothermal σ phase dissolution experiments are shown in Fig. 8. According to the ageing time at 1123 K, two different percentages of σ phase (10.8 and 24.0 vol.%) were obtained as described in previous section.

The comparison between experimental and analytical results of σ evolution during the continuous heating is shown in Fig. 9, while Table 2 summarizes the most relevant kinetic parameters obtained.

As expected, from Fig. 9 it can be seen that the amount of σ phase precipitated during continuous heating depends on initial percentage of σ phase. At constant heating condition, the lower the initial amount of σ phase, the higher the σ phase amount precipitated prior to dissolution.

Fig. 7 Temporal isothermal evolution of σ phase volume fraction (x) at 1273 K; the discrete symbols are from experiments, and the curve is from Eq. (13) ($V_{\sigma}^i = 24.0$ vol.%, $n_d = 1.6$, $c_d = 0$, $\omega_0 = 1.9 \times 10^5$ s⁻¹, $Q_d = 202$ kJ mol⁻¹)

Fig. 8 Micrographs showing the initial percentage of σ phase (dark phase V_0' ; white phase austenite; grey phase ferrite), before the non-isothermal dissolution heat treatments: **a** $\sigma = 10.8$ vol. %, **b** $\sigma = 24.0$ vol. %

Fig. 9 Temporal non-isothermal evolution of σ phase amount (V) for different initial σ phase contents: **a** $V_0 = 10.8$ vol.%, **b** $V_0 = 24.0$ vol.%. The discrete symbols are from experiments, and the curve is from the model ($n_d = 1.6$, $c_d = 0$, $Q_d = 202$ kJ mol $^{-1}$)

Table 2 Most relevant kinetic parameters obtained for the σ phase non-isothermal precipitation and dissolution

Precipitation				Dissolution			
V_0 (vol.%)	n	c	Q_{eff} (kJ mol $^{-1}$)	ω_0 (s $^{-1}$)	n_d	c_d	Q_d (kJ mol $^{-1}$)
10.8	1.6	0	205	16×10^5	1.6	0	202
24.0				3.9×10^5			

The same values of time exponent and impingement factor obtained for both precipitation and dissolution reaction (Table 2) suggest the same kinetic mechanism for both dissolution and precipitation. In particular, the time exponent equal to 2 is associated in the literature [24] with grain edge nucleation after nucleation site saturation is reached, while the time exponent value greater than $2^{1/2}$ is associated with increasing nucleation rate (diffusion-controlled growth). Obviously, for the σ phase dissolution the time exponent is related to δ ferrite grain boundary precipitation.

It is worth mentioning that uncertainties on the kinetic mechanism of precipitation and dissolution based on the

Avrami exponent may be associated with the dependence of the time exponent on the particle distribution. As a matter of fact, Sun et al. [40] demonstrated that an inhomogeneous distribution of nuclei can result in a decreasing Avrami exponent.

A good correspondence with the experimental results were obtained by setting the activation energy for both precipitation and dissolution very close to that of Cr grain boundary diffusion (218 kJ mol $^{-1}$) [41], suggesting that σ particle precipitation/dissolution kinetics is controlled by Cr grain boundary diffusion. The dependence of sigma formation on Cr diffusion in ferrite is expected, since nucleation of sigma phase always occurs at ferrite–

austenite interfaces [39], and growth of the sigma phase is strongly related to consumption of ferrite. Similarly, nucleation of δ ferrite, associated with σ phase dissolution, always occurs at σ/γ or σ/δ interfaces, and growth of δ ferrite is strongly related to the consumption of σ phase.

About the σ phase redissolution temperature, experimental results show a good agreement with those obtained by Wong *et al.* [27] who found values which range from 1156 to 1190 K by differential thermal analysis.

It is interesting to note that almost all the kinetic parameters were constant after the conversion from the isothermal to the non-isothermal model. Only the pre-exponential factor (ω_0) value obtained for the non-isothermal dissolution heat treatment was found different from that calculated for the isothermal one (Fig. 7). This discrepancy is supposed to be related to the experimental difficulty in calculating the theoretical TTT diagram. In fact, as in all experimental determinations of TTT diagrams concerning rapid transformations, the time to reach the isothermal temperature is critical [4].

Finally, ω_0 was found to depend on the σ phase content at the beginning of the non-isothermal heat treatment (V_0) (Table 2). According to Wong *et al.* [27], this phenomenon could be due to a variation of the ratio between σ/γ boundaries and σ phase volume fraction induced by different ageing times [27]. However, more in-depth investigations may be needed for a conclusive relationship between the ω_0 parameter and the initial σ phase content.

4 Conclusions

1. Based on the additivity rule, a model for non-isothermal σ particles dissolution was developed by using information from experimental calibration of both isothermal precipitation and dissolution models.
2. The model was applied to the dissolution of σ phase in a 2205 DSS during continuous heating, showing a good agreement with experimental measurements.
3. The time and impingement exponents were found equal for both precipitation and dissolution, suggesting the same kinetics mechanisms for both precipitation and dissolution.
4. The grain boundary-controlled growth/dissolution was explained by the values of precipitation and dissolution activation energies obtained, which are similar to the chromium grain boundary diffusion activation energy found in the literature.

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