

Design and modelling of ultra-high strength steels: nanoprecipitation and plasticity

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Preface

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Cambridge. The research reported herein was conducted under the supervision of Dr Pedro Rivera in the Department of Materials Science and Metallurgy, University of Cambridge, between October 2010 and September 2013.

This work is to the best of my knowledge original, except where acknowledgment and references are made to previous work. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text. Neither this, nor any substantially similar dissertation has been, or is being, submitted for any other degree, diploma, or other qualification at any other university. This dissertation does not exceed 60,000 words in length.

Some of the work described herein has been presented in the following publications:

- B. Kim, D. San Martín, J. Chao and P. E. J. Rivera-Díaz-del-Castillo, The effect of silicon on the $\varepsilon \rightarrow \theta$ transformation in ultra-strong spring steels, in *Proceedings of the international conference Materials Science and Technology*, 7-11 October 2012, Pittsburgh PA: 1086-1093
- B. Kim, C. Celada, D. San Martín, J. Chao, J. Vara and P. E. J. Rivera-Díaz-del-Castillo, Interrupted ageing in steels: Hardness improvement and microstructural stabilization, *Scripta Materialia*, 68:945-948, 2013
- B. Kim, C. Celada, D. San Martín, T. Sourmail and P. E. J. Rivera-Díaz-del-Castillo, The effect of silicon on the nanoprecipitation of cementite, *Acta Materialia*, 61:6983-6992, 2013

- B. Kim, E. Boucard, T. Sourmail, D. San Martín, N. Gey and P. E. J. Rivera-Díaz-del-Castillo, Understanding the microstructure-properties relationship in tempered martensite: 0.5–0.6 wt.% C steels, to be submitted in *Acta Materialia*.

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Abstract

Understanding the changes occurring in the mechanical properties during martensite tempering is essential in the development of new industrial grades. The aim of this research was to develop new ultra-high strength steels via nanoprecipitation control, which requires an understanding of the processing-microstructure-property relationship in medium carbon (0.5–0.6 wt.%) steels throughout tempering. Much of the work has been centred in understanding the role of silicon at the precipitation level and in the recovery of martensite.

By using an existing spring steel grade, the effect of interrupted ageing (IA) in tempered martensite has been studied. In IA, an intermediate step between quenching and tempering is introduced, where quenched martensite is left to rest at room temperature for a defined period of time. By allowing carbon segregation into dislocation cores, the incorporation of IA resulted in a more stable microstructure and hardness improvement.

The effect of silicon in the epsilon to cementite carbide transition has also been studied. The classical nucleation theory was applied in order to model cementite formation under paraequilibrium conditions, thus incorporating silicon during nucleation. Characterisation using high energy X-rays showed the inhibiting effect of silicon in the overall cementite precipitation.

The second effect of silicon was observed in the martensite recovery. A series of experiments were carried out in order to capture the various microstructural changes taking place during tempering: precipitation, grain size and dislocation density evolution. It was observed that the addition of silicon reduces the rate of martensite recovery, owing to the reduced cross-slip in the ferrite lattice.

A plasticity model based on irreversible thermodynamics and EBSD characterisation was applied to identify the effective grain size. The results from these two techniques require further research. Nevertheless, based on the post-failure analysis

by TEM, it appears that at relatively early tempering stages, even low angle lath boundaries can contribute to strengthening, where piled-up dislocations have been observed at lath boundaries.

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Chapter 1

Introduction

The progress in materials science has led to the development of advanced engineered materials. Taking the example of the automotive steel industry, one of the main driving forces has been the quest for stronger and lighter materials. The development of such advanced structural materials provide car manufacturers greater flexibility in the design. The main focus of this research has been centered around spring steels technology. Suspension springs act together with shock absorbers, with their main role consisting in damping vibrations that may be transferred from the road to the passengers. For instance, in the case of spring steels, the development of special high-strength grades allows a reduction in the number of coils used, as shown in Figure 1.1. For example, by reducing the number of coils by one, a significant spring weight reduction of over 20% can be achieved [1]. From the consumers perspective, lower vehicle weight results in reduced fuel consumption. This also contributes to the ever-increasing demand for lower carbon dioxide emissions.

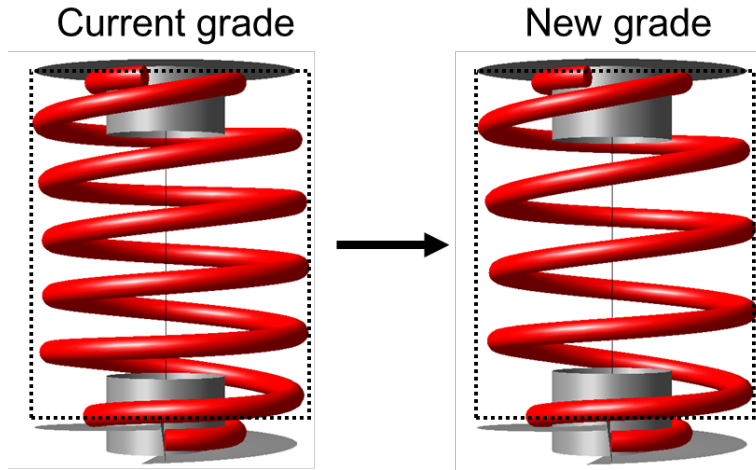


Figure 1.1: Weight reduction achieved by the use of improved grades in spring steels [1].

In compensating for the reduction in weight, the component must meet higher mechanical properties demands. One important family of engineered materials used in structural applications is tempered martensite. Martensite tempering is a very complex topic on its own, being accompanied by a series of microstructural changes which is reflected in the mechanical properties. During the early stages of tempering, martensite exhibits ultra-high strength, but the alloy is extremely brittle for commercial use. On the other hand, as tempering progresses, the initial ultra-high strength is lost while ductility is recovered. In order to understand the trade-off between these two properties, it is necessary to understand the changes occurring at the microstructural level.

One particular phenomenon that has attracted immense attention is precipitation hardening. When steel is quenched, carbon atoms initially occupy the interstitial sites within the Fe-lattice. Once tempering occurs, carbon participates in the precipitation of carbides.

The effect that the presence of dispersed phases have on the strength increment,

$\Delta\tau$, can be described by the Ashby-Orowan relationship:

$$\Delta\tau = 0.84 \left(\frac{1.2\mu b}{2\pi L} \right) \ln \left(\frac{x}{2b} \right), \quad (1.1)$$

where μ is the shear modulus of the matrix, b is the magnitude of the Burgers vector, L is the spacing between particles, and x is the particle diameter.

From Equation (1.1), it is possible to establish that the principal microstructural parameter that dictates the degree of precipitation hardening is the spacing between the particles, followed by the size of particles.

Described by the three-link chain model, Figure 1.2, microstructure tailoring is achieved by controlling the processing stage, which in turn determines the mechanical properties and final performance. In the processing stage, the two main variables are heat treatment and alloying. All the possible combinations of heat treatments and alloying systems give rise to a very large number of possible microstructural outcomes.

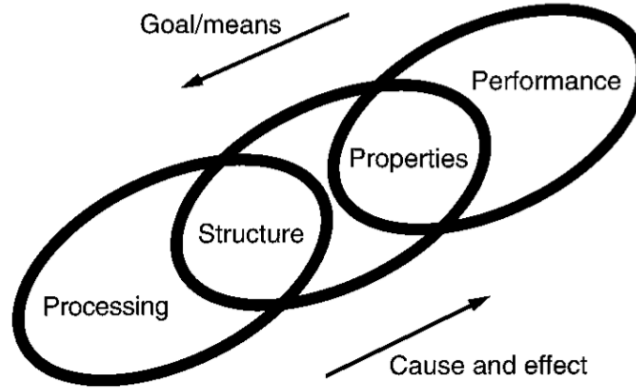


Figure 1.2: Three-link chain model of the central paradigm of materials science and engineering [2].

In spring steels technology, usually medium carbon steels containing 0.5 to 0.6 wt.% carbon, are used. The typical industrial process takes place in the 350–450 °C tem-

perature range. This corresponds to the relatively early stages of martensite tempering, involving the ε - and cementite θ -carbides, where the former is the preceding metastable phase that forms before the latter. Early literature has attributed the exceptional ultra-high strength in tempered martensite to the presence of ε -carbide within martensitic laths [3]. Furthermore, silicon has been reported to delay the $\varepsilon \rightarrow \theta$ carbide transition. In order to relate to the mechanical properties of the steel, the effect of silicon on the aforementioned transition is of great technological importance. Chapter 2 provides a literature review centred around carbide precipitation during martensite tempering, and the effect of silicon in carbide precipitation.

In understanding the effect of heat treatment in carbide precipitation, Chapter 3 explores the effect of interrupted ageing in martensitic steels. During interrupted ageing, the quenched martensite is left to age at room temperature for a specified period of time, prior to tempering. Using a single grade, a series of heat treatments have been designed to understand the effect of interrupted ageing time, tempering time and temperature on carbide precipitation. By allowing carbon segregation during interrupted ageing, the number of effective nucleation sites is increased, which aids in improving and stabilising the microstructure and hardness properties ($\sim 10\%$ increase). Such carbon segregation behaviour was modelled using the Kalish-Cohen model [4] and thermoelectric power measurements.

Aiming at understanding the sequence of precipitation in tempered martensite, Chapter 4 looks into the early precipitation stages of ε and θ . In order to understand the effect of silicon on carbide precipitation, a model alloy of composition Fe-0.55C-2Si wt.% was studied. The nucleation of cementite was modelled under paraequilibrium conditions, in order to account for the silicon entrapment in cementite during low-temperature tempering. Carbides were characterised using electron and X-ray diffraction methods, where trial runs were carried out using high energy X-rays from a synchrotron source. The knowledge built from the ternary model alloy was then applied to more complex alloy compositions in Chapter 5. *In situ*

tempering was characterised using synchrotron radiation, and showed that silicon inhibits cementite precipitation by enveloping the growing precipitate. Gathering data from literature, a new mechanism by which silicon retards cementite growth is suggested.

Although precipitation hardening accounts for a significant strengthening contribution in tempered martensite, there are other microstructural properties evolving during martensite tempering that determine the overall mechanical properties. In order to model stress-strain behaviour of martensitic steels in Chapter 6, an irreversible thermodynamics-based approach to plasticity has been taken in order to bring multiscale plasticity phenomena together. Experimentally determined microstructural features in Chapter 5 such as lath size, precipitate size and volume fraction, dislocation density, and carbon content in solid solution, are incorporated, thus integrating the role of silicon on the mechanical properties of martensitic steels.

Finally Chapter 7 gives the general conclusions, highlighting the contributions of this PhD thesis in further understanding the properties of tempered martensitic steels. Furthermore, a series of suggestions for further work are given, raising further topics of interest that are beyond the scope of this work.

Chapter 2

Literature review:

carbide precipitation in martensite

2.1 Existing spring steels grades

This section aims at giving a brief overview of the physical metallurgy of spring steels, giving examples of high performance grades and details on typical chemical compositions and heat treatments. Two common grades used for making spring steels within the European market are 54SiCr6 and 54SiCrV6 [5], where the chemical composition specified by the European norm is detailed in Table 2.1.

Table 2.1: 54SiCr6 and 54SiCrV6 compositions specified by the EN10089 [5], (in wt.%, Fe to balance).

	C	Si	Mn	Cr	V
54SiCr6	0.51–0.59	1.2–1.6	0.5–0.8	0.5–0.8	-
54SiCrV6	0.51–0.59	1.2–1.6	0.5–0.8	0.5–0.8	0.1–0.2

Table 2.2: Summary of heat treatment and minimum mechanical properties specified by the European norm [5].

$\ddagger$	T_γ (°C)	Quenching media	T_{temp} (°C)	$\sigma_{0.2}$ (MPa)	σ_{UTS} (MPa)	A (%)	Z (%)	I (J)
54SiCr6	860	oil	450	1300	1450-1750	6	25	8
54SiCrV6	860	oil	400	1600	1650-1950	5	35	8

$\ddagger$ T_γ and T_{temp} are the austenitising and tempering temperatures respectively, and $\sigma_{0.2}$, σ_{UTS} , A, Z and I refer to 0.2% proof yield stress, ultimate tensile stress, elongation, reduction of area and impact energy respectively.

In the 54SiCrV6 grade, vanadium is added to the base 54SiCr6 grade. Usually vanadium is present as a microalloying addition, where the formation of precipitates would account for an improvement in mechanical properties. The aimed mechanical properties for both alloys are summarised in Table 2.2.

One alloying element that has drawn significant industrial interest is silicon. In studying the effect of silicon for spring steel applications, Choi [6] compared two steel grades: SAE9254 (Fe-0.55C-1.5Si-0.7Mn-0.7Cr wt.%), and POSHIS120D (Fe-0.48C-2.1Si-0.65Mn-0.7Cr wt.%). Improved mechanical properties were obtained in terms of both tensile strength and area reduction in the higher silicon grade, POSHIS120D. The microstructural feature responsible for such increased strengthening was the precipitation of fine $\text{Fe}_{2.4}\text{C}$ carbides, and the suppression of the transition from this carbide to spheroidised cementite. Therefore in optimising the mechanical properties of spring steels, understanding carbide precipitation throughout processing becomes essential.

2.2 Tempered martensite

The typical heat treatment of tempered martensitic steels is represented in Figure 2.1. The main stages encountered are: austenitisation, quenching and tempering. Each of these stages are very important, and are carefully controlled in industry.

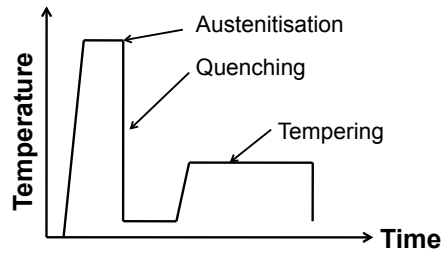


Figure 2.1: Typical heat treatment for tempered martensitic steels.

2.2.1 Austenitisation

The austenitisation stage has two principal objectives: (i) complete austenitisation so there is no ferrite left in the microstructure prior to quenching, and (ii) carbon levelling, in order to ensure homogeneity in composition. The latter point is especially important, as uneven distributions of carbon would cause martensite transformation in carbon-rich areas, whereas lower bainite formation is promoted in carbon-poor regions [7]. Such inhomogeneity in the microstructure has a detrimental impact on the mechanical properties of the steel. Although sufficient time is required for such even distribution of carbon in the austenite, another factor that needs to be considered is the growth of austenite grains. In literature, austenite grain size has been reported to affect the martensitic start temperature [8, 9], as well as the mechanical properties. After quenching, smaller prior austenite grains (PAGs), would lead to a higher density of ‘barriers’ to dislocation motion [7]. This last point will be further explored in Chapter 6.

2.2.2 Quenching

When steel is quenched from its austenite state to room temperature, it undergoes a martensitic transformation. The stable form of iron at low temperatures is ferrite (α), a body centred cubic (bcc) structure; the presence of carbon atoms occupying the interstitial sites gives rise to tetragonality. Hence, as-quenched martensite (α') adopts a body centred tetragonal (bct) structure. Carbon being insoluble in α -Fe, the matrix is initially in a super saturated solid solution (s.s.s.) form.

The quenching process is very important, as the cooling rate needs to be sufficiently high in order to avoid pearlite formation and to minimise the degree of autotempering. As-quenched martensite has a distinct microstructure, consisting of needle- or lath-like structures that are reported to have formed following the Kurdjumov-Sachs orientation relationship with respect to the previous austenite phase [10]. The martensitic microstructure is dependent on the carbon content of the alloy, Figure 2.2 [10]. On closer inspection, martensite consists of a series of sub-structures, as illustrated in Figure 2.3. Within a prior austenite grain, packets are observed, which are composed of blocks that contain individual laths with small angle misorientations. The effect of each constituent substructure will be further explored in Chapter 6.

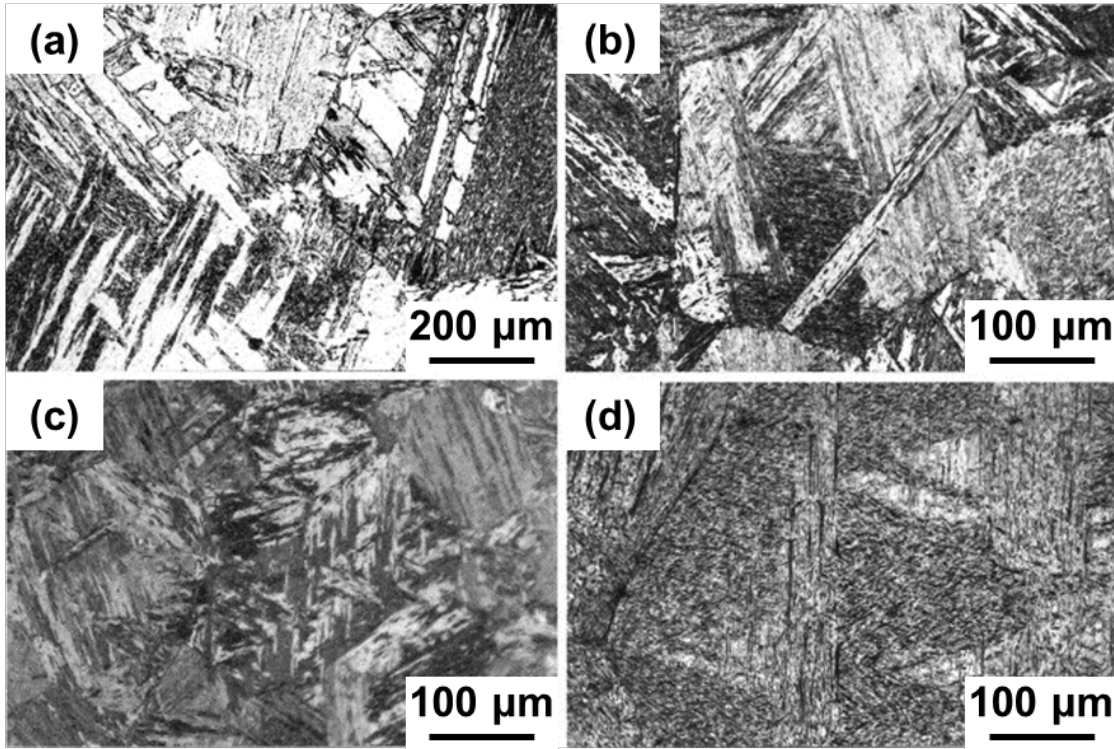


Figure 2.2: Optical micrographs of lath martensite for Fe–C alloys containing (a) 0.0026, (b) 0.18, (c) 0.38, (d) 0.61 wt.% carbon [10].

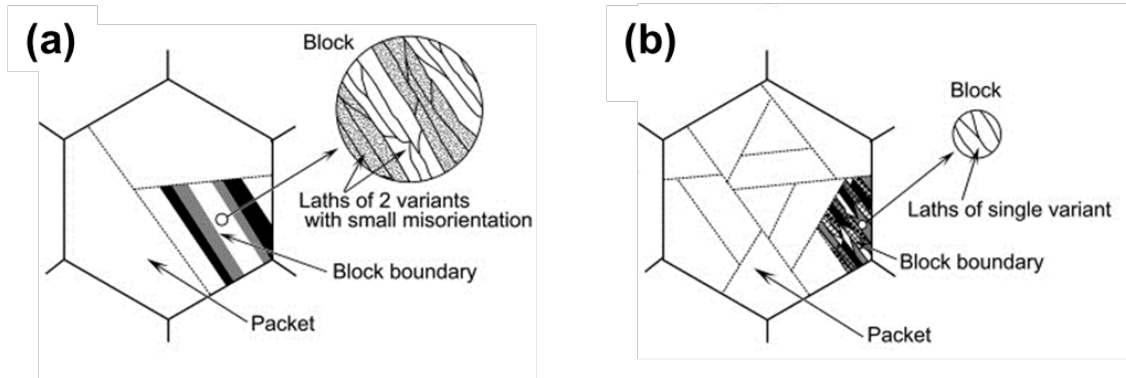


Figure 2.3: Schematic illustration of lath martensite structure for (a) low carbon (0–0.4 wt.% C) and (b) high carbon (0.6 wt.% C) alloys [10].

2.2.3 Tempering

Table 2.3: Sequence of the changes occurring in the microstructure during the tempering of martensite [11].

Stage	Temperature range (°C)	Changes occurring throughout stage
T1	100–250	Decomposition of supersaturated martensite to low-carbon martensite and transition carbides (ε or η)
T2	200–300	Decomposition of retained austenite to bainite
T3	250–350	Transformation of the reaction products of T1 and T2 into ferrite and/or cementite
T4	>350	Growth and spheroidisation of cementite
T5	>500	Intermetallic precipitation and further carbide formations in alloy steels

Table 2.3 summarises the typical sequence of events occurring during the tempering of martensite. Throughout martensite tempering, carbon leaves the interstitial sites and takes part in carbide precipitation. Consequently, a reduction in tetragonality is observed, until the matrix reverts back to its original bcc form. Furthermore, although the main microstructural feature is martensite, there will always be some retained austenite (γ_R) left on the as-quenched condition. It is thought that its presence even at room temperatures, is due to the enrichment of the interstitials, e.g. carbon, during isothermal holding [12]. The amount of retained austenite can be estimated from the Koistinen-Marburger equation [13]:

$$1 - V_{\alpha'} = \exp \left(\beta (M_s - T_q) \right), \quad (2.1)$$

where $V_{\alpha'}$ is the volume fraction of martensite, $\beta = -0.011 \text{ K}^{-1}$, M_s is the martensite start temperature and T_q is the temperature to which the sample is cooled. From (2.1), typically in medium carbon martensitic steels, γ_R is under 10%. Owing to the enrichment of carbon in the austenite phase, the decomposition of the retained phase is thought to lead to further carbide precipitation [12, 11].

At this stage, it is important to note that there is an intermediate stage between quenching and tempering, called ageing [11]. As most alloy have an M_s temperature above room temperature, inevitable martensite ageing takes place at room temperature. During ageing, only interstitial elements, such as carbon atoms, are sufficiently mobile. The structural rearrangements of carbon atoms taking place during martensite ageing have been extensively studied by Génin [14], and Taylor and Cohen [15]. Investigating the effect of ageing prior to tempering on carbide precipitation, constitutes the base of Chapter 3.

2.3 Carbides in martensite

From a precipitation hardening perspective it is of great interest to characterise and understand the carbide phases present within the matrix. The principal iron carbides that have been reported in literature are the ε and the θ carbides, where the former is the preceding metastable phase that forms before cementite θ -carbide. The basic properties of these two carbides are summarised in Table 2.4.

Typically in martensitic steels, during early stages of tempering, the material exhibits ultra-high strength. However, its brittleness limits its industrial usability. Throughout continuous tempering, ductility of the material is recovered at the expense of strength. Therefore, throughout the heat treatment, there is always a compromise between strength and ductility. This softening transition, which typically occurs around 300–350 °C, also corresponds to the temperature regime where the $\varepsilon \rightarrow \theta$ carbide transition takes place.

Table 2.4: Summary of properties of cementite and ε -carbides.

	ε -carbide	θ -cementite
Chemical composition	$\text{Fe}_{2.4}\text{C}$	Fe_3C
Crystal structure	hexagonal close packed	orthorhombic
Space group	P6 ₃ 22	Pnma
OR [‡]	Jack [16]	Bagaryatski [17]
	$(0001)_\varepsilon \parallel (011)_{\alpha'}$	$[100]_\theta \parallel [0\bar{1}1]_{\alpha'}$
	$(10\bar{1}0)_\varepsilon \parallel (2\bar{1}1)_{\alpha'}$	$[010]_\theta \parallel [1\bar{1}\bar{1}]_{\alpha'}$
	$(10\bar{1}1)_\varepsilon \parallel (101)_{\alpha'}$	$[001]_\theta \parallel [211]_{\alpha'}$

[‡] OR refers to the most commonly reported orientation relationship existing between the carbide and the matrix.

In early literature, the ultra-high strength observed in tempered martensite has been attributed to the presence of microstrains between ε and the matrix [3]. Early literature has reported the effect that silicon has in delaying the aforementioned transition [18, 19]. Numerous researches have reported strength increments at higher temperatures, as a consequence of increasing silicon content within the alloy [18, 19, 20, 21, 22, 23, 24, 25].

Gordine and Codd [22] proposed a mechanism by which silicon retards the $\varepsilon \rightarrow \theta$ carbide transition: the third stage of tempering (T3 on Table 2.3) originally taking place in two steps:

- Stage IIIA- the remaining carbon atoms in the matrix are taken up for cementite precipitation while ε -carbide persists in the matrix. At this stage, both carbides co-exist in the material
- Stage IIIB- once the matrix becomes depleted, the ε -carbide decomposes in order to assist in the further precipitation of cementite.

The rate-controlling factors were seen to be the diffusion of carbon through the

low-carbon martensite for IIIA, and the mobility of substitutional elements or the self-diffusion of Fe for step IIIB. On the other hand, it was proposed that in the presence of silicon, steps IIIA and IIIB would merge, and shift the reactions to higher temperatures, consequently stabilising ε at higher temperatures [22].

In understanding the carbide transition and the influence of silicon, numerous studies have been carried out. Miyamoto *et al.* [26] used electron diffraction techniques in order to characterise the carbides present within martensite throughout tempering under the influence of manganese and silicon as alloying elements, summarised in Table 2.5.

Table 2.5: Carbide transition seen in the tempering of martensite in Fe-0.6C-2(Si,Mn), from Miyamoto *et al.* [26].

Alloy system	250 °C		450 °C			
	30 s	1200 s	30 s	120 s	300 s	1200 s
Fe-0.6C	ε	θ	θ	-	-	θ
Fe-0.6C-2Mn	ε	θ	θ	-	-	θ
Fe-0.6C-2Si	ε	ε	ε	ε/θ	θ	θ

Comparing Fe-0.6C with Fe-0.6C-2Mn, the addition of manganese does not appear to have a significant effect on the carbide transition. However a marked effect is seen when silicon is added, as ε is seen throughout longer tempering conditions, both time- and temperature-wise. Taking the Fe-0.6C-2Si alloy tempered at 450 °C, according to Table 2.5, 30 s tempering results in ε being formed, whereas after 300 s, θ is seen. Figure 2.4 shows the SAD patterns for the ε and θ conditions. The measured interplanar spacing (shown in Figure 2.4) were ① 4.36 and ② 2.40 Å, for ε , and ① 4.10 and ② 2.29 Å, for cementite.

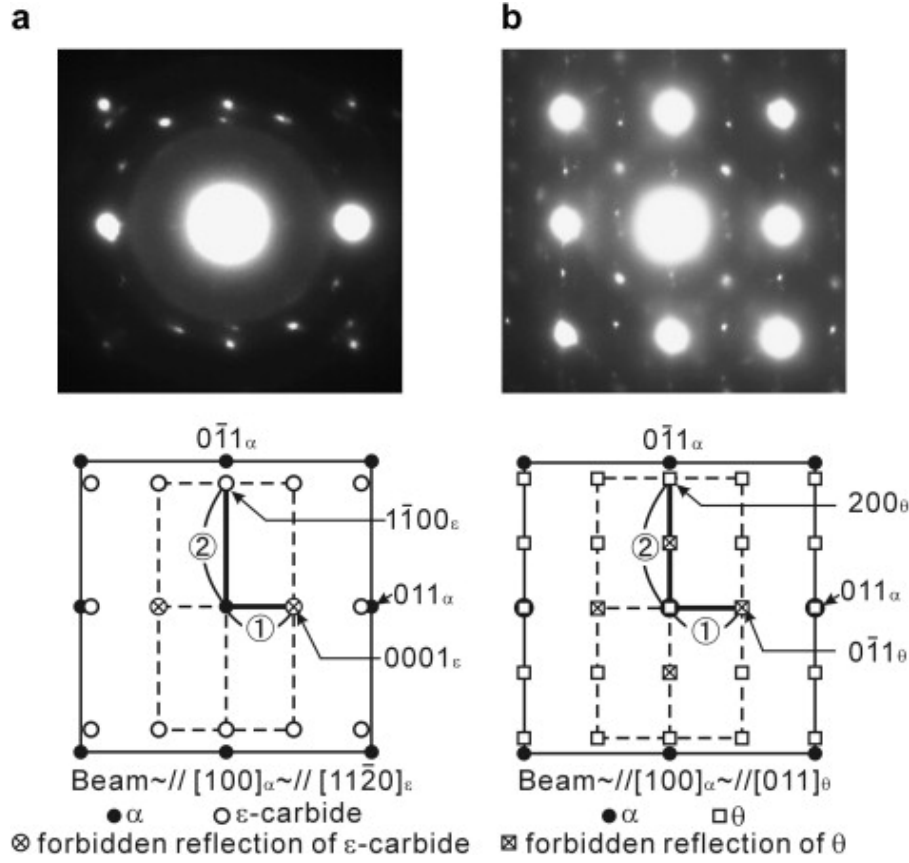


Figure 2.4: SAD patterns for the Fe-0.6C-2Si alloy tempered at 450 °C for (a) 30 s, and (b) 300 s, where the present carbide phases are ϵ and θ , respectively [26].

Furthermore in the work by Miyamoto *et al.* [26], by means of atom probe tomography (APT), there was a slight indication of silicon being built up at the cementite/matrix interface after the material was tempered at 450 °C for 1200 s. This result is in agreement with the earlier work by Chang and Smith [20], where a Si-rich region of 1–2 nm was observed at the cementite/matrix interface using APT, Figure 2.5. Such partitioning behaviour of silicon from the carbide to the matrix has been frequently reported in the APT literature, e.g. [26, 27, 28, 29].

Such findings led to the conclusion that silicon inhibits cementite growth. The suggested mechanism presumes that the Si-rich region at the interface acts as a barrier, where carbon diffusion is slowed down, reducing the overall carbide growth kinetics [20]. This further adds to the inhibited cementite growth observed due to

the relatively slow diffusion of silicon during partitioning.

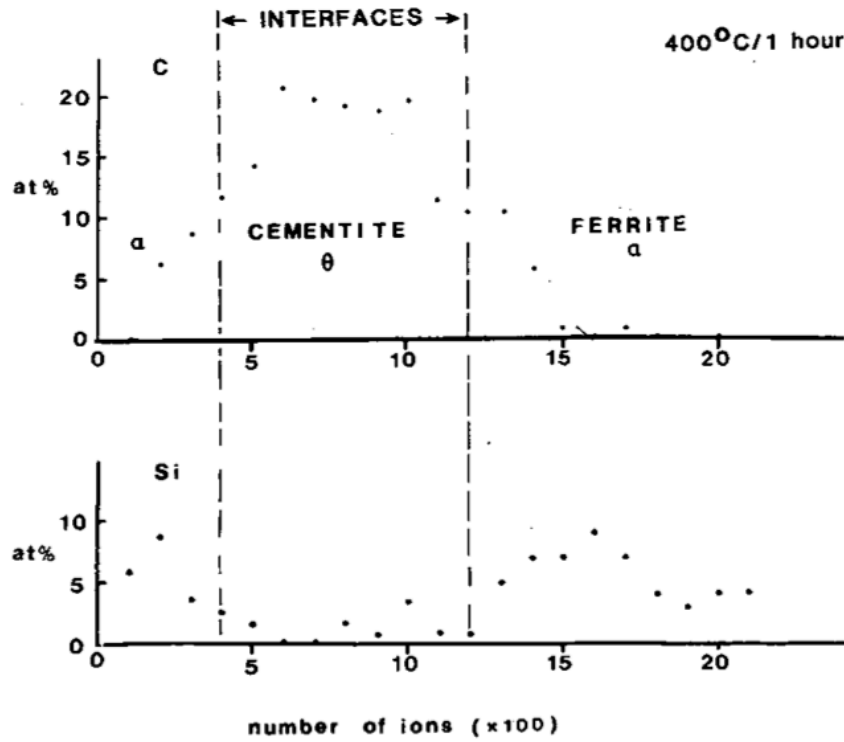


Figure 2.5: Composition profiles across the cementite/matrix interface after 1 hour tempering at 400 °C for the EN45 commercial grade containing 0.6 carbon and 2 silicon by weight % [20].

For silicon partitioning to take place during the growth stage, there should have been silicon present during the initial cementite nucleation process. This concept of cementite nucleation under paraequilibrium conditions has been well-received in literature. During nucleation under paraequilibrium conditions, cementite traps the inherent chemical composition of the matrix phase, including silicon. However, as tempering progresses, the silicon content within the carbide decreases, as observed by Reisdorf [3]. Given that silicon is not present under equilibrium conditions within cementite, it is inferred that silicon partitioning takes place as the system tends to equilibrium.

Based on the growth kinetics experimentally observed, it is possible to infer the conditions at which cementite nucleated in the first place. Extensive effort has been

put into understanding θ -nucleation, and different conditions under which cementite was seen to nucleate have been reported, out of which, three are listed as examples:

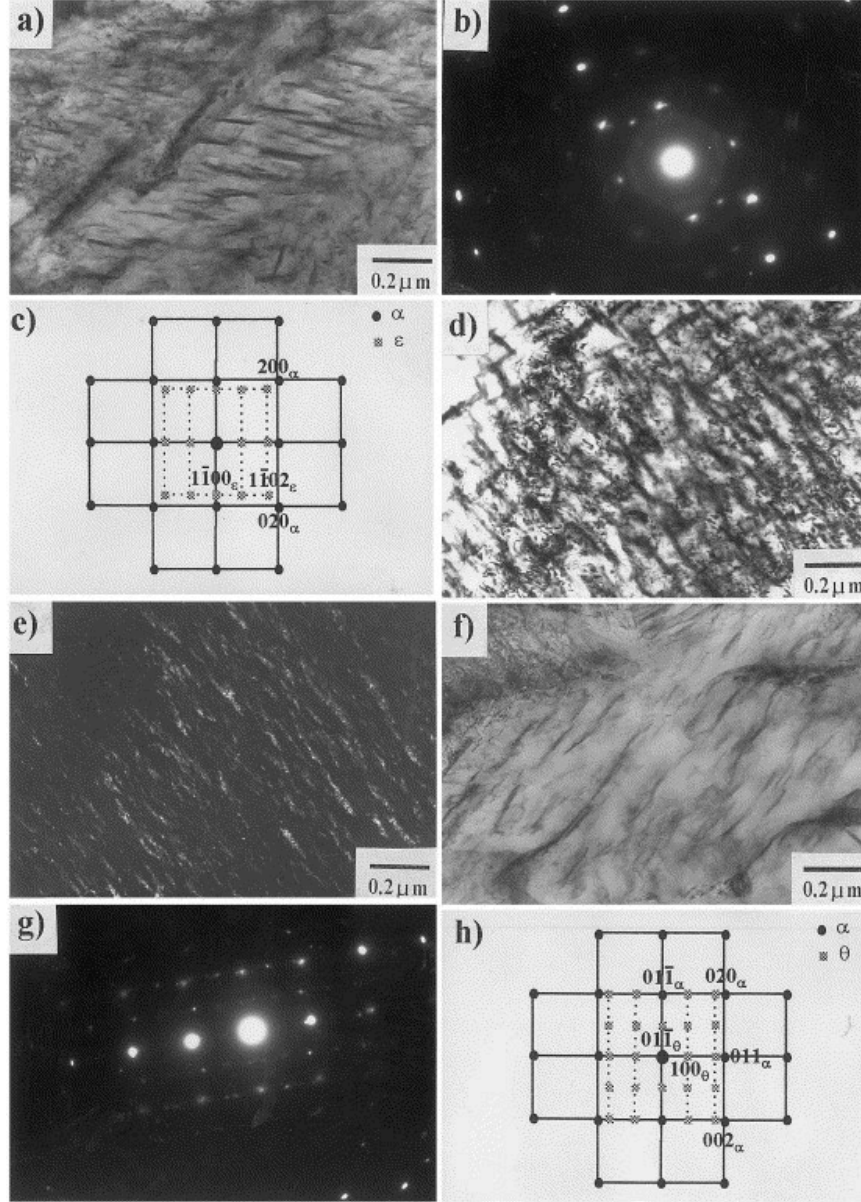


Figure 2.6: TEM diffraction work by Nam *et al.* on a Si-Cr steel, where (a) ε carbide is seen at 250 °C, (b) the corresponding diffraction pattern of (a) on the $[001]_{\alpha}$ zone, (c) schematic representation of the diffraction pattern of (b), (d) tempered at 350 °C, (e) dark field image of (d) using $(1\bar{1}01)_{\varepsilon}$ reflection, (f) cementite seen at 400 °C, (g) diffraction pattern of (f), and (h) schematic representation of diffraction pattern of (g) zone axes $[100]_{\alpha}$ and $[011]_{\theta}$ [25].

- Nam *et al.* [25] have shown that ε carbide forms when a spring steel is tempered at 250 °C, and as temperature increases to 350 °C, further ε -carbide precipitates. Simultaneously, θ nucleation takes place, either at dislocations or at the ε /matrix interface. As cementite nucleates, dissolution of the ε phase takes place. See Figure 2.6.
- Perez and Deschamps [30] have based their work on the condition that co-precipitation of ε and θ carbides occurs during tempering, and that solute competition defines the carbide being precipitated. See Figure 2.7.

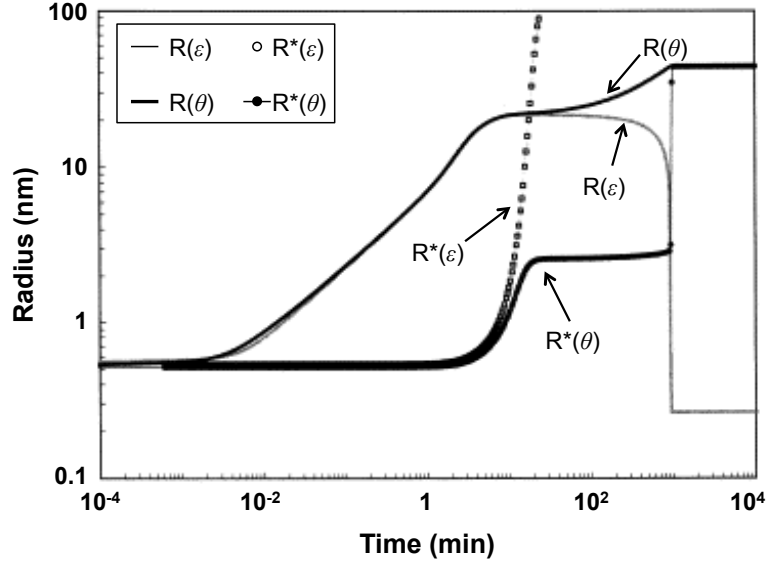


Figure 2.7: Simulation of carbide growth for the metastable ε -phase and the stable θ precipitates at 200 °C. Initially, both phases grow simultaneously in a similar manner. Once the critical radius for dissolution of the metastable phase, $R^*(\varepsilon)$, exceeds the value of the mean radius, $R(\varepsilon)$, it destabilises the metastable phase, and dissolution occurs in order to allow the growth of the stable phase θ [30].

- Andrews [31] stated that cementite can precipitate in steels at temperatures below 200 °C. The proposed mechanism consisted of a ‘zig-zag’ movement by which a slight displacement of iron atoms breaks the cubic symmetry of the ferrite phase and builds the orthorhombic unit cell. Furthermore, in high

carbon steels, it has been observed that defects play a significant role in offering powerful nucleation sites where, for instance, cementite has been reported to nucleate along twin boundaries [11].

Due to its metastable nature, ε carbide phase is absent from commercial thermochemical databases. Instead, most of the computational thermodynamics work has been on the formation of cementite from ferrite, under both ortho- and paraequilibrium conditions, such as the work by Ghosh and Olson [32], and Kozeschnik and Bhadeshia [33].

Paraequilibrium (PE) is a kinetically constrained form of growth, where only interstitial atoms are able to diffuse and the diffusivity of substitutional species is considered negligible. Thus, a growing phase under PE conditions would inherit the substitutional alloy content from the parent phase. Since the substitutional elements cannot partition, instead of considering the individual chemical potential of each element, instead they are referred to collectively by one hypothetical element, Z.

Figure 2.8 shows the method of determining the driving force of cementite under paraequilibrium conditions [32]. The thermodynamic driving force, ΔG^N is given by:

$$\Delta G^N = (\mu_Z^{N,PE-\theta} - \mu_Z^{N,PE-\alpha})x_Z^{N,PE-\theta} + (\mu_C^{N,PE-\theta} - \mu_C^{N,PE-\alpha})x_C^{N,PE-\theta}, \quad (2.2)$$

where $x_i^{N,\phi}$ is the mole fraction of element i in the critical nucleus, and $\mu_i^{N,\phi}$ is the corresponding chemical potential for phase ϕ , where $\phi = PE-\alpha, PE-\theta$.

The chemical potential of Z, μ_Z^ϕ , is given by the sum of each individual substitutional alloying element:

$$\mu_Z^\phi \equiv \sum y_j \mu_j^\phi, \quad (2.3)$$

where y is the site fraction for the substitutional alloying element j .

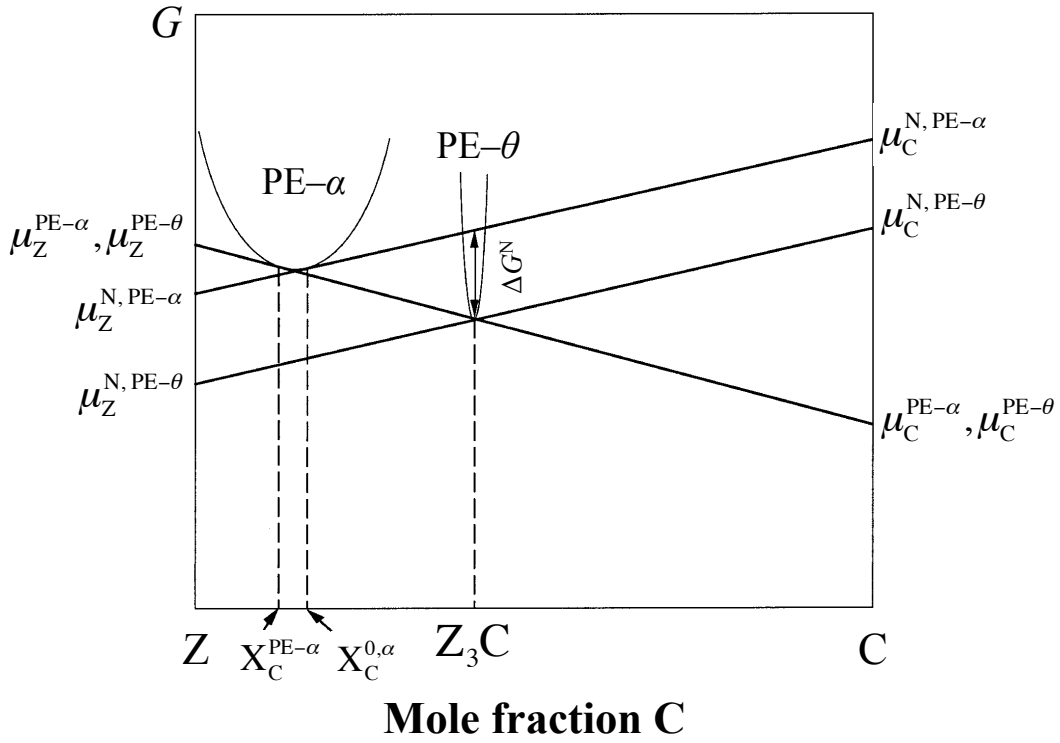


Figure 2.8: Schematic plot of Gibbs energy *vs.* composition for determining the driving force for cementite nucleation under paraequilibrium conditions based on the parallel tangent construction, where ΔG^N is the driving force for nucleation, μ is the chemical potential for paraequilibrium ferrite (PE- α) and cementite (PE- θ). $X_C^{PE-\alpha}$ is the initial carbon content in the alloy and $X_C^{0,\alpha}$ is the carbon content in PE- α after complete precipitation of PE- θ . After Ghosh and Olson [32].

Kozeschnik and Bhadeshia [33] modelled cementite precipitation under paraequilibrium conditions for two 0.4 wt.% C alloys containing 1.6 wt.% (high) and 0.3 wt.% (low) silicon. Inconsistent with the widely accepted effect of silicon in retarding the formation of cementite during martensite tempering, there was no meaningful difference between the high and low silicon alloys. The only appreciable retarding effect of silicon was seen at low carbon contents only, Figure 2.9 (a). An example of a set of calculations under paraequilibrium conditions are shown in Figure 2.9 (b), for the high silicon alloy containing 1.6 wt.% silicon.

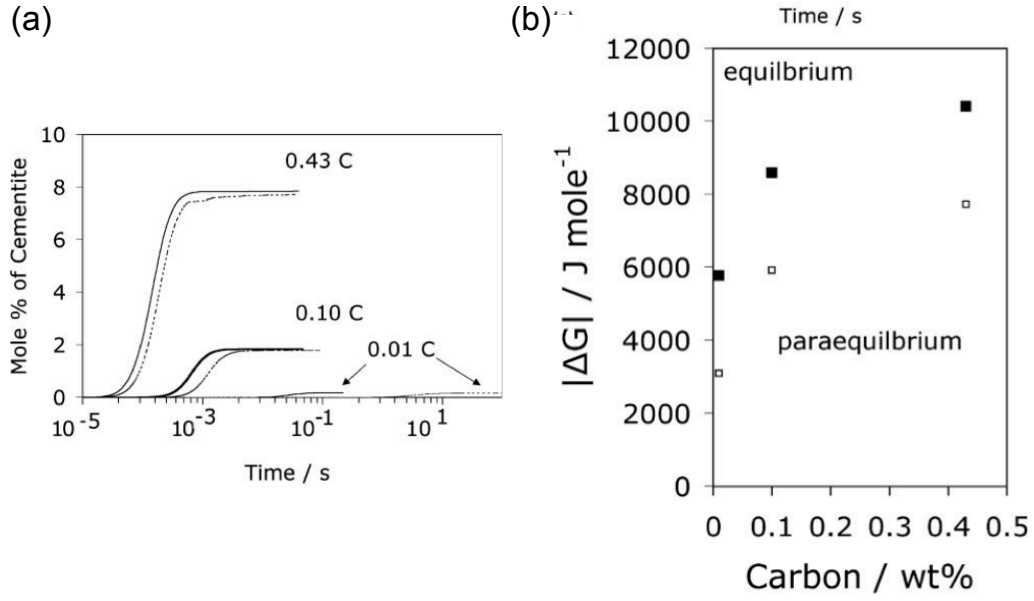


Figure 2.9: (a) Kinetics of paraequilibrium cementite precipitation at 315 °C for the low silicon alloy (solid line) and high silicon alloy (dotted) as a function of carbon content, and (b) computed ΔG for $\alpha \rightarrow \alpha + \theta$ at 315 °C for the 1.6 wt.% Si alloy. After Kozeschnik and Bhadeshia [33].

They went further in explaining the counterintuitive results of the effect of silicon in the tempering kinetics. Following the work by Kalish and Cohen [4], where it was shown that carbon preferentially segregates to dislocations rather than forming carbides, Kozeschnik and Bhadeshia have postulated that the apparent effect of silicon, in reality is due to the time taken for the dissolution of defects in order to make the carbon available for precipitation. Therefore, as less carbon will be available for precipitation (assuming that the majority has been segregated to dislocations), then the silicon will greatly affect tempering kinetics, as shown by the 0.01 wt.% case in Figure 2.9 (a).

In further understanding the effect of substitutional elements such as silicon, aluminium and manganese, Jang *et al.* [34] have performed Density Functional Theory (DFT) calculations to obtain the formation energy for ε and θ carbides. In this modelling approach, the formation energy is given by the energy difference between

the products and the reactants:

$$\Delta U = E(\text{Fe}_l\text{C}_m\text{X}_n) - lE(\text{Fe}) - mE(\text{C}) - nE(\text{X}), \quad (2.4)$$

where $E(\text{Fe}_l\text{C}_m\text{X}_n)$ is the total energy at the corresponding equilibrium lattice parameters, $E(\text{Fe})$ is the total energy of the bcc phase, and $E(\text{C})$ is the total energy of the carbon (graphite) phase. X is the substitutional element, such as Si, Al or Mn. $E(X)$ is the total energy of the substitutional element at the corresponding equilibrium lattice constants.

The substitution of silicon into Fe_3C - θ was simulated with an orthorhombic structure of composition $(\text{Fe}_{11}\text{Si})\text{C}_4$, which corresponds to 4.07 wt.% silicon content, i.e. one out of the twelve iron atoms constituting the unit cell is substituted by silicon [35]. The structure is shown in Figure 2.10. In the case of ε -carbide, one substitutional atom was introduced into a unit cell containing 6 Fe atoms [34]. The values are summarised in Table 2.6.

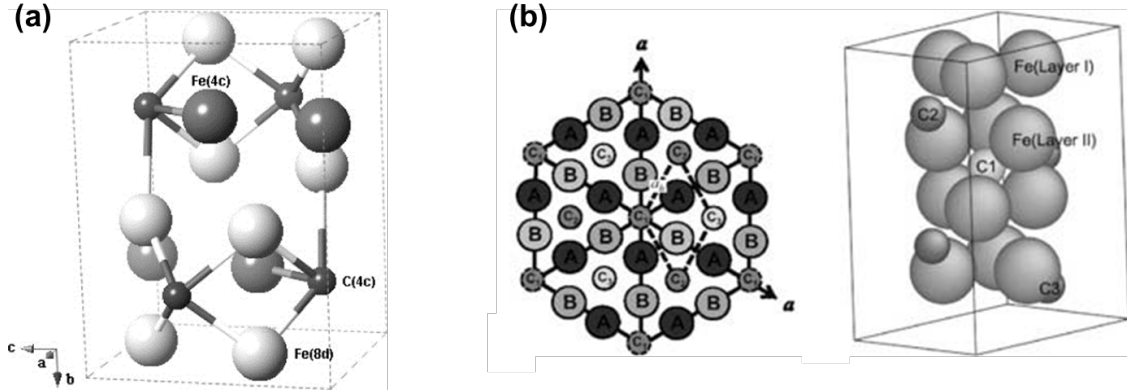


Figure 2.10: (a) Unit cell of cementite (orthorhombic, $Pnma$) containing 12 Fe atoms and 4 C atoms [35], and (b) ε -carbide (hexagonal, $P6_322$), with the basal plane shown on the left and the unit cell on the right [34].

Table 2.6: Formation energies (kJ mol^{-1} of unit cells containing 12 Fe atoms. The values in brackets are the differences between the pure carbide and when one Fe atom per unit cell is substituted by an alloying element [34].

System	ε -carbide	Cementite
Pure carbide	106.0	86.1
Si-substituted	154.4 (+48.4)	123.2(+37.1)
Al-substituted	84.7 (-21.3)	72.5 (-13.6)
Mn-substituted	74.8 (-31.2)	81.1 (-5.0)

From the DFT results, it appears that it is less favourable to substitute silicon into ε than in cementite. Jang *et al.* have interpreted these results in light of the enhancement of ε precipitation when silicon is incorporated into the lattice not being a thermodynamic effect. Instead, they have postulated that since silicon substitution in the iron lattice leads to a contraction in lattice parameters, the presence of silicon would reduce the c-axis, improving the coherency between the ε -carbide and the matrix during nucleation.

2.3.1 Characterising carbides

Two recent techniques that have been developed over the past decade for characterising carbides have been 3D atom probe tomography (3D ATP), and high energy X-ray diffraction methods using synchrotron radiation sources. The former has been considered useful especially in studying the alloying elements distribution across the matrix/carbide interface, as exemplified by the work carried out by Miyamoto *et al.* [26], Zhu *et al.* [28, 29] and Caballero *et al.* [27]. Nevertheless, care should be taken when identifying carbides using this method, as this particular technique does not provide direct evidence of the crystallographic structure of the phase. In the case of the APT technique, the detected carbon level is used to distinguish the carbides

present.

Characterising carbides becomes a particular challenge, as often in literature, different chemical compositions have been reported for the ε -carbide phase. If the chemical composition of the iron-carbide is to be expressed in the form of Fe_xC , in most cases, the orthorhombic cementite case is reported to have a value of $x=3$. However, in the case of ε , many researches have found that the value of x can range between 2 and 2.4, as reviewed by Génin [14]. Furthermore, Génin proposed a Fe_9C_4 structure, as this would ensure the highest occupancy of carbon sites within a hcp ordered structure.

Additional transitional carbides that have been reported in the literature are η - and χ -carbides. The former, an orthorhombic structure of composition Fe_2C , has been reported be an intermediate phase between ε and θ . The latter carbide, χ , also known as the Häag carbide, was hypothesised to have a monoclinic crystal structure, of composition $(\text{Fe,Mn})_5\text{C}_2$ [36, 37], which was thought to occur in Mn-containing alloys, also as an intermediate carbide between ε and θ .

Table 2.7 summarises the carbides that have been reported, with their corresponding carbon content in weight percent. Note that in the case of ε -carbide, the most widely accepted form of $\text{Fe}_{2.4}\text{C}$ has been considered. Given the similarity in carbon content, it thus becomes a challenge to distinguish the carbides from each other solely based on the carbon content.

Table 2.7: List of possible carbides occurring in tempered martensite.

Phase	ε	η	χ	θ
Carbon content in wt.%	8.2	8.7	7.9	6.7

The other experimental technique that has gained strength is high-energy X-rays from a synchrotron source. As it is based on crystal diffraction methods, it overcomes the challenge of distinguishing the carbides phases. Given its high energy

X-rays, it allows further penetration into the sample, offering a more representative analysis of the bulk material. Although for precise details such as size of the carbides, the TEM would be the technique of choice, X-ray diffraction (XRD) methods allow a better estimate of the volume fraction of the carbide phase present. Furthermore, there are other aspects that are better resolved using XRD methods than TEM, such as dislocation density and tetragonality of the matrix phase. Given the abundant information that can be extracted from XRD methods, in the current work X-ray diffraction plays a significant role in understanding the effect of silicon in carbide precipitation and throughout martensite tempering.

The ultimate aim of this research is to elucidate the microstructural parameters that determine strengthening in martensitic steels. The research carried out by Choi [6] showed that by optimising the microstructure via controlled precipitation, outstanding mechanical properties of 2350 MPa tensile strength and 25% reduction area have been achieved. In his work, a combination of heat treatment and silicon additions to retard the $\varepsilon \rightarrow \theta$ carbide transition was explored.

Chapter 3

Interrupted ageing in steels

This chapter looks at the effect of interrupted ageing in tempered martensite. Interrupted ageing is an intermediate step between quenching and tempering, where quenched martensite is left to rest at room temperature for a defined period of time, during which carbon segregates into dislocation cores. As exemplified by aluminium metallurgy, the incorporation of interrupted ageing (IA) allows microstructural tailoring, where Lumley *et al.* [38, 39] reported simultaneous improvements of both strength and ductility through interrupted ageing in aluminium alloys.

This chapter presents the effect of interrupted ageing in martensitic steels, and models carbon segregation to dislocations with the aim of understanding carbon behaviour throughout the heat treatment. The study has been conducted in a commercial spring steel grade, where for a single alloy, by manipulating the heat treatment a wide range of microstructural and hardness properties have been obtained.

3.1 Introduction

3.1.1 Ageing in steels

As-quenched martensite has a very high density of crystal defects, such as dislocations. Dislocations act as carbon-sinks, where the strain fields surrounding the

dislocation cores attract carbon atoms [40], forming Cottrell atmospheres that cancel the dislocation strain. Initially, carbon would be present in interstitial sites, forming a super-saturated solid solution; however, the metastability of these structures causes redistribution of carbon atoms during ageing and tempering [41]. Thus, freshly quenched martensite is known to undergo ageing even at room temperature [11]. During room temperature ageing, the diffusion of solutes is restricted due to slow kinetics, and only interstitials such as nitrogen and carbon diffuse appreciably. Understanding such redistribution of interstitials is of significant interest as the distribution of carbon atoms immediately after quenching has a marked effect on the subsequent heat treatment [4].

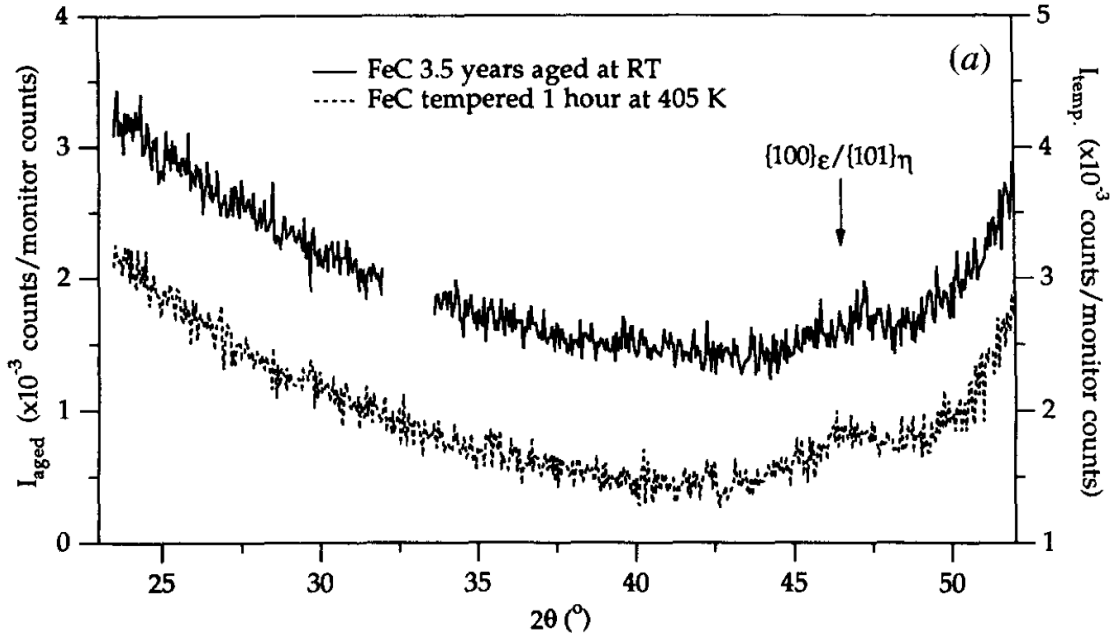


Figure 3.1: XRD patterns obtained using synchrotron radiation, ($\lambda = 0.189821$ nm) for Fe–1.13C wt.% aged at room temperature for 3.5 years, where prolonged room temperature ageing (solid line) shows peaks corresponding to transitional carbides [41].

Van Genderen *et al.* [41] reported room temperature formation of transitional carbides (either ϵ or η) in a binary alloy of composition Fe–1.13C wt.% that has

been aged for 3.5 years, Figure 3.1. It is evident that appreciable microstructural changes occur even at room temperature. By introducing an intermediate stage between quenching and tempering called interrupted ageing (IA), the aim of this chapter is to explore the effect IA can have on carbide precipitation, in particular microstructural properties such as particle spacing and size.

3.1.2 Thermoelectric power

A technique that has been employed in order to study carbon-controlled reactions, such as precipitation, is thermoelectric power (TEP) [42, 43, 44, 45, 46, 47]. The main benefit of TEP is attributed to its sensitivity in detecting variations in the concentration of atoms in solid solution. This feature can be exploited for studying the kinetics of carbon diffusion during IA. TEP operation consists in clamping the two extremes of the material in the form of a rectangular block on two metallic reference blocks (copper was used in this work). One block is kept at 15 °C, while the other is at 25 °C, and given the temperature gradient, ΔT , of 10 °C, the response in voltage, ΔV is recorded. The set-up is illustrated in Figure 3.2.

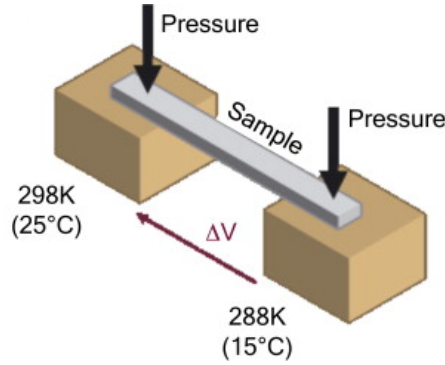


Figure 3.2: Experimental set-up of the TEP system [43].

The TEP, S^* , of the tested material is given by:

$$S = S^* - S_{\text{Cu}}^* = \frac{\Delta V}{\Delta T}, \quad (3.1)$$

where S is the observed TEP, S_{Cu}^* is the TEP of the reference blocks (pure copper, 99.99 wt.%), $S_{\text{Cu}}^* = 1.91 \mu\text{V K}^{-1}$ at 20 °C.

In steels, the observed TEP is the result of various additive terms [48]:

$$S^* = S_0^* + \Delta S_{\text{ss}} + \Delta S_{\text{d}} + \Delta S_{\text{pcpt}}, \quad (3.2)$$

where S_0^* is the TEP of the base metal, ΔS_{ss} is due to the elements in solid solution, ΔS_{d} is due to dislocations, and ΔS_{pcpt} is due to the presence of precipitates. Such an observation has been related to the interaction between free carbon atoms in solid solution and dislocations in pre-strained ultra-low carbon steels [47].

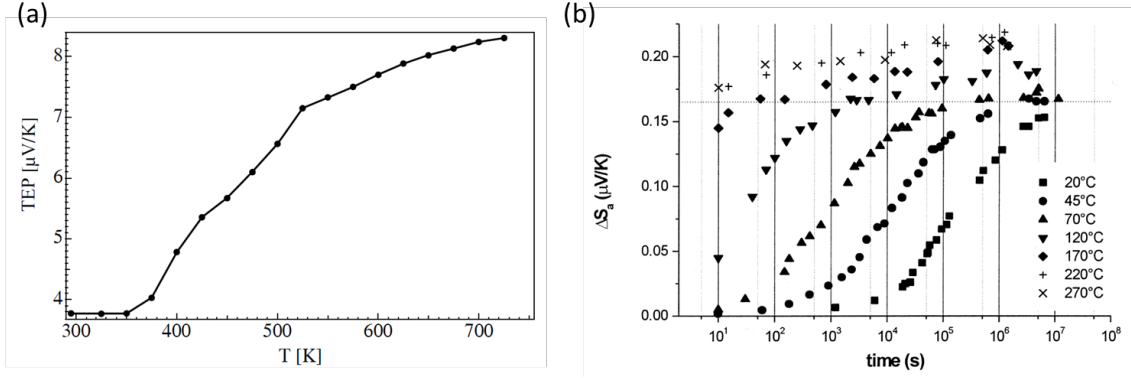


Figure 3.3: (a) Room temperature TEP signal after tempering 25 minutes at different temperatures for an Fe-1.23C-0.64Cr-0.34Mn-0.22Si-0.07Ni-0.12Mo-0.10Cu wt.% alloy [49], and (b) Room temperature TEP evolution after various strain ageing treatments on an Fe-4C-7N-225Mn-22Al-11P-9S ($\times 10^{-3}$ wt.%) alloy, where ΔS_{a} is the TEP value after the strain-ageing treatment [47].

Tkalcec *et al.* [49] recorded the TEP value after 25 minutes tempering at different temperatures, for a Fe-1.23C-0.64Cr-0.34Mn-0.22Si-0.07Ni-0.12Mo-0.10Cu wt.% alloy (Figure 3.3 (a)). It was observed that the TEP signal varied inversely with the amount of carbon in solid solution. Furthermore, Lavaire *et al.* [47] recorded the room temperature TEP evolution after strain ageing experiments. For an ultra low carbon (ULC) steel of composition Fe-4C-7N-225Mn-22Al-11P-9S ($\times 10^{-3}$ wt.%)

that had been cold-rolled to a 50% reduction, the TEP evolution differed between tempering conditions, Figure 3.3 (b).

Lavaire *et al.* [47] attributed the observed TEP differences to the ability of the strained steel to trap carbon atoms on dislocations, and concluded that the observed TEP evolution was due to the diffusion of carbon in ferrite. All conditions saturate after some time, which appears to be shorter as the tempering temperature increases. This saturation level would infer complete carbon segregation. Although the dislocation density was not stated in their work, and some carbon segregation would have inevitably occurred immediately after cold-rolling, it is clear that TEP evolution can be used for studying carbon segregation to dislocations during martensite ageing.

TEP measurements, combined with the model originally devised by Kalish and Cohen [4], are used for gaining further understanding of the interrelationship between processing, microstructure and the mechanical properties of mid-carbon steels undergoing IA.

3.2 Experimental procedure

The 54SCV6 automotive grade used in spring steels was selected for this current study. Table 3.1 summarises the measured chemical composition.

Table 3.1: Measured chemical composition of the 54SCV6 grade used, with Fe to balance.

	C	Si	Mn	Cr	Cu	Ni	Mo	V
wt. %	0.56	1.59	0.71	0.54	0.12	0.06	0.02	0.13

The as-received material was in the form of rods, with an initial hardness of 317 HV1.

3.2.1 Heat treatment

Cylindrical rod-like specimens of 3 mm in diameter and 12 mm in length were machined. The heat treatment of these specimens was carried out in an Adamel Lhomargy dilatometer (model DT1000) as shown in Figure 3.4. The conventional heat treatment consists in tempering immediately after quenching. In the heat treatment involving interrupted ageing, a dwell time is introduced between quenching and tempering, where the sample is removed from the dilatometer and kept at room temperature for a prescribed time.

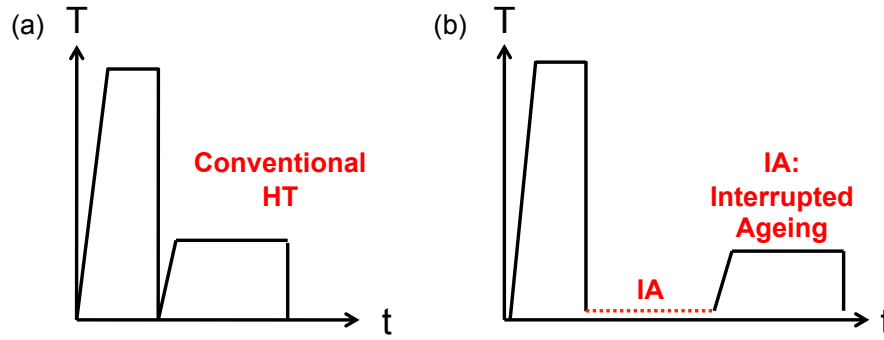


Figure 3.4: (a) Conventional heat treatment for tempered martensite, and (b) heat treatment used for interrupted ageing.

A series of heat treatments were designed in order to study the effect of:

- The duration of the interruption.
- The duration and temperature of the tempering stage.
- Austenitisation temperature.

Table 3.2 shows a summary of all the 11 conditions studied, where T is the temperature, t is time and subscripts 1 and 2 refer to the austenitisation and the tempering stages respectively. t_{IA} is the duration of the interruption time at room temperature.

The choice of the austenitisation conditions reflects the typical industrial process for spring steels, where austenitisation is carried out at 880 °C for 180 s. Tempering

is usually carried out in the range of 350–450 °C for 1800–3600 s. However lower tempering temperatures were selected in this study in order to optimise hardness properties. Furthermore, a relatively low tempering temperature would ensure incomplete reactions, where carbon would still remain in solid solution. This gives greater flexibility in studying the effects of interrupted ageing, as will be shown further on.

Table 3.2: Summary of heat treatments in order to study the effect of interrupted ageing.

	T_1 (°C)	t_1 (s)	t_{IA}	T_2 (°C)	t_2 (s)
L1	880	180	7.2 hours	250	1800
L2	880	180	3 days	250	1800
L3	880	180	30 days	250	1800
L4	880	180	30 days	250	300
L5	880	180	-	-	-
L6	880	180	-	250	1800
L7	880	180	-	250	5400
L8	880	180	-	300	1800
L9	880	180	30 days	300	1800
L10	1000	180	-	250	1800
L11	1000	180	-	300	1800

3.2.2 Determining the prior austenite grain size

As there are two austenitisation temperatures being used, 880 and 1000 °C, this will result in a microstructural difference. The conditions austenitised at 1000 °C are bound to have a larger prior austenite grain (PAG) size, which is likely to affect the

subsequent martensite formation [7].

Typically, in industry, austenitisation is carried out at temperatures near 880 °C. 1000 °C was chosen to account for the dissolution of ‘reluctant carbides’ [50] such as vanadium carbide, V_4C_3 . Given the list of alloying elements of the 54SCV6 grade, it is likely that vanadium carbide is present within the as-received state. ThermoCalc predicts the dissolution of vanadium carbide at 983 °C for the given alloying system. Although grain coarsening will only take place after the dissolution of the carbide phases [51], it is still worth comparing the PAG sizes for the austenitisation conditions.

The PAG boundaries were revealed by the thermal etching method [52], where samples of 5 mm diameter and 12 mm length were polished down to a 1 μ m diamond paste and etched with 2% nital solution. Austenitisation was carried out in an 805 Bähr dilatometer at the respective temperatures, and quenched. The specimens were later examined under an optical microscope, at which the grain boundaries were visible. The average grain size was estimated using the mean linear intercept method [53].

3.2.3 Mechanical testing

Hardness

Dilatometry samples were polished to a 1 μ m diamond paste finish. Two sets of hardness measurements were carried out. The first set shortly after heat treatment in the dilatometer, and the second set after a six months period from the first set of measurements. Vickers hardness tests were carried out using a Mitutoyo MVK-H2 microhardness indenter with a 1 kg load. 10 measurements were taken from each condition.

Tensile testing

Tensile tests were performed on dilatometry samples of 3 mm diameter and 15 mm length. The heat treatments described on Table 3.4 were followed and the tensile tests were carried out immediately after removal from a LK02 dilatometer. 3 runs were made per condition, using a Microtest tensile machine.

Compression testing

In addition to the tensile tests, the conditions L3, L5 and L8 were selected for compression testings. Dimensions of 5 mm diameter and 8 mm length were used.

3.2.4 Microstructural characterisation

Microstructural characterisation was carried out using transmission electron microscopy (TEM) on a Philips CM30 model. 3 mm discs were cut from the dilatometry samples, and were electropolished using a solution composed of 15 ml perchloric and 85 ml ethanol. A twinjet electropolisher Struers Tenupol-5 was used, operated under a voltage of 20.5 V, at 16 °C, and a flow rate set at 12. Over 500 intralath precipitates were analysed per condition, taken from three to four different TEM frames, all under the same magnification, $\times 52$ k. Characteristics such as particle length, width and centre-to-centre spacing were manually measured using ImageJ. Using bright field imaging techniques, features down to ~ 5 nm could be resolved by TEM. Stereological corrections were applied [54]. Furthermore, for comparison purposes, given the length, l , and width, w , an expression for the equivalent radius, r_{equiv} was derived:

$$r_{\text{equiv}} = \left(\frac{3}{16} (w_{\text{average}})^2 l_{\text{average}} \right)^{\frac{1}{3}}, \quad (3.3)$$

where the subscript ‘average’ stands for average values.

3.2.5 Thermoelectric power

Thermoelectric power (TEP) measurements were carried out on quenched specimens of dimensions $30 \times 2 \times 1 \text{ mm}^3$, using a TechLab-GEM-PPM INSA Lyon model. The TEP evolution in the as-quenched state was recorded over a period of 3 months. For the austenitisation at $880 \text{ }^\circ\text{C}$ condition, 3 runs were made for reproducibility.

3.3 Characterisation by dilatometry

3.3.1 Summary of critical temperatures

The dilatometry curves obtained during the heat treatment were analysed in order to extract the critical transformation temperatures, such as the austenitisation start and finish temperatures (A_{c1} and A_{c3} , respectively) and the martensitic start temperature (M_s). These are summarised in Table 3.3.

Table 3.3: Summary of critical temperatures obtained from dilatometry.

A_{c1}	A_{c3}	M_s
$798 \pm 3 \text{ }^\circ\text{C}$	$832 \pm 3 \text{ }^\circ\text{C}$	$238 \pm 9 \text{ }^\circ\text{C}$

Given that A_{c3} is below the austenitisation temperature, complete austenitisation is guaranteed during the heat treatment. A typical dilatometry curve is shown in Figure 3.5 for the austenitisation and quenching part. The transformation temperatures were manually measured, where the point at which a change in slope occurred was estimated by eye, as shown in the magnified view in Figure 3.5. The values in Table 3.3 represent an average of 11 readings.

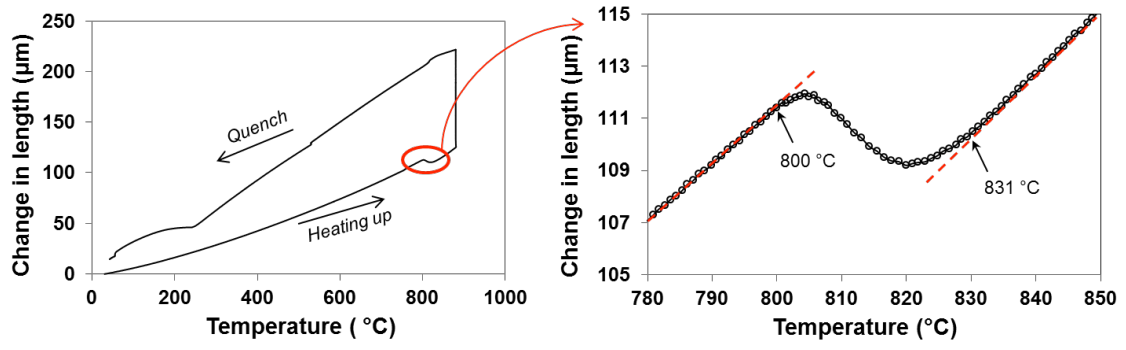


Figure 3.5: Typical dilatometry curve showing the transformations for the austenitisation stage.

3.3.2 PAG size

Figure 3.6 shows typical optical micrographs after thermal etching for 3 minutes at (a) 880 and (b) 1000 °C. The PAG boundaries are hardly visible for the 880 °C austenitisation temperature due to the small grain size. The average PAG size was measured to be $5.1 \pm 0.4 \mu\text{m}$ for 880 °C and $23.3 \pm 0.6 \mu\text{m}$ for 1000 °C. Increasing the austenitisation temperatures results in a five-fold increase in the PAG size.

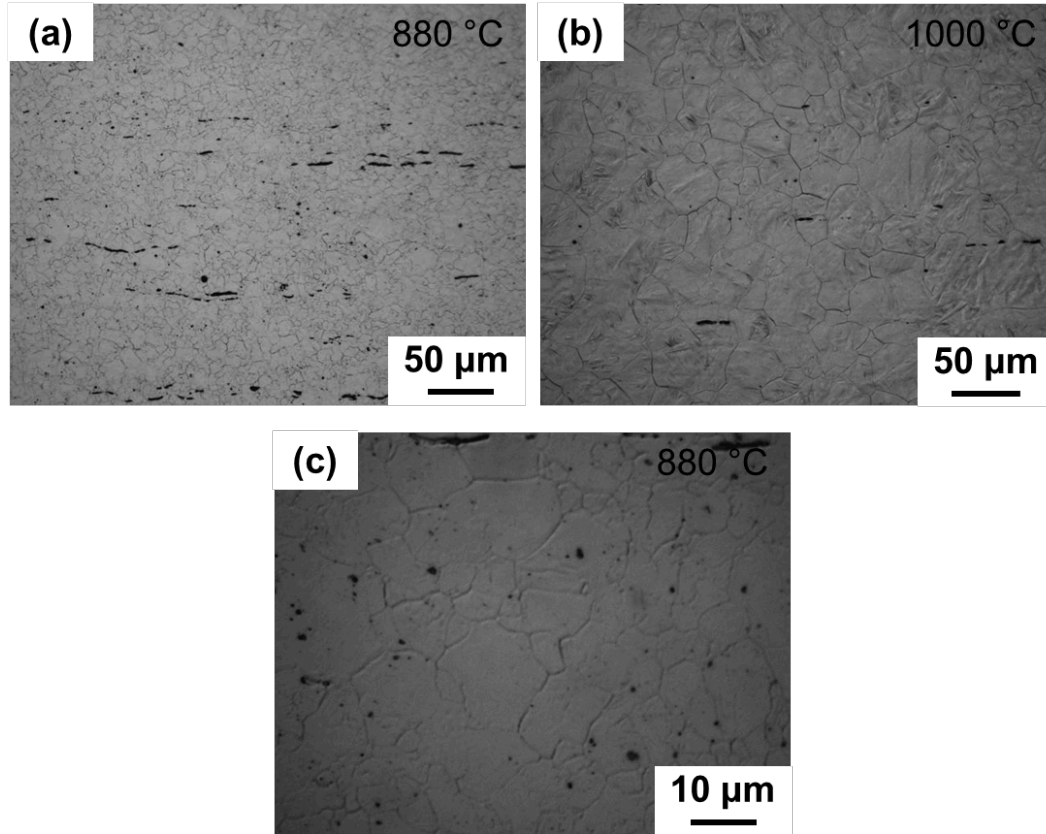


Figure 3.6: Optical micrograph revealing prior austenite grain size by the method of thermal etching for 3 minutes austenitisation at (a) 880 and (b) 1000 °C, and (c) 880 °C taken at a magnification of $\times 1000$.

3.4 Hardness and microstructural analysis

3.4.1 Hardness testing

The hardness for the various heat treatment conditions listed in Table 3.2 are shown in Figure 3.7. Three immediate trends can be spotted. The first is that the initial hardness (dark grey) is higher for the conditions undergoing interrupted ageing (L1–L4, with the exception of L9). The second is that hardness properties become stable via interrupted ageing, whereas for those undergoing direct tempering an increase in hardness is observed. Finally, the third is that after the 6 months following the initial readings, the conditions undergoing direct tempering (L6–L8) as well as L9,

reach hardness values approaching the interrupted ageing ones ($\sim 700\text{HV1}$).

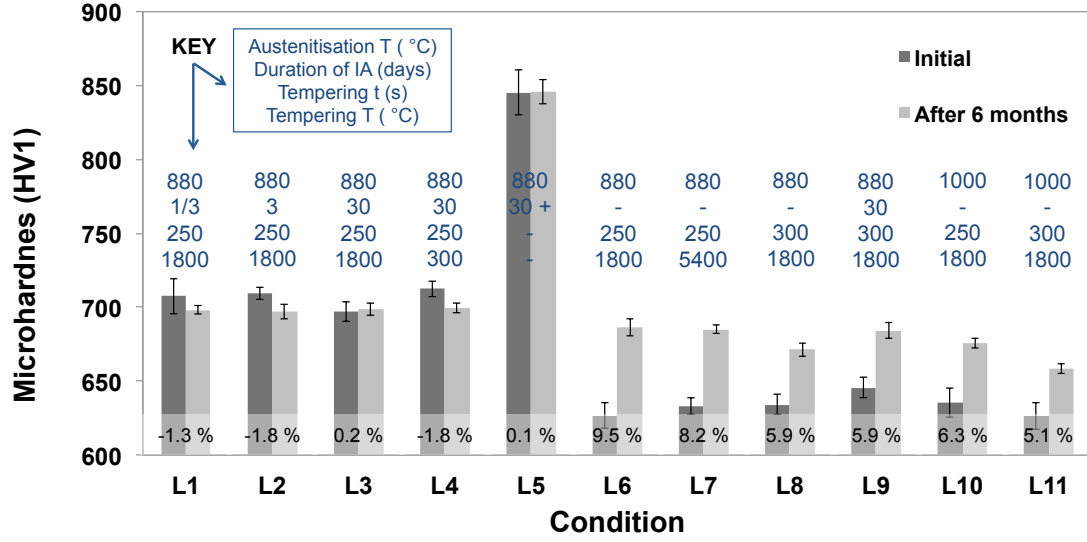


Figure 3.7: Hardness measurements after heat treatment (dark grey) and 6 months after (light grey). The percentage increase in hardness is shown at the bottom of the bars, and the error bars indicate one standard deviation.

Upon quenching, the formation of martensite is accompanied by a lattice expansion. During tempering, decomposition of martensite takes place, as the initially trapped carbon diffuses out. The tetragonality is reduced and the process is accompanied by the following: lattice contraction due to the decomposition of martensite, and a corresponding expansion due to the decomposition of retained austenite [55]. On the series of work by Averbach *et al.* where the dimensional stability of components has been studied, it was shown that even after the final manufacturing stage, further dimensional changes were observed due to transformations taking place at room temperature: “In all cases, the martensite contractions are quite additive in that if the transformation at a higher temperature is stopped, it proceeds at room temperature at the same rate it would have if all the shrinkage had occurred at room temperature” [55].

This seems to confirm the postulate that at low temperatures such as 250 °C, the precipitation process does not come to a completion, but instead continues at room

temperatures, although most probably at a reduced kinetics. For example, studying the effect of tempering in the dimensional stability of martensite, Averbach *et al.* showed that tempering 1 hour at 120 °C causes the same contraction as tempering 1050 days (~ 35 months) at 20 °C.

By incorporating the IA stage before the conventional tempering, a higher degree of reaction completion is achieved, as during the IA stage, ‘ordering’ of carbon atoms takes place. In this sense, having an interruption stage prior to tempering provides a more efficient solute take-up. This could also be the reason why in industry, tempering is conventionally carried out at higher temperatures between 400 and 450 °C, as from the dimensional stability point of view, this would ensure reaction completion.

For condition L9, despite the interrupted ageing, the hardness is significantly lower than conditions L1–L4, and it is not stabilised even after the 30 days of interruption time. A possible explanation for this discrepancy is presented in the forthcoming microstructural analysis.

A second set of experiments for conditions L1 and L6 were performed using a lower quenching rate of 15 °C/s. In this case, the measured hardness for L1₁₅ and L6₁₅ were 661.8 ± 3.1 and 659.9 ± 5.8 HV1, respectively. Comparing these values with the ones obtained using the maximum quenching rate achieved by the dilatometer, 75 °C/s (Figure 3.8), this shows that the effect of the interrupted ageing is limited to high quenching rates.

So far, only the effects of precipitates have been considered for understanding hardness properties. Nevertheless, there are other microstructural aspects that must be taken into account: carbon content in solid solution, dislocation density and structure, and whether dislocations are mobile or locked due to segregated carbon atoms. Understanding the different strengthening contributions will be explored in detail in Chapter 6 on Plasticity.

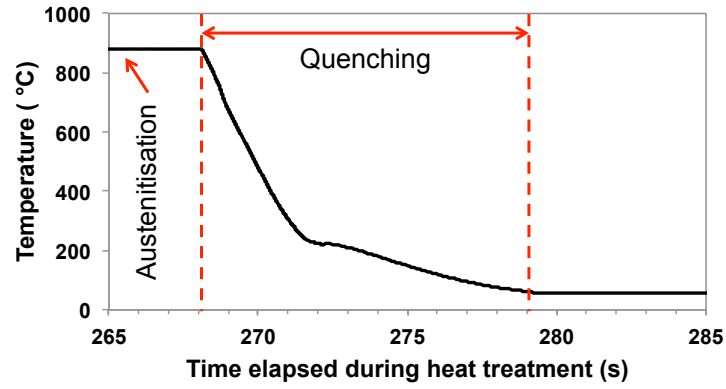


Figure 3.8: Representative dilatometry curve showing temperature-time during sample heat treatment.

3.4.2 TEM

Selected bright field images are shown in Figures 3.9 and 3.10. The differences in the intralath carbides are not very obvious at first, but quantitative metallography shows obvious trends. The values obtained for length, l , and width, w , of intralath carbides, and the corresponding aspect ratio for each condition are summarised in Table 3.4. Furthermore the extracted equivalent radius, r_{equiv} , in Equation (3.3) and the centre-to-centre spacing between carbides are also given. Conditions L10 and L11 have been omitted due to the different austenitisation conditions and L5 as no intralath carbides were observed for the as-quenched condition.

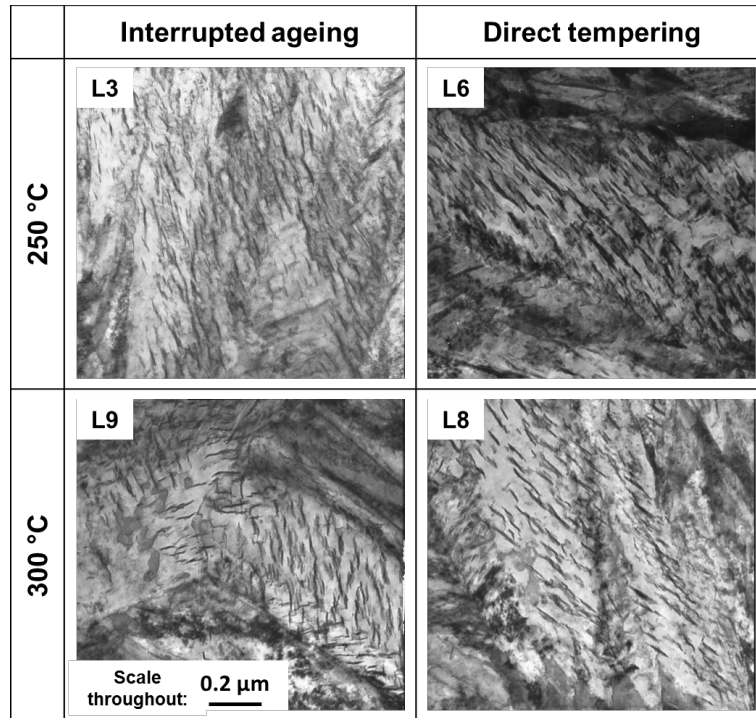


Figure 3.9: Representative bright field images showing intralath carbides for conditions L3, L6, L8 and L9, where the effect of interrupted ageing and tempering temperature are compared.

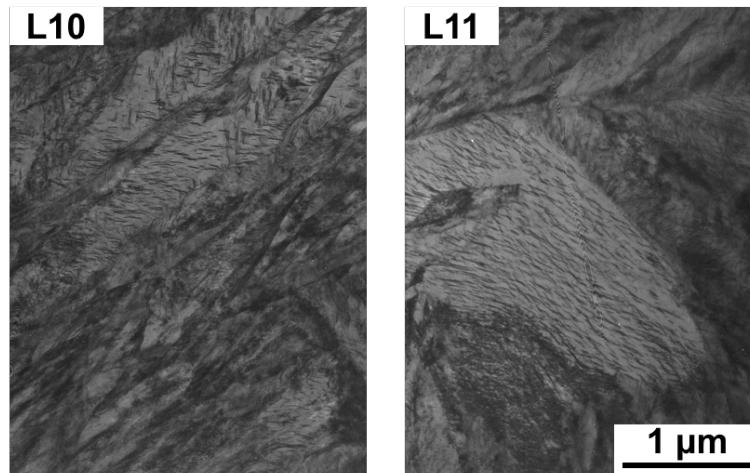


Figure 3.10: Bright field images for conditions L10 and L11 (austenitisation at 1000 °C). Notice the inhomogeneity of the microstructure.

Table 3.4: Summary of the microstructural analysis.

	l (nm)	w (nm)	Aspect ratio	r_{equiv} (nm)	Spacing (nm)
L1	51.5	8.8	5.9	9.1	36.4
L2	51.7	9.1	5.7	9.3	33.2
L3	48.0	7.0	6.9	7.6	29.0
L4	40.6	7.8	5.2	7.7	28.4
L6	56.1	8.7	6.5	9.2	32.2
L7	48.2	8.4	5.8	8.6	39.9
L8	46.9	7.1	6.6	7.6	33.1
L9	42.9	5.4	7.9	6.2	29.1

Histograms for the length, width and spacing measurements for condition L3 are shown in Figure 3.11.

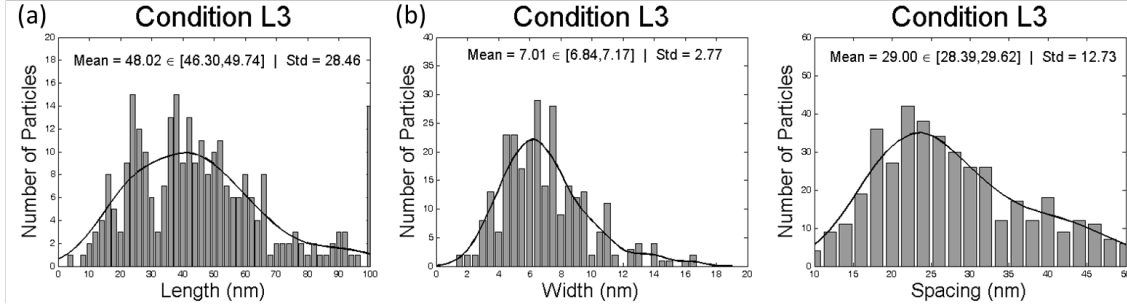


Figure 3.11: Histograms for (a) length, (b) width, and (c) spacing measurements for condition L3.

Kolmogorov–Smirnov two sample test

A statistical method is needed in order to systematically compare the size and spacing distributions of carbides. The Kolmogorov–Smirnov (K-S) statistical test [56] is carried out between two conditions in order to compare the distribution of two sample data sets, x_1 and x_2 . In the K-S test, the null hypothesis states that x_1 and x_2 are from the same continuous distribution. The output of the test is as

follows:

- 1: reject null hypothesis, i.e. x_1 and x_2 are not from the same continuous distribution;
- 0: valid hypothesis.

The null hypothesis is rejected when the p-value is less than the significance level (5%), i.e. $p \leq 0.05$. The K-S test can be applied to distinguish and compare the microstructure of two given conditions. The results from the test are summarised in Table 3.5.

The observed trend is that IA results in a finer microstructure in terms of smaller particle size and spacing (L3 vs. L6 and L9 vs. L8), and that the duration of tempering after 30 days of IA does not influence the microstructure (L3 vs. L4). Tempering at a higher temperature after IA leads to smaller carbides, without altering their spacing (L3 vs. L9). In general, the incorporation of the IA stage leads to finer microstructures.

The last two columns from Table 3.4 are represented in Figure 3.12 on a r_{equiv} vs. spacing plot.

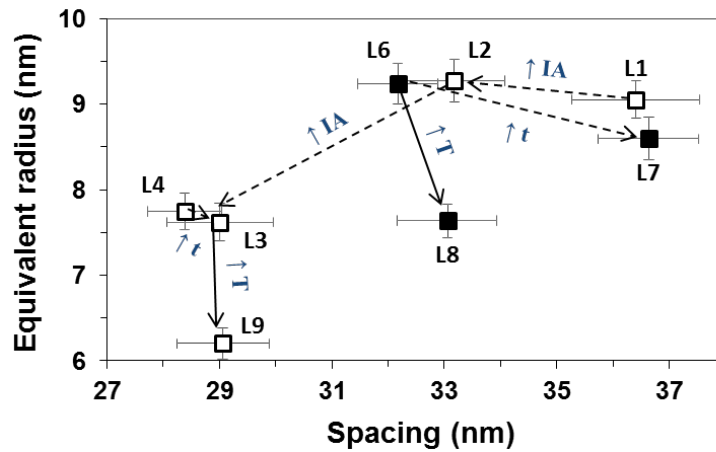


Figure 3.12: Summary for intralath carbide equivalent radius and spacing for conditions L1 to L9, except L5.

Table 3.5: Summary of the outcome from the K-S test, where p-values are given in brackets (when p-values are less than 0.001 they are indicated as ~ 0).

Conditions	Particle size	Particle spacing	Interpretation
L3 vs. L6	1 (~ 0)	1 (~ 0)	30 days of IA gives a finer microstructure (both precipitate size and spacing)
L1 vs. L2	0 (0.541)	1 (0.0013)	Size does not change but the spacing decreases between 1/3 and 3 days of IA
L3 vs. L4	0 (0.121)	0 (0.5535)	After 30 days of IA, the tempering time does not influence precipitation
L2 vs. L6	0 (0.633)	0 (0.2827)	3 days of IA does not alter the microstructure significantly
L6 vs. L7	1 (0.003)	1 (~ 0)	In direct tempering, longer tempering decreases carbide size and increases spacing
L6 vs. L8	1 (~ 0)	0 (0.1736)	In direct tempering, increasing tempering temperature decreases carbide size
L3 vs. L9	1 (~ 0)	0 (0.6750)	After 30 days of IA, increasing tempering temperature decreases carbide size

A clear trend is observed in Figure 3.12: as the duration of the interrupted ageing increases, the spacing between carbides decreases; whereas as tempering temperature increases, the size of the carbides decreases. Hardness measurements showed

that the hardness value was significantly lower than the conditions undergoing interrupted ageing. Condition L9 presents the finest microstructure in terms of particle size and spacing. The low hardness could be due to a lesser degree of precipitation hardening if particle shearing mechanism is assumed [57]. The increase in hardness in L9 over the 6 months period is not understood yet. However, an initial postulate is that due to the small spacing between carbides, dissolution of carbides or carbon clusters may have taken place, increasing the carbon content in matrix.

Overall, the reason for the finer microstructures obtained via IA is based on the postulate that IA provides a more efficient take-up of carbon atoms from the solid solution. The following sections aims at understanding and modelling carbon segregation to dislocations by means of thermoelectric power measurements, adopting the Kalish-Cohen model [4] for carbon segregation.

3.5 Modelling carbon segregation during interrupted ageing

3.5.1 The Kalish-Cohen model

In understanding the microstructural changes occurring during strain-ageing of martensite, Kalish and Cohen [4] presented a model to describe the process by which carbon segregates into dislocation fields. Consider a carbon atom in solid solution in freshly quenched martensite. Due to the strain fields spanning around dislocation lines, the carbon atom will be attracted to the core of the dislocation. At this stage it is necessary to state the assumption made that the only carbon-sink acting within the microstructure are dislocations.

If the spacing between two adjacent dislocations is given by $d_{\perp}$ then, as illustrated in Figure 3.13 (a), the maximum distance that a carbon atom would need to diffuse before reaching the nearest trapping site is given by $x_{\max}$.

During dilatometry experiments, the M_s was determined to be 238 ± 9 °C. This would correspond to a dislocation density, ρ , of around $8 \times 10^{15} \text{ m}^{-2}$ [58]. Assuming a homogeneous distribution of dislocations throughout the material, the average spacing between two adjacent dislocations, Figure 3.13 (a), is given by $\rho^{-\frac{1}{2}}$; hence $d_{\perp} \approx 11.2 \text{ nm}$, yielding a value of 5.6 nm for $x_{\max}$. For simplicity, the ρ value for the as-quenched condition is used. Nevertheless, this value will vary throughout different heat treatment conditions. For instance, in the case of direct tempering, the dislocation density will reduce after tempering and this will slightly change the process of carbide precipitation.

The interaction energy between the carbon atom and the dislocation strain fields at the dislocation core has been stated to be 0.46 eV at a distance of one Burgers vector ($1b$) [4], where b is taken to be 0.25 nm . Furthermore, it is known that at the limit of interaction radius, r_i , Figure 3.13 (b), the interaction energy experienced by the carbon atom is equivalent to the thermal energy $kT = 0.026 \text{ eV}$, where $k = 8.62 \times 10^{-5} \text{ eV K}^{-1}$ and $T = 298 \text{ K}$, equivalent to a distance of $17.8b$. [4].

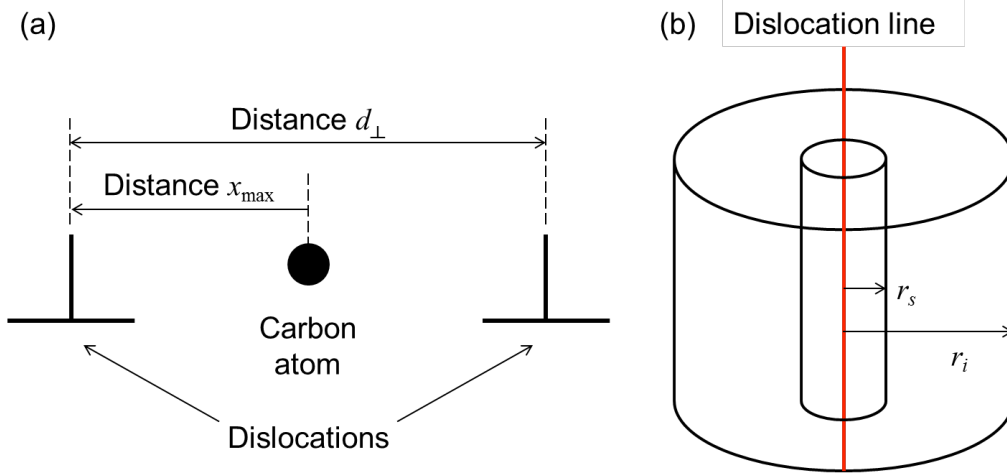


Figure 3.13: (a) Illustration of the distance that a carbon atom needs to travel before being segregated into the core of the dislocation, and (b) schematic diagram of the dislocation core, where r_s and r_i are the segregation and the interaction radius, respectively.

The process suggested by Kalish and Cohen for carbon segregation into dislocation strain fields is summarised in Figure 3.14.

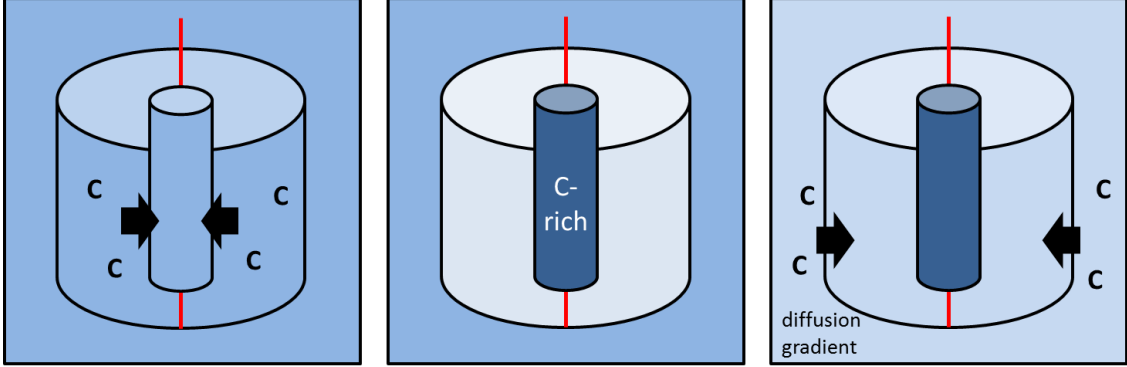


Figure 3.14: Illustration of the carbon segregation process by Kalish and Cohen [4].

It has been suggested that initially carbon within the interaction region, r_i , segregates into the segregation zone, r_s . This leaves a temporary carbon-depleted region within the $r_i - r_s$ zone, while the dislocation core remains carbon rich. This establishes a diffusion gradient between the $r_i < r < r_s$ region and the region beyond r_i , which will draw the carbon into the depleted zone in order to even out the carbon content within the matrix. The following section attempts at explaining the process occurring during interrupted ageing by applying the Kalish-Cohen model interpreted in light of TEP measurements.

3.5.2 Thermoelectric power

The TEP evolution recorded over a 3 month period is shown in Figure 3.15.

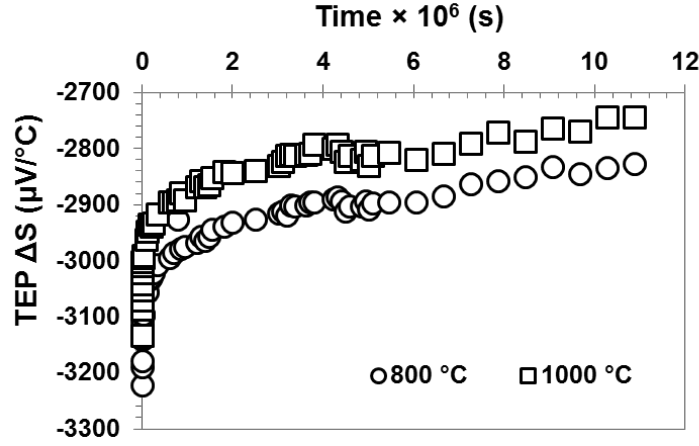


Figure 3.15: TEP evolution for as-quenched martensite over a 3 month period for austenitisation at 880 and 1000 °C.

The TEP signal for the 1000 °C condition is higher than for 880 °C. TEP is very sensitive to the state of the microstructure [49]. Differences in the microstructure between the two samples such as prior austenite grain size, and carbon concentration in solid solution after the dissolution of secondary carbides, could contribute to a difference in TEP signal. Recalling Equation (3.2), the total TEP signal is a contribution from solid solution (ΔS_{ss}), dislocations (ΔS_d) and precipitate effects (ΔS_{pcpt}).

During room temperature ageing of quenched martensite, carbon segregation into dislocation cores would cancel out the dislocation strain fields, hence the ΔS_d term would change. Similarly, the signal due to solid solution would also evolve, as less free carbon in solid solution remains. The ΔS_{pcpt} term becomes significant only in the case of small, coherent precipitates [45]. For the sake of simplicity, the following assumptions are made in interpreting TEP evolution:

- Quenching is sufficiently fast to avoid the formation of small coherent carbide precipitates during cooling.
- The carbon/dislocation interaction energy remains constant until the dislocation core becomes saturated; i.e., ΔS_d remains constant during early segrega-

tion stages.

- Following the work by Lavaire *et al.* [47], in the first instances after quenching, the decrease in TEP magnitude is due to C segregation alone.

Studying the TEP response for the individual effects of each microstructural contribution goes beyond the scope of the current research. Instead, focus has been on the 880 °C condition with the aim to study the evolution of the TEP throughout room temperature ageing. Three runs have been made for reproducibility and the curves are shown in Figure 3.16.

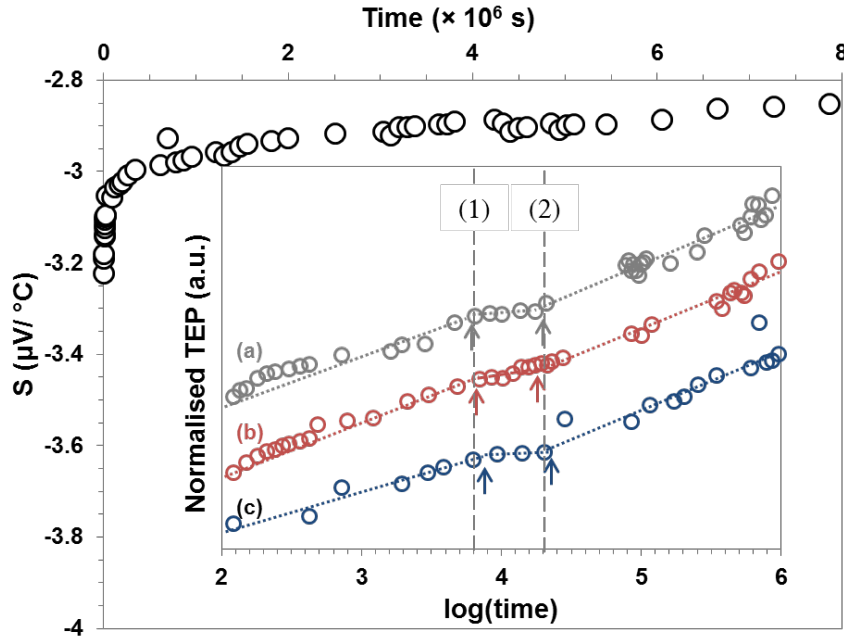


Figure 3.16: TEP evolution for as-quenched martensite from austenitisation at 880 °C, where the inset shows a detailed view of the three runs (a), (b) and (c).

From the central frame in Figure 3.16, it can be seen that the gradient of the curve changes twice, where the changing points are marked with an arrow. It appears that first there is an increase (slightly linear) in TEP signal, although some scattering of the data occurs at first quenching instances. At (1), the TEP curve flattens out, as it approximately reaches a plateau for some time, followed by further increase in

TEP from (2). The aim of the following sections is to extract from the TEP curves semi-quantitative information regarding carbon segregation.

The first step is to mark the moment at quenching, time= 0 seconds, as the beginning of carbon segregation. Therefore, the time elapsed since quenching is an indication of the carbon segregation in martensite. Then, given the time lapse, and with a suitable diffusivity value, the distance diffused by a carbon atom could be determined.

3.5.3 Semi quantitative analysis

The time elapsed at (1) and (2) (Figure 3.16) were found to be 1.8 ± 0.2 and 5.5 ± 0.6 hours, respectively. Given the times at points (1) and (2), the diffusing distance of the carbon atom can be determined. Using reported value from literature for the diffusivity of carbon in ferrite at room temperature, $D_{C,\alpha} = 2.8 \times 10^{-22} \text{ m}^2 \text{ s}^{-1}$ [59], the diffusing distance, $\langle x \rangle$, can be determined:

$$\langle x \rangle = \sqrt{2D_{C,\alpha}t}, \quad (3.4)$$

Moreover, by finding the equivalent distance in terms of b units, and assuming that the interaction energy between the core of the dislocation and at the r_i limit varies linearly, it is possible to estimate the interaction energy between the diffusing carbon atom at the dislocation. Knowing that at a distance of $1b$ the interaction energy is 0.46 eV, and that at a distance of $17.8b$ the interaction energy decreases to 0.026 eV [4], a linear decrease is assumed between these two ranges. The values are summarised in Table 3.6.

Table 3.6: Estimating diffusing distances and carbon-dislocation interaction energies from TEP results.

	Time (h)	$\langle x \rangle$ (nm)	$\langle x \rangle$ (b)	IE (eV)
(1)	1.8 ± 0.2	1.9	$7.7b$	0.060
(2)	5.5 ± 0.6	3.3	$13.3b$	0.034

At time (2), the estimated interaction energy is 0.034 eV. Previously it was determined that at the limit of r_i the interaction energy is 0.026 eV, equivalent to a distance of $17.8b$. Thus it can be inferred that at even after 5.5 hours of quenching, the carbon within the $r_s < r < r_i$ region is still reaching the dislocation core.

This is consistent with the microstructural observations made by TEM. Results from the Kolmogorov-Smirnov statistical test on Table 3.5 show that when comparing conditions L1 vs. L2, increasing the interruption time from 7.2 hours to 3 days the average spacing between intralath carbides becomes smaller, also shown in Figure 3.12.

Initially, the plateau region of the TEP curve (marked by (1) and (2)) was thought to correspond to the stage in the Kalish-Cohen model where the $r_s < r < r_i$ region temporarily becomes depleted, and further carbon from the matrix is drawn due to the established diffusion gradient. Thus, it would relate to a period of time where minimum carbon diffusion takes place due to carbon competition between neighbouring dislocations. However, between (1) and (2) there is a time lapse of ~ 3.7 hours, which appears to be rather high, especially given that one would expect such flux of carbon should be continuous instead of maintaining the depleted region for 3.7 hours.

Nonetheless, the quantification is sensitive to the value of $D_{C,\alpha}$ used for estimating carbon diffusion. For instance, Veiga *et al.* [60] have computed $D_{C,\alpha}$ values using different computational methods (atomistic simulations, elasticity calculations and

simple random walk) for both screw and edge dislocations, in order to determine the kinetics of Cottrell atmosphere formation at 300 K. The values are summarised in Table 3.7.

Table 3.7: Diffusion coefficient values from literature [60].

Dislocation	Method	$D_{C,\alpha}$ ($\text{m}^2 \text{s}^{-1}$)
Edge	Atomistic simulations	4.2×10^{-21}
Edge	Elasticity calculations	2.5×10^{-21}
Edge	Simple random walk	2.6×10^{-21}
Screw	Atomistic simulations	2.3×10^{-21}
Screw	Elasticity calculations	1.7×10^{-21}
Screw	Simple random walk	2.6×10^{-21}

The values reported by Veiga *et al.* [60] are approximately one order of magnitude lower than the value used [59]. The use of smaller $D_{C,\alpha}$ values would slightly overestimate the diffusing distances. For instance, using the value from elasticity calculations for an edge dislocation, the diffusing distances at points (1) and (2) will be $22.8b$ and $39.8b$ respectively. The diffusing distance at (2) almost corresponds to the actual distance between adjacent dislocations, $d_{\perp} = 11.2 \text{ nm}$, equivalent to $44.8b$.

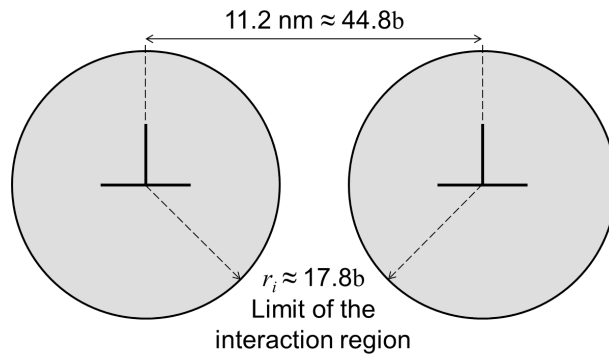


Figure 3.17: Schematic representation of the region around dislocations.

Figure 3.17 schematically represents the distances between neighbouring dislocations. At high dislocation densities there is solute competition between adjacent dislocations [61]. A carbon atom sitting in the region beyond r_i will experience a ‘pull’ from two dislocation fields simultaneously, which would reduce the effective segregation.

The accuracy of the numerical results presented here strongly depends on the validity of the assumptions made for the analysis. For the sake of simplicity, it has been assumed that the dislocation interaction energy varies linearly with distance, although it has been reported that the variation is parabolic [4]. Furthermore, the change in TEP signal has been attributed solely to the diffusion of carbon. However, as carbon segregates into dislocations, the TEP will gradually change as dislocation strain fields become relaxed due to carbon migration to sites where energy is minimised.

Nonetheless, the conclusion that can be reached remains the same: the duration of the interruption time is related to the process of carbon segregation to dislocation sites. Hence longer interruption time leads to increased carbon segregation, which increases the number of effective nucleation sites. By ‘concentrating’ the carbon atoms enables a more homogeneous dispersion of carbides, manifested by smaller size and spacing between carbides.

3.6 Tensile and compression testing

3.6.1 Tensile testing

The results for the tensile tests are shown in Figure 3.18 and detailed in Table 3.8. All conditions showed very little ductility and, on average, one out of three samples per condition failed before reaching the elastic limit. In the case of conditions L5 and L10, all three samples failed prematurely. Part of the premature failure might be due to poor surface finish of the tensile specimens. Nevertheless, a comparative

study can still be made between the conditions.

The general trend observed is that samples undergoing interrupted ageing show very little ductility. This is due to the fact that there will always be some carbon remaining within the dislocation cores that does not precipitate [62, 63]. This point will be further explored in Chapter 6 (Plasticity).

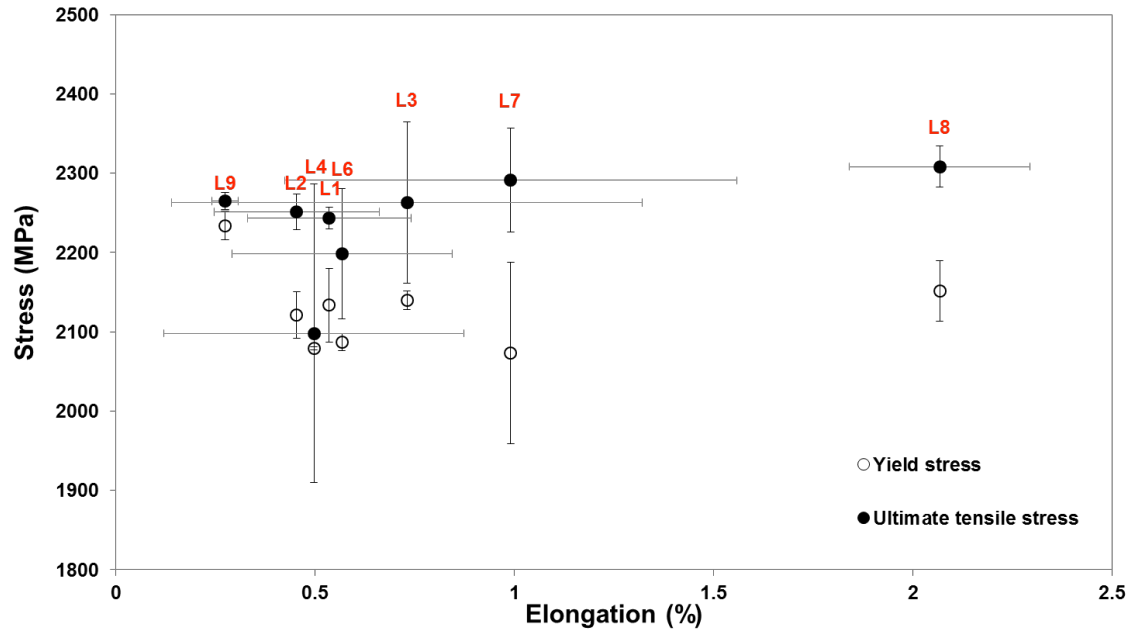


Figure 3.18: Summary plot of tensile properties.

Table 3.8: Summary of tensile properties. The heat treatment for each condition is given within brackets, in the form of ('austenitisation temperature ($^{\circ}\text{C}$)' - 'duration of IA (hours)' - 'tempering temperature ($^{\circ}\text{C}$)' - 'tempering time (s)').

Condition	σ_y (MPa)	σ_{UTS} (MPa)	Elongation (%)
L1 (880 - $\frac{1}{3}$ - 250 - 1800)	2134 ± 50	2244 ± 14	0.54 ± 0.2
L2 (880 - 3 - 250 - 1800)	2121 ± 30	2251 ± 20	0.45 ± 0.2
L3 (880 - 30 - 250 - 1800)	2140 ± 12	2263 ± 100	0.73 ± 0.6
L4 (880 - 30 - 250 - 300)	2079 ± 2	2098 ± 190	0.50 ± 0.4
L5 (880 - 30+ - x - x)	-	-	-
L6 (880 - x - 250 - 1800)	2087 ± 11	2073 ± 80	0.57 ± 0.3
L7 (880 - x - 250 - 5400)	2073 ± 110	2291 ± 70	0.99 ± 0.6
L8 (880 - x - 300 - 1800)	2151 ± 40	2308 ± 30	2.07 ± 0.2
L9 (880 - 30 - 300 - 1800)	2234 ± 20	2265 ± 11	0.27 ± 0.03
L10 (1000 - x - 250 - 1800)	-	-	-
L11 (1000 - x - 300 - 1800)	2070 ± 42	2120 ± 195	0.54 ± 0.45

3.6.2 Compression testing

Further to the tensile tests, conditions L3, L5 and L8 were tested under compression. The yield stress obtained has been compared with the tensile properties, Table 3.9. In comparing the σ_y values for conditions L3 and L8, the results are inconclusive, as they are within experimental error. Although the hardness properties show a marked difference between the two conditions (Figure 3.7), there is no appreciable difference in the yield stress.

Table 3.9: Comparison of compression and tensile results.

Condition	Compression σ_y (MPa)	Tensile σ_y (MPa)
L3	2467 ± 80	2140 ± 16
L5	3047 ± 12	-
L8	2390 ± 17	2151 ± 60

The linear relationship between Vickers hardness and yield stress initially proposed by Tabor [64], and then confirmed by Hutchinson *et al.* [65] with a proportionality constant of 3, is not evident in this case (Figure 3.19).

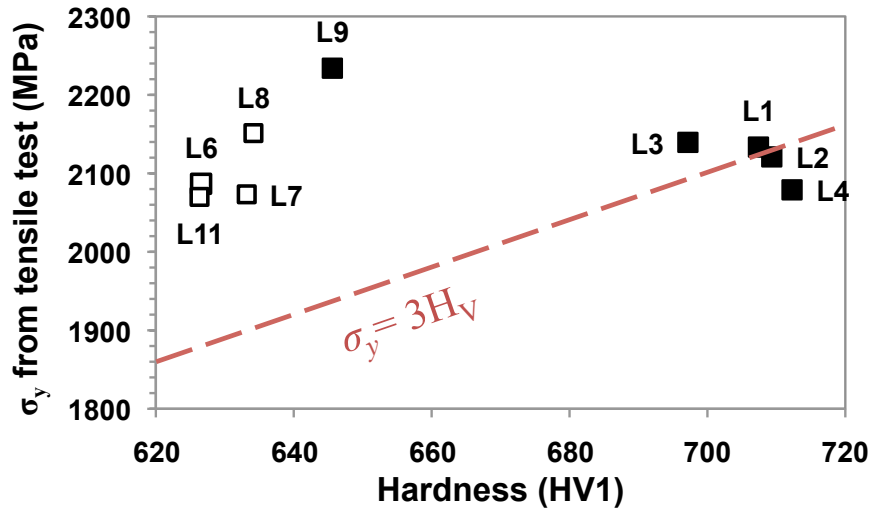


Figure 3.19: Plot of σ_y vs. Vickers hardness.

What becomes evident is that in tempered martensitic steels different terms contribute to the yield stress, such as precipitate hardening and carbon in solid solution, as well as the initial dislocation density in the material. A quantification of the influence of the different contributions is presented in Chapter 6.

3.7 Conclusion

The effect of interrupted ageing in a mid-carbon commercial steel was studied. It was found that interruption increases hardness by $\sim 10\%$, and stabilises properties. Microstructural characterisation by TEM shows that a finer precipitation distribution is obtained through interrupted ageing.

From the systematic microstructural analysis using the Kolmogorov-Smirnov analysis, some important conclusions can be drawn:

- 30 days of IA leads to a finer microstructure, both in precipitate size and spacing.
- After 30 days of IA, the duration of the subsequent tempering stage does not influence precipitation; while increasing the tempering temperature, decreases carbide size.
- In direct tempering, longer tempering time decreases carbide size and increases spacing; whereas increasing the tempering temperature, decreases carbide size.

With the aid of TEP measurements, and invoking the Kalish-Cohen model, it is understood that for freshly quenched martensite the interruption at room temperature allows carbon migration towards dislocation cores. Such uniform redistribution is consistent with the formation of nuclei, where the spacing between precipitates is reduced with interruption time. Therefore by introducing interrupted ageing into the heat treatment, effective and efficient carbon distribution takes place, reflected on the microstructure and properties. Although there is a limit on the scaling-up due to component size and quenching rates required, this may be exploited in applications where dimensional stability and constant hardness are required throughout component life.

Chapter 4

Modelling θ nucleation: the Fe-C-Si model alloy system

This chapter looks at the effect of silicon in cementite nucleation during martensite tempering. The literature review presented in Chapter 2 showed that there is still some controversy around the nucleation and growth stages in cementite precipitation, especially under the influence of silicon. Aiming to further understand the cementite nucleation process, a model based on the classical nucleation theory (CNT) is presented. To account for the effect of silicon, paraequilibrium conditions have been set for cementite nucleation. The driving force for nucleation was evaluated from the chemical and misfit energy terms.

4.1 The Fe-C-Si model alloy system

Preliminary studies were carried out on a Fe-C-Si ternary alloy system in order to observe carbide transition under the influence of silicon. The measured chemical composition of the steel is shown in Table 4.1.

Table 4.1: Measured chemical composition of model alloy (Fe to balance).

	C	Si	Mn	Cr	Mo	V	Ti	S	P	Ni
wt.%	0.57	1.97	0.002	0.005	0.005	0.000	0.002	0.009	0.006	0.000

The model alloy was cast using an Arc Melter AM (Edmund Buhler GmbH). A laboratory cast of 65 g was produced, which was then homogenised at 1200 °C for 48 hours in vacuum and then furnace cooled to room temperature. Figure 4.1 shows an image taken by optical microscopy of the as-received state, etched using 2% nital. Notable features include the pearlite microstructure, some ferrite shown in a lighter shade near prior austenite grain boundaries, and circular dark regions most probably owing to impurities or porosity. Prior austenite grain boundaries were also visible, and the PAG size was $\sim 300\text{ }\mu\text{m}$ of the initial microstructure.

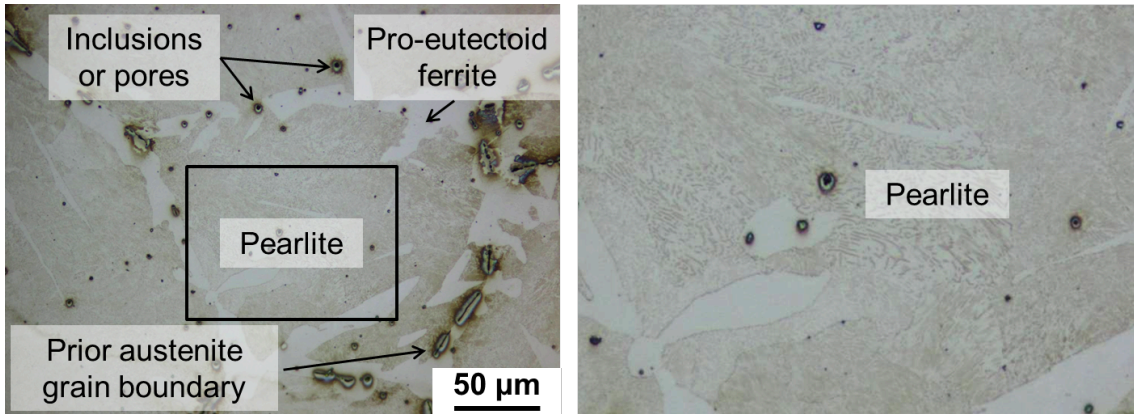


Figure 4.1: Optical micrograph of the initial microstructure of the as-cast material following homogenisation treatment, where the image on the right is a magnified view of the marked pearlite microstructure on the right.

Table 4.2: Heat treatment for the model alloy.

Condition	T_{γ} (°C)	t_{γ} (s)	T_{temp} (°C)	t_{temp} (s)
250 °C	880	180	250	1800
300 °C	880	180	300	1800
350 °C	880	180	350	1800
400 °C	880	180	400	1800

The conditioning of the specimens was carried out using an Adamel Lhomargy DT1000 dilatometer. The list of heat treatments is summarised in Table 4.2. These were in the shape of cylindrical rods of 3 mm diameter and 12 mm length. Quenching was done using a helium flux, potentially achieving cooling rates of about 300-500 °C per second, although a close inspection of the dilatometry curve in the previous chapter showed an actual quenching rate of ~ 75 °C/s.

During the heat treatment, the critical transformation temperatures Ac_1 , Ac_3 and M_s were recorded, and are summarised in Table 4.3.

Table 4.3: Summary of critical temperatures.

Condition	Ac_1 (°C)	Ac_3 (°C)	M_s (°C)
250 °C	810	853	280
300 °C	814	855	275
350 °C	815	851	276
400 °C	814	850	269
Average	813	852	275
Standard deviation	2	2	4

Given that Ac_3 is below the austenitisation temperature, the austenitisation condition chosen for this steel (880 °C) ensures complete austenitisation. Furthermore, from the dilatometry curves, some unexpected slope changes were detected, Figure 4.2.

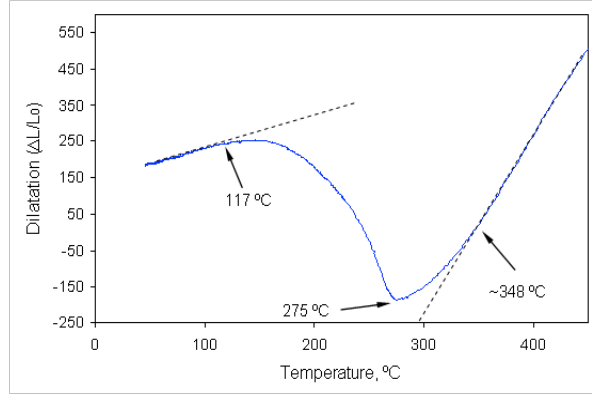


Figure 4.2: Segment of the dilatometry curve, where the martensitic transformation has been highlighted.

The strongest signal detected at 275 $^{\circ}\text{C}$ has been taken as the martensitic start temperature. However, in some conditions an early slope change was detected. In Figure 4.2, this was seen near 348 $^{\circ}\text{C}$. This early detection of the M_s has been reported in the literature for steels containing Cr. The observed splitting phenomenon was associated with an incomplete dissolution of secondary phases [66]. This is unlikely to be the case in the model alloy as the only alloying elements are silicon and carbon.

Another possible cause is the inhomogeneous distribution of carbon. Given that the M_s temperature strongly depends on the carbon content, the local concentration of carbon may cause fluctuations in the M_s . Andrews [67] derived an empirical expression for determining the M_s (in $^{\circ}\text{C}$) based on the chemical composition of the alloys (in wt.%):

$$M_s = 539 - 423C - 30.4Mn - 17.7Ni - 12.1Cr - 7.5Mo \quad (4.1)$$

The change in signal observed near 117 $^{\circ}\text{C}$ is likely to correspond to the end of the martensitic transformation, M_f .

4.1.1 Mechanical properties

Vickers hardness tests were carried out on dilatometry specimens, as they provide fast and relatively accurate results for the mechanical properties of the samples. The measurements were carried out using an LH Vickers Hardness Tester with a 5 kg load, and an indentation dwelling time of 10 s. The reported value for each condition is an average obtained from 5 readings, as shown in Figure 4.3 (a). Furthermore, compression tests were also carried out using a MicroTest model at room temperature, where the strain rate used was $7 \times 10^{-4} \text{ s}^{-1}$, Figure 4.3 (b). The compressive yield stress, $\sigma(y)$, was recorded, as well as the maximum engineering stress before rupture, $\sigma(e, \max)$, and the corresponding strain values, $\varepsilon(e)$ at $\sigma(e, \max)$, were also recorded. Strictly speaking, the last two values do not represent a true property of the material. However, they have been reported for comparative purposes between the four conditions.

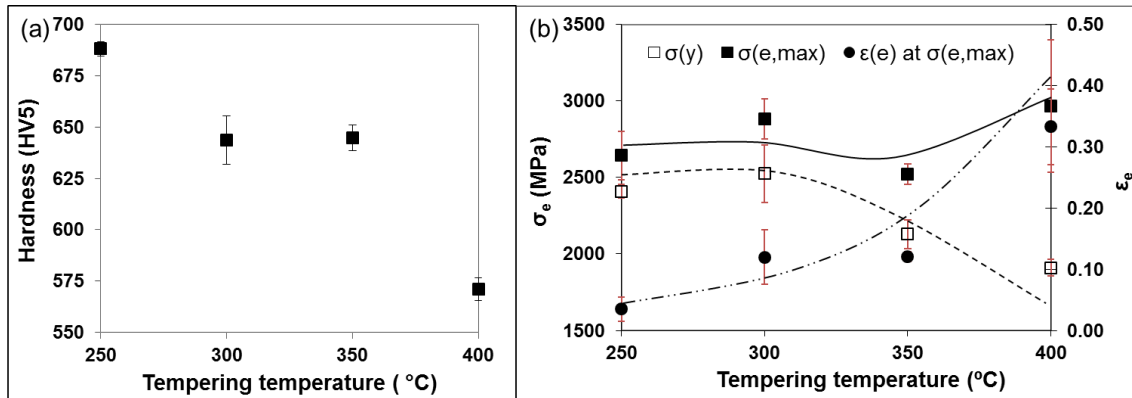


Figure 4.3: (a) Hardness values and (b) summary from compression testing for the model alloy.

In both tests, the yield strength was seen to decrease with increasing tempering temperature. In the case of hardness, a dramatic decrease is seen between 350 and 400 °C, whereas during compression testing, the softening transition was seen to occur near 350 °C. The properties are further elucidated in light of microstructural analysis.

4.1.2 Microstructural analysis

Representative micrographs for all conditions are shown in Figure 4.4. The same microstructural analysis of the intralath carbides has been followed as in Chapter 3, where over 250 particles have been analysed, coming from 3-4 TEM frames, under the same magnification ($\times 52k$). The principal features are summarised in Table 4.4.

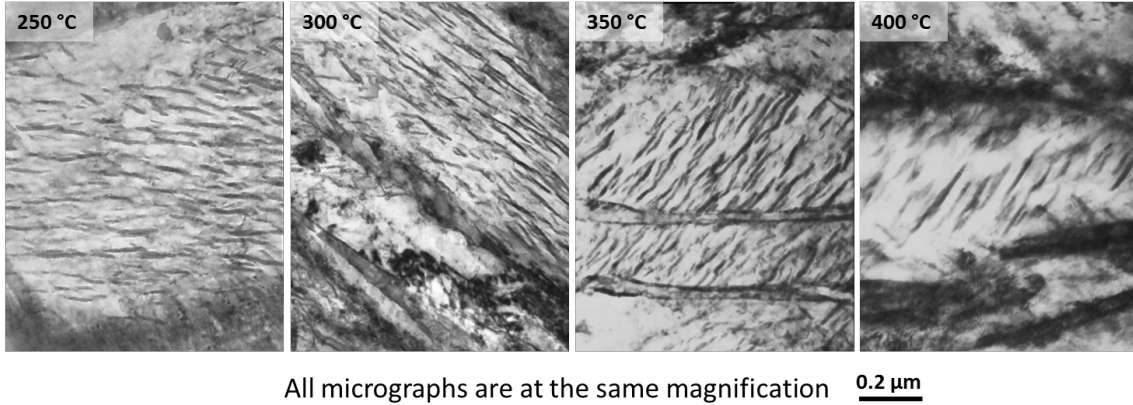


Figure 4.4: Representative bright field TEM micrographs for each condition, where intralath carbides are shown.

Table 4.4: Summary of the microstructural analysis.

Condition	Aspect ratio	r_{equiv} (nm)	Spacing (nm)
250 °C	7.9	10.4	37.3
300 °C	7.4	10.7	37.3
350 °C	7.0	11.1	40.8
400 °C	7.2	11.7	50.3

Notice that through tempering, the size of intralath carbides does not change significantly. This will be considered in Chapter 5, where silicon is shown to have a pronounced effect on the growth kinetics of cementite. One thing to notice is that the spacing between intralath carbides increases, while the size remains relatively constant with increasing temperature. This implies a decrease in the volume fraction

of intralath carbides. During microstructural analysis, only the intralath carbides were characterised. It is hypothesised that at increasing tempering temperatures, there are other favourable nucleation sites in competition, such as lath and other subgrain boundaries. The decreasing volume fraction of intralath carbides is consistent with the drop in hardness and strength observed in Figure 4.3.

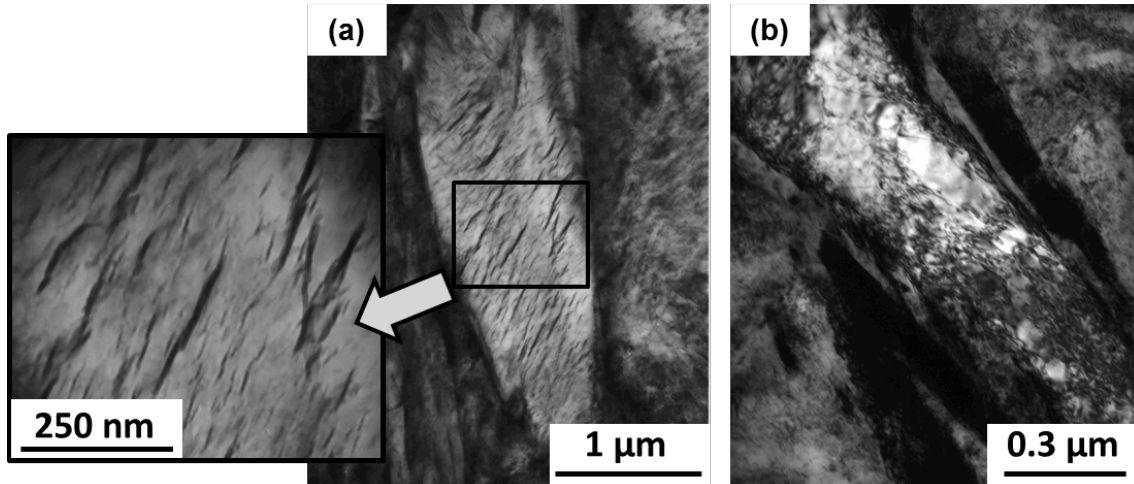


Figure 4.5: Representative bright field images for the 250 °C condition, showing (a) intralath carbides within the lath, where the inset shows a higher resolution image of the corresponding carbides, and (b) considerably high dislocation density within the lath unit.

Other noticeable features observed on the TEM are presented in Figure 4.5, where a high dislocation density can be seen within a single martensitic lath. Figure 4.6 shows the diffraction patterns taken from representative areas. One observation is the confirmation of the presence of ε -carbide after tempering at 300 °C, where the reported Jack orientation relationship (OR) between the carbide and the matrix has been observed (Table 2.4). Furthermore, cementite was also observed near twinned regions for the 250 °C condition, where the Bagaryatski OR exists. Therefore it becomes evident that although the $\varepsilon \rightarrow \theta$ transition occurs throughout tempering, there are circumstances under which cementite nucleates independent of ε .

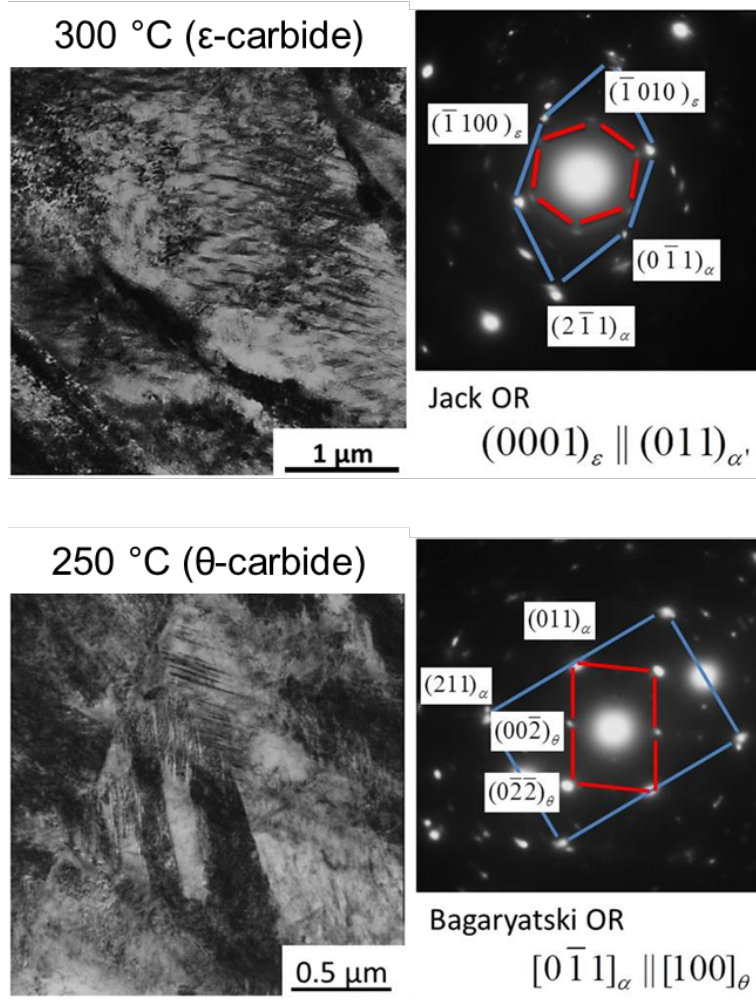


Figure 4.6: The presence of ϵ obeying Jack OR at 300 °C was confirmed using diffraction pattern analysis, and cementite satisfying Bagaryatski OR was seen to be present after tempering 1800 s at 250 °C.

Retained austenite was not detected during TEM work. In order to obtain a more representative analysis of the bulk material, X-ray diffraction was carried out.

4.1.3 X-ray diffraction

A Phillips X'Pert PW3020 model equipped with a copper radiation source ($\lambda \approx 1.540598 \text{ \AA}$) was used. Scans were taken from 35 to 105° 2θ , using a step size of 0.035° and a dwell time of 15 s. Note that in order to distinguish the cementite carbide from the Bragg angle, θ is used for the former, while ϑ is used for the latter.

Diffraction analysis and Rietveld refinement were carried out using HighScore Plus software.

Dilatometry samples were used for X-ray analysis. Cylinders of 3 mm diameter were sliced into several discs. The surface of the samples was polished to a colloidal silica finish (5 minutes), in order to relieve the residual stresses from the surface during sample preparation. The 3 mm discs were then stuck to the surface of a silicon sample holder, which has no background noise, so that the reflection from the sample holder does not interfere with the diffraction pattern from the specimens. The scans for conditions 250 and 400 °C have been plotted together, for easier comparison, Figure 4.7.

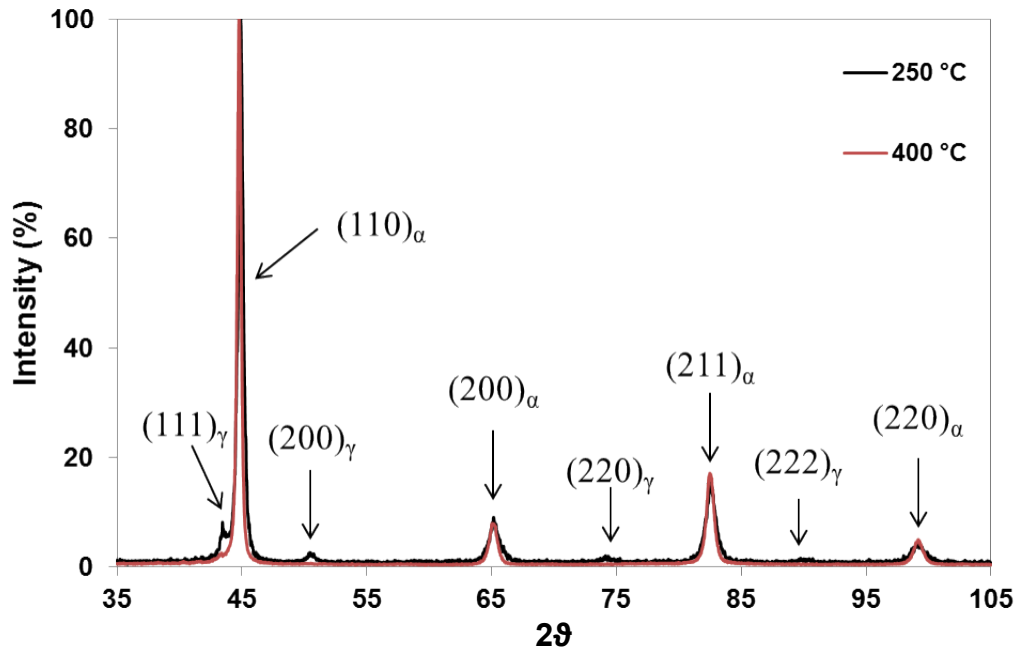


Figure 4.7: Diffraction patterns for conditions 250 and 400 °C.

A clear difference between the two conditions is that at 400 °C the retained austenite peaks no longer become visible. Furthermore, slight sharpening of the ferrite peaks also occurs at 400 °C, which is attributed to the decrease in the dislocation density during martensite recovery at higher temperatures. The method of quantifying dislocation density by XRD methods will be discussed in Chapter 5.

Rietveld refinement was carried out with two phases present: γ -austenite ($\text{Fm}\bar{3}\text{m}$) and α -ferrite ($\text{Im}\bar{3}\text{m}$). For the 250 °C condition, some tetragonality was observed, refinement was carried out with phase α' -martensite ($\text{I4}/\text{mmm}$) instead of $\text{Im}\bar{3}\text{m}$, to account for the tetragonality of the matrix phase. The lattice parameters for condition 250 °C were determined to be $a= 0.2862$ and $c= 0.2876$ nm, giving a tetragonality of 1.005. The measured volume fraction of retained austenite is summarised in Table 4.5.

Table 4.5: Retained austenite volume fraction during tempering.

Condition	Volume fraction of γ_R (%) $\ddagger$
250 °C	6.8
300 °C	5.5
350 °C	4.3
400 °C	-

$\ddagger$ The values obtained are after refining to a goodness of fit $\left(\text{GOF} = \frac{R_{\text{wp}}}{R_{\text{exp}}}\right) < 2\%$.

4.2 Modelling cementite nucleation using the classical nucleation theory

In order to model cementite nucleation, the classical nucleation theory is considered. Typically in the case of homogeneous nucleation, the overall Gibbs free energy change per nucleus, ΔG , is defined as:

$$\Delta G = -V(\Delta G_V - \Delta G_S) + A\gamma, \quad (4.2)$$

where G_V , G_S and γ are the chemical, strain and interfacial energy terms for the newly forming nucleus of volume V and area A .

Differentiating Equation (4.2), an expression for the activation energy barrier for

the nucleation process (ΔG^*) can be obtained.

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_V - \Delta G_S)^2}, \quad (4.3)$$

From Equation (4.3), it appears that maximising the denominator would minimise the activation energy barrier. The denominator evaluates the quantity by which the chemical driving force, ΔG_V , is reduced by the counteracting strain energy, ΔG_S , term. The effective driving force for nucleation is therefore given by $(\Delta G_V - \Delta G_S)$ [68]. In other words, nucleation may theoretically occur when $\Delta G_V > \Delta G_S$, but will most likely require $\Delta G_V - \Delta G_S \gg 0$.

The process of nucleation is very sensitive to the value of γ . Perez and Deschamps [30] reported the interfacial energy of ε and θ for the nucleation process based on the Becker-Döring theory: $\gamma(\alpha'/\varepsilon) = 0.147 \text{ J m}^{-2}$ and $\gamma(\alpha'/\theta) = 0.174 \text{ J m}^{-2}$. Nevertheless if one were to consider that the $\varepsilon \rightarrow \theta$ transition is a two-step process, where the intralath cementite nucleates at the α'/ε boundary [25], in order to successfully model the interfacial energy there are three interfaces to be considered: α'/ε , ε/θ and α'/θ , Figure 4.8.

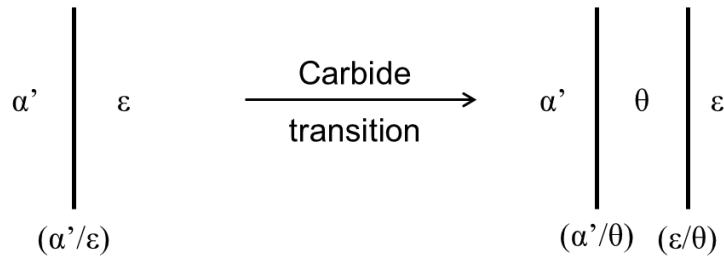


Figure 4.8: Representation of the three interfaces involved during the $\varepsilon \rightarrow \theta$ transition.

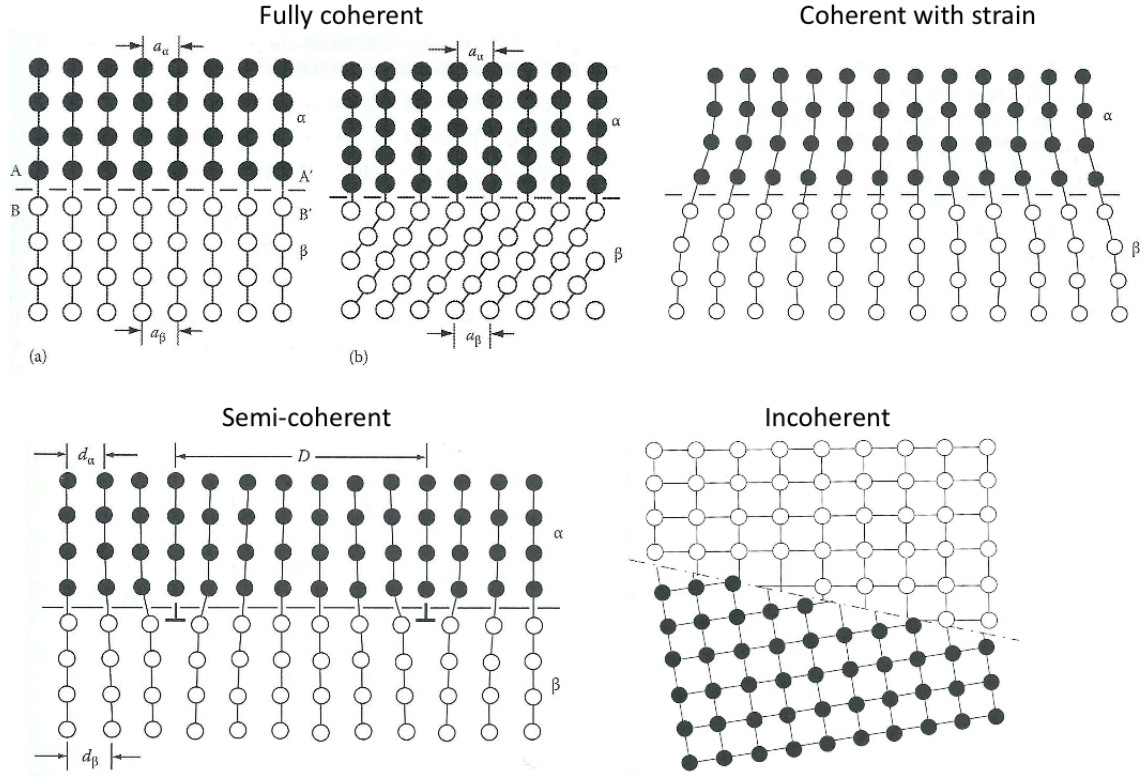


Figure 4.9: Four different types of interfaces presented depending on the degree of coherency: fully coherent, coherent with strain, semicoherent and incoherent. After Porter, Easterling and Sherif [68].

The interface between two phases, α and β , can be of four types, depending on the degree of coherency, Figure 4.9. During early stages of nucleation, the coherency between the matrix and the precipitate phase is full, yielding a very low interfacial energy, γ between 1–200 mJ m^{-2} [68]. However as a precipitate grows, coherency is lost. Due to discontinuity in the lattice parameter across the interface, straining occurs. During continuous growth, there comes a point where it becomes more favourable to replace interfacial strain by the introduction of a dislocation. For semicoherent interfaces, the interfacial energy is in the range of 200–500 mJ m^{-2} [68], whereas for incoherent interfaces, the value of γ can go up to 1000 mJ m^{-2} [68].

By the time the carbide transition takes place, ε reaches a considerable size, as seen by TEM. Supposing that a semicoherent interface exists between the matrix

and ε prior to θ nucleation, then $\gamma(\alpha'/\varepsilon)_{\text{semicoherent}} > \gamma(\alpha'/\theta)_{\text{coherent}}$, as the nucleating cementite will be coherent with the matrix during such early stages. Thus during the ε to θ transition, the formation of the new interfaces given by the sum of $\gamma(\varepsilon/\theta)_{\text{coherent}}$ plus $\gamma(\alpha'/\theta)_{\text{coherent}}$ might counterbalance the annihilation of the existing interface $\gamma(\alpha'/\varepsilon)_{\text{semicoherent}}$.

Due to the absence of the necessary interfacial energy values, only the $(\Delta G_V - \Delta G_S)$ contribution for ΔG^* will be evaluated. The values for G_V and G_S are evaluated in sections 4.2.1 and 4.2.2 respectively.

4.2.1 Thermodynamics- ΔG_V

At the early stages of carbide precipitation during martensite tempering (generally temperatures below 350 °C), the diffusivity of most elements is substantially low. The only elements that will be able to diffuse significantly are interstitials such as carbon. Therefore paraequilibrium conditions need to be considered.

Consider the process of nucleation of cementite (θ) occurring in ferrite (α) under paraequilibrium conditions, in a ternary system Fe–C–Si. At the carbide/matrix interface, due to the relatively high mobility of carbon, the chemical potential of carbon, μ_C , will have equilibrated in a short time, i.e. $\mu_C^\alpha = \mu_C^\theta$. On the other hand, iron and silicon would have different chemical potentials [69], i.e. $\mu_{\text{Fe}}^\alpha \neq \mu_{\text{Fe}}^\theta$ and $\mu_{\text{Si}}^\alpha \neq \mu_{\text{Si}}^\theta$. At this stage, given the restricted diffusivities of Fe and Si, X is used to collectively refer to Fe and Si. This state of ‘constrained’ equilibrium is defined as paraequilibrium.

The driving force for nucleation, ΔG^N of paraequilibrium cementite is given by [32]:

$$\Delta G^N = (\mu_X^\theta - \mu_X^\alpha)x_X^\theta + (\mu_C^\theta - \mu_C^\alpha)x_C^\theta \quad (4.4)$$

where x_i^ϕ is the mole fraction of element $i = \text{C, X}$, within phase ϕ , where $\phi = \alpha, \theta$. Furthermore, since paraequilibrium cementite inherits the matrix composition, the

concentration of the elements will be the same across the interface, thus the u -fraction is considered, which is defined as [69]:

$$u_i = \frac{x_i}{\sum x_X}, \quad (4.5)$$

where x_i is the mole fraction of element i , and $\sum x_X$ is the sum taken for Fe and the other substitutional elements. In order to achieve paraequilibrium conditions at the interface, the product of chemical potential μ_X and u_X must be the same in both phases.

Having defined the alloy system and conditions, the u -fraction was determined in order to calculate the paraequilibrium driving force. The TCFE6 (v 6.2) database [70] was used in ThermoCalc to obtain the ΔG^N term. Once obtained, the volume Gibbs free energy can be determined by:

$$\Delta G_V = \frac{\Delta G^N}{V_{m,\theta}}, \quad (4.6)$$

where ΔG^N is the chemical Gibbs free energy obtained from ThermoCalc expressed in J mol^{-1} , and $V_{m,\theta}$ is the molar volume of cementite, which will be determined in section 4.2.2. The values obtained for ΔG^N are shown in Figure 4.10. Both paraequilibrium and full equilibrium conditions have been computed.

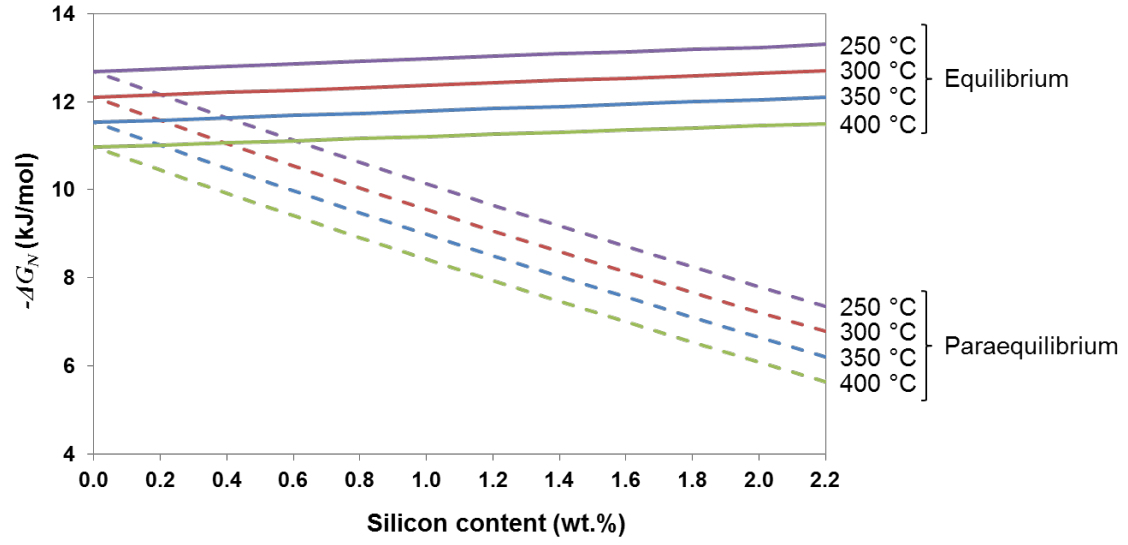


Figure 4.10: Driving force for nucleation obtained using ThermoCalc for cementite nucleation under both para and full equilibrium conditions for a Fe-0.55C-(0-2.2)Si wt.% ternary system.

Table 4.6: Computed equilibrium composition (in mass fraction) of cementite for Fe-0.55C-2.0Si wt.% system, where silicon is seen to have negligible solubility in cementite.

Temperature	Fe	C	Si
250 °C	9.33×10^{-1}	6.69×10^{-2}	~ 0

Table 4.6 summarises the chemical composition for cementite under equilibrium conditions for the Fe-0.55C-2.0Si wt.% alloy. It can be seen that under equilibrium conditions in ThermoCalc, silicon has negligible solubility in cementite.

The driving force for cementite nucleation under paraequilibrium conditions is lower than for full equilibrium. These values are comparable with those reported by Kozeschnik and Bhadhesia [33] and Ghosh and Olson [32, 71].

4.2.2 Misfit strain- ΔG_S

The second aspect to consider in determining the effective driving force is the ΔG_S term. The elastic strain energy stored in the matrix surrounding an inclusion is approximated by [72]:

$$\Delta G_S = 6\mu\delta^2 \cdot E\left(\frac{H}{D}\right), \quad (4.7)$$

where μ is the matrix shear modulus, δ is the volumetric misfit and the term within brackets indicate functional dependence of E with $\frac{H}{D}$, accounts for the shape factor of the inclusion, where D is the equatorial diameter and H is the polar diameter of the inclusion. The volumetric misfit is a function of the lattice parameters:

$$\delta = \frac{1}{3} \left(\frac{V_1 - V_2}{V_2} \right), \quad (4.8)$$

where V_i refers to the atomic volumes for phases $i=1$ and 2 . The atomic volume of a phase is given by:

$$V_{\text{atomic}} = \frac{V_{\text{unit cell}}}{n}, \quad (4.9)$$

where $V_{\text{unit cell}}$ is given by the product of lattice parameters $a \times b \times c$, and n is the number of atoms sitting within the defined unit cell.

The presence of silicon leads to contraction in the Fe-lattice, owing to its small size. In order to incorporate the effect of silicon during nucleation, one must consider the variation in the matrix properties, as this will have an impact on the δ misfit value. One method of estimating the lattice parameters of ferrite based on chemical composition is by empirical formulae, such as the one shown below, where the elements

within the brackets refer to the alloying element content in atomic percent [73]:

$$a_{\alpha,0} = 0.28664 + 0.00006(\text{Mn}) - 0.00003(\text{Si}) - 0.00005(\text{Cr}), \quad (4.10)$$

The lattice parameter for Fe-0.55C-2.0Si wt.% was determined to be 0.2826 nm using XRD methods. This is used as a benchmark. From Equation (4.10), the presence of silicon leads to a contraction of -0.00003 per 1 at.% silicon, therefore the lattice parameter, $a_{\alpha,0}$, as a function of silicon content can be determined. Furthermore, since carbide precipitation occurs at temperatures above ambient, temperature dependency of the shear modulus and the lattice parameters should be considered. Those will be explored next.

Shear modulus

The temperature dependency of the shear modulus has been extracted from a similar alloy in literature (Fe-0.4C-0.14Si-0.86Mn wt.%) [74]. The values are listed in Table 4.7.

Table 4.7: Matrix shear modulus variation as a function of temperature [74].

T (°C)	25	250	300	350	400
μ (GPa)	81	75	73	71	68.5

These values are to be substituted into Equation (4.7) in order to obtain more accurately the strain energy during actual tempering conditions.

Lattice parameters

The $a_{\alpha,0}$ values need further readjustments in order to incorporate the effect of temperature. The effect of temperature on the lattice parameter should be incorporated

in the following manner [75]:

$$a_{\alpha} = a_{\alpha,0}[1 + \beta(T - 800 \text{ K})], \quad (4.11)$$

where β is the linear expansion coefficient and T is the absolute temperature. The value of β was reported to be $17.5 \times 10^{-6} \text{ K}^{-1}$ for ferrite containing up to 0.6 wt.% carbon [75] (NB. although these reported values were determined for a temperature range between 800 and 1200 K (527 and 927 °C), where 800 K was used as the reference temperature, they will still be used given the similar carbon contents in the matrix).

Furthermore, at the early stages of tempering, the tetragonality of the matrix phase also needs to be considered. The lattice parameters obtained by XRD showed that at 250 °C the tetragonality of the matrix was 1.005, while at higher temperatures, no sign of tetragonality was observed. The tetragonality has also been considered when computing the atomic volume of the matrix phase.

The tetragonality in the as-quenched state can be estimated by [76]:

$$c/a = 1 + 0.045x_w, \quad (4.12)$$

where x_w is the mass % of carbon. Thus, the expected tetragonality in the as-quenched state is calculated to be 1.025. There might be some confusion as to which tetragonality value for the matrix should be used for estimating the lattice parameters of the matrix phase. However, it is assumed that cementite forms after ε -carbide, by which time, considerable reduction of matrix tetragonality would have already occurred due to the precipitation of ε [77].

Carbides

The lattice parameters for the carbide phases were obtained from literature: $a = 0.2752$ and $c = 0.4353 \text{ nm}$ for ε -carbide and $a = 0.4516$, $b = 0.5077$ and $c = 0.6727$

nm for θ -carbide [78], giving an atomic volume of 0.0101 and 0.0096 nm³ respectively. Using these parameters, the molar volume of cementite term from Equation (4.6), $V_{m,\theta}$, was determined to be 5.86×10^{-6} m³ mol⁻¹. Although strictly speaking the lattice parameters of the carbide phases would also change due to thermal expansion, a constant value has been used for their atomic volume.

Table 4.8: The misfit between the different phases in Fe-0.55C-2.0 wt.% at 250 °C.

Interface	α'/ε	α'/θ	ε/θ
δ	4.52×10^{-2}	6.32×10^{-2}	2.2×10^{-2}

The estimated misfit δ values at 250 °C for the different interfaces are summarised in Table 4.8. Closer inspection of these values shows that $\delta(\alpha'/\theta) \approx \delta(\alpha'/\varepsilon) + \delta(\varepsilon/\theta)$, as represented in Figure 4.11. This could be a way of understanding the role of a metastable phase, as the transitional phase offers an intermediate misfit energy path. This is consistent with Nam's postulate, that the nucleation of cementite has been suggested to take place at the matrix-epsilon interface [25].

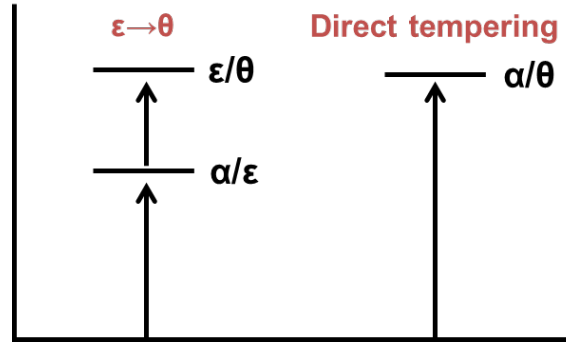


Figure 4.11: The presence of the metastable ε phase offers an intermediate misfit energy path during cementite precipitation.

4.2.3 Computing the effective driving force ($\Delta G_V - \Delta G_S$)

Now that ΔG_V and ΔG_S have been determined, the effective driving force can be computed, as shown in Figure 4.12 for θ -nucleation. It should be noted that

for nucleation to take place, the chemical driving force should be higher than the opposing strain term, i.e. for nucleation to be favourable, the effective driving force $(\Delta G_V - \Delta G_S) > 0$. The x -axis, shown in red in Figure 4.12, corresponds to $(\Delta G_V - \Delta G_S) = 0$. Therefore the horizontal axis can be used as a criterion to decide whether nucleation is favourable or not. With the incorporation of ΔG_S , the total driving force for nucleation is reduced. The contribution from each individual energy term is shown in Figure 4.13.

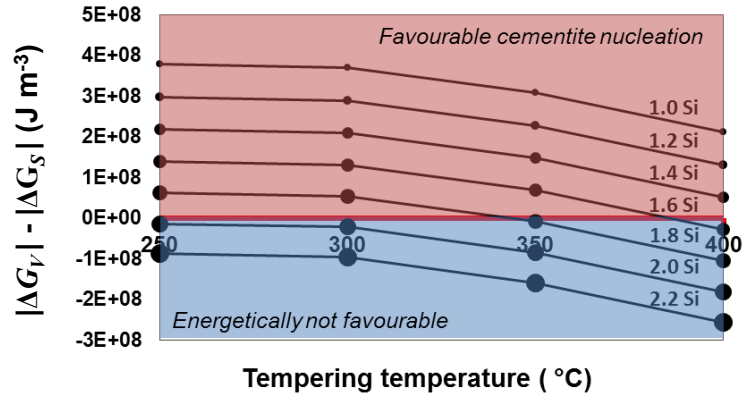


Figure 4.12: Driving force for cementite nucleation, ΔG^N under paraequilibrium conditions.

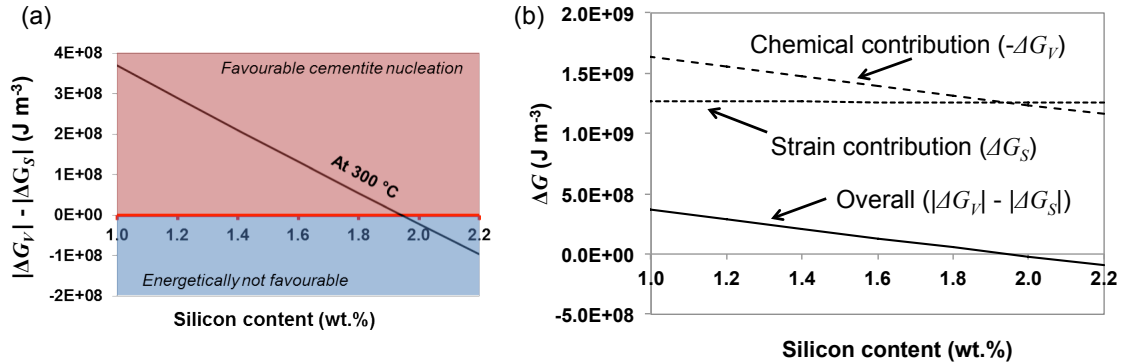


Figure 4.13: (a) Driving force for cementite nucleation as a function of Si content at 300 °C, and (b) contribution from each of the energy terms.

For instance, at 300 °C (Figure 4.13 (a)), it appears that when the silicon content is above ~ 1.95 wt.%, cementite nucleation is not favoured. This is consistent with the

diffraction pattern work in Figure 4.6, where ε -carbide was seen present at 300 °C.

One aspect to notice is that, in the presence of crystal defects, an extra energy term needs to be considered. Thus, Equation (4.2) becomes:

$$\Delta G = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d, \quad (4.13)$$

where the ΔG_d term accounts for the reduction in the nucleation energy barrier owing to the presence of crystal defects in the material.

The incorporation of the ΔG_d term will further reduce the overall ΔG^* value in Equation (4.3), facilitating the nucleation event by reducing the activation barrier. This will favour the nucleation of θ in higher silicon contents. This is observed in Figure 4.6, where cementite was seen present near twin regions at 250 °C. Furthermore, this agrees with results presented by Andrews [31], where it was demonstrated the formation of cementite at 250 °C is possible, as cementite nucleation is strongly related to twin density [79].

In order to refine the model, precise lattice parameters of the carbide phases need to be determined.

4.3 Characterising carbides using high energy synchrotron radiation

Given the limited resolution of laboratory X-ray diffractometers, trial runs were made using a high energy source on the I11 beamline (high resolution powder diffraction) [80] of Diamond Light Source (Didcot, UK). The sample, needle in shape, was spun and measured under transmission mode. A 15 keV beam was used ($\lambda \approx 0.817157$ Å) for the trial tests. The conditions that were analysed *ex situ* were 250 and 400 °C after tempering for 1800 s. The dilatometry samples were manually round until they were 0.8 mm diameter and 6 mm length.

Trial runs were made using both high resolution MAC detectors and the time-resolved position sensitive detector (PSD) [81], where room temperature measurements were taken. Out of the two detectors, the latter gave a better signal-to-noise ratio. The diffraction peaks obtained using the PSD detector are shown in Figure 4.14.

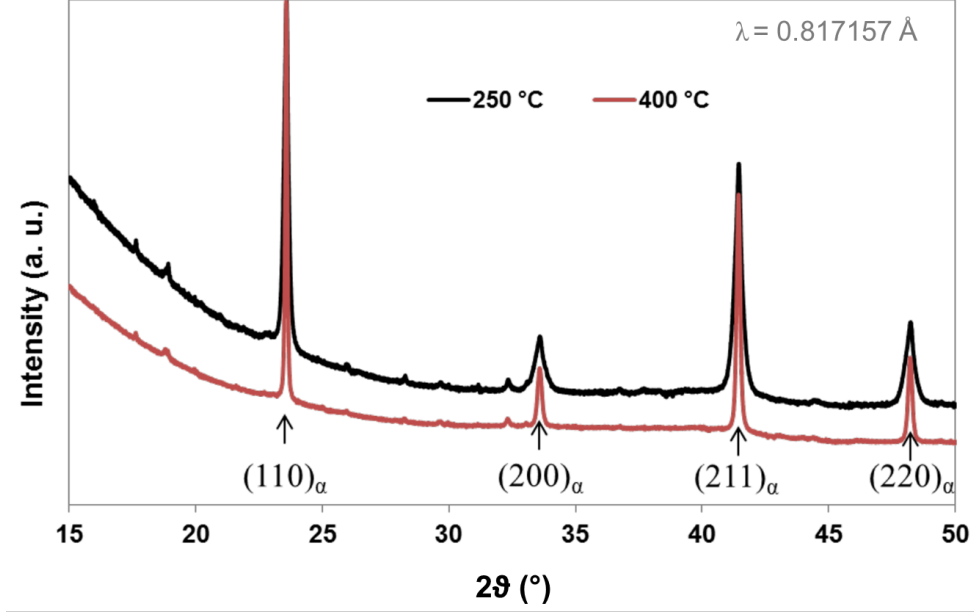


Figure 4.14: Diffraction peaks for conditions 250 and 400 °C using an exposure time of 120 s with the PSD detectors.

In order to account for the straining on the sample surface during sample preparation, the peak positions were analysed. The ferrite peaks can be used as a benchmark in order to estimate the peak shift that occurred due to sample straining. Bragg's equation (4.14) can be used in order to determine the d_{hkl} -spacing of a peak of index (hkl) , taking $n=1$ and given that λ and ϑ are known:

$$n\lambda = 2d_{hkl}\sin\vartheta, \quad (4.14)$$

For cubic structures, the d_{hkl} -spacing and the lattice parameter a have the following

relationship:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \quad (4.15)$$

For instance, taking the (110) reflection of the ferrite peak, $\lambda = 0.817157 \text{ \AA}$, and $2\vartheta = 23.588^\circ$, which by Equation (4.14), this corresponds to a d_{hkl} -spacing of $1.999 \text{ \AA}$. This value is slightly smaller than the one obtained from laboratory XRD measurements, where for $\lambda = 1.540598 \text{ \AA}$, and $2\vartheta = 44.880^\circ$, $d_{hkl} = 2.018 \text{ \AA}$, which would be equivalent to an angle of $2\vartheta = 23.360^\circ$ on the synchrotron results. The sample preparation for the latter case was done carefully to remove the residual stress built on the surface due to mechanical grinding. Therefore due to the straining of the material, in the $2\vartheta \sim 23^\circ$ region, the peaks from the synchrotron measurements will be shifted to slightly higher angles by $\sim 0.2^\circ$ to the right.

Whilst bearing this in mind, the region $27^\circ < 2\vartheta < 32^\circ$ is considered, as in this interval no ferrite and austenite peaks are present and so the peaks will occur only due to carbides. Three carbides have been considered from the Inorganic Crystal Structure Database (ICSD) [82]: ε -carbide (collection code 44354, source Nagakura [78]), η -carbide (collection code 87128, source Hirotsu and Nagakura [83]) and θ -carbide (collection code 99017, source Wood *et al.* [84]). The relevant carbide peaks in the range $27^\circ < 2\vartheta < 32^\circ$ are summarised in Table 4.9, and their positions labelled in Figure 4.15.

The peaks were further matched against possible forms iron oxides from the ICSD database (e.g. collection codes 26410, 15840, 35000). Within the $27^\circ < 2\vartheta < 32^\circ$ region, relatively strong oxide peaks should be observed at $2\vartheta \sim 31.9^\circ$, with additional peaks at $2\vartheta \sim 27.6^\circ$ and 29.3° . The absence of these oxide peaks shows that the peaks in Figure 4.15 are better indexed as carbide peaks.

Table 4.9: Carbide reflections in the range of $27^\circ < 2\vartheta < 32^\circ$, where only those peaks that are strong have been included ($> 10\%$ of the most intense peak, which are the $(111)_\varepsilon$, $(211)_\eta$ and $(031)_\theta$ peaks).

Carbide	Structure	Space group	hkl reflection	2ϑ	d_{hkl}	I
ε	h.c.p.	P6 ₃ 22	(112)	29.45 °	1.6074	16 %
η	orthorhombic	Pnnm	(211)	29.36 °	1.6125	100 %
η	orthorhombic	Pnnm	(220)	29.77 °	1.5905	47.5 %
θ	orthorhombic	Pnma	(230)	28.07 °	1.6848	11 %
θ	orthorhombic	Pnma	(301)	29.86 °	1.5857	17 %
θ	orthorhombic	Pnma	(222)	31.41 °	1.5095	11 %

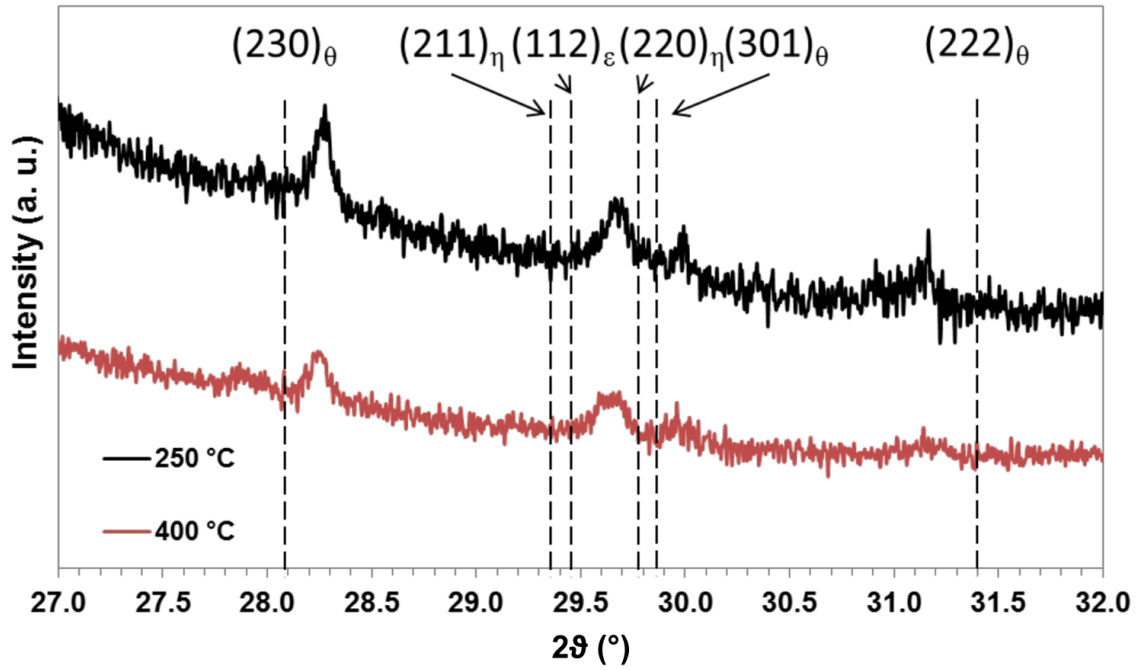


Figure 4.15: Carbides within the $27^\circ < 2\vartheta < 32^\circ$.

From Figure 4.15, most peaks can be indexed as either ε , η and θ carbides, although due to the inappropriate sample preparation, precise indexing is not possible. Nevertheless, this shows that the resolution of the synchrotron is potentially good enough for detecting carbides. This led to the planning of experiments involving *in situ* tempering of martensite on the I11 in order to observe carbide precipitation in alloys containing a range of silicon contents. This will be explored in Chapter 5.

4.4 Conclusion

Preliminary work was carried out on an Fe-0.55C-2.0Si wt.% model alloy, in order to become familiar with cementite precipitation in martensitic steels. Cementite nucleation was modelled within the classical nucleation theory framework, where it was observed that as silicon content increased, the driving force for cementite decreased. According to the theoretical result at 300 °C, a silicon content of 2.0 wt.% would not favour cementite nucleation, which was consistent with the electron diffraction work from TEM, where ε was seen to be stable at 300 °C. This could explain the peak in mechanical properties observed for the 300 °C condition during compression testing. On the other hand, it was also seen that cementite nucleation is favoured under the presence of defects, such as twins, at temperatures as low as 250 °C.

Furthermore, simulation of the misfit at the carbide/matrix interface, showed that the precipitation of ε before cementite lowered the misfit at the interface. This is a way of understanding the carbide precipitation sequence, as the preceding metastable phase offers an alternative path that reduces the misfit energy during nucleation.

Chapter 5

The effect of silicon on tempered martensite

Following the ternary model alloy system, this chapter further elaborates on the understanding of the effect of silicon during martensite tempering on more complex alloying systems. The studied compositions have been inspired from commercial alloys. *In situ* tempering was carried on the synchrotron, in order to study cementite growth under the influence of silicon. Furthermore, based on the broadening of the ferrite peaks, the dislocation density throughout tempering was measured. Combined with microstructural analysis, this experimental chapter provides a clearer picture of the microstructural transitions occurring during martensite tempering.

5.1 Alloys

Three alloys containing different silicon contents have been considered, the measured chemical compositions are listed in Table 5.1, as determined by supplier ASCOmetal. The notation used throughout is HS, MS and LS, for the high (2.3 wt.%), medium (1.7 wt.%) and low (1.4 wt.%) silicon contents, respectively.

Table 5.1: Measured chemical composition of alloys, in weight %, Fe to balance.

	C	Si	Mn	Cr	Mo	V	Ti	Ni	Cu	S	P
HS	0.56	2.30	0.69	0.89	0.02	0.10	0.03	0.20	0.15	0.02	0.01
MS	0.55	1.71	0.71	0.89	0.02	0.10	0.03	0.20	0.16	0.03	0.01
LS	0.55	1.43	0.72	0.91	0.02	0.10	0.03	0.21	0.16	0.02	0.01

These were casts made specifically for this study, where laboratory heats were manufactured as 20 kg ingots using a vacuum induction furnace. The ingots, of section 100×100 mm, were left to cool to room temperature. Approximately 2/10 and 1/10 of the total material was cut from the top and bottom of the ingot respectively, keeping the more homogeneous and sound material from the remaining 7/10. This was then homogenised at 1200 °C, and forged into a bar of 40 mm diameter. To reduce hardness and to ease cutting, the bars thus forged were slowly cooled in a furnace rather than in air.

Heat treatment and dilatometry

The heat treatment consisted in austenitising at 880 °C for 180 s, quenching and tempering. Two sets of heat treatments were carried out. The first set was heat treated in a DT1000 dilatometer, where quenching was done using helium flux. The samples were characterised using microscopy (both optical and electron), hardness and high energy X-rays using synchrotron radiation. Tempering was carried out at 250, 300, 350, 400 and 450 °C for 1800 s. The critical transformation temperatures determined by dilatometry are summarised in Table 5.2.

Table 5.2: Summary of critical temperatures obtained by dilatometry.

	A_{c1} °C	A_{c3} °C	M_s °C
HS	822 ± 2	857 ± 3	222 ± 10
MS	809 ± 1.5	843 ± 1.7	233 ± 6
LS	802 ± 1.8	838 ± 1.4	231 ± 8

Given that for all three alloys, the A_{c3} is below the austenitisation temperature, complete austenitisation is ensured prior quenching.

The second set of heat treatments were performed using laboratory furnaces. The samples were wrapped within a stainless steel foil, and quenching was carried out using ice brine. The samples for synchrotron use were left in the as-quenched form, whereas those used for lab-based X-ray diffraction were tempered as follows:

- 1800 s at 300 °C
- 3600 s at 300 °C
- 1800 s at 350 °C
- 3600 s at 350 °C
- 1800 s at 400 °C

5.2 Microstructure and properties

5.2.1 Hardness

Vickers hardness measurements were carried out using a microhardness machine (Wilson Wolpert model 401 MVA), with a 1 kg load, where average values from 5 measurements have been determined per condition. The as-received microstructure consisted of pearlite, with an initial hardness of 328 ± 3 , 327 ± 2 and 311 ± 4

HV1 for alloys HS, MS and LS, respectively. The hardness evolution throughout tempering is summarised in Figure 5.1.

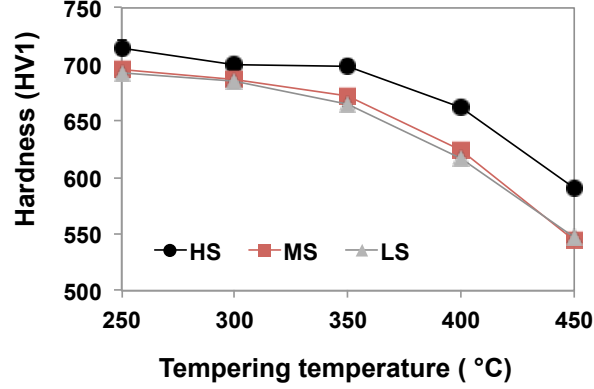


Figure 5.1: Average hardness properties (error bars within marker size).

It is observed that the hardness decreases with tempering temperature. However, there is a slight difference in the trend between the HS and the other two alloys. In the case of HS, the hardness remains relatively constant on tempering up to 350 °C. At 400 and 450 °C, there is a dramatic drop in HS hardness. On the other hand, in both MS and LS, the decrease in hardness occurs gradually from 250 °C. This observation is consistent with the reported cases in literature [23], where this delay in the softening transition has been attributed to the role of silicon in delaying the $\varepsilon \rightarrow \theta$ transition.

5.2.2 Optical and scanning electron microscopy

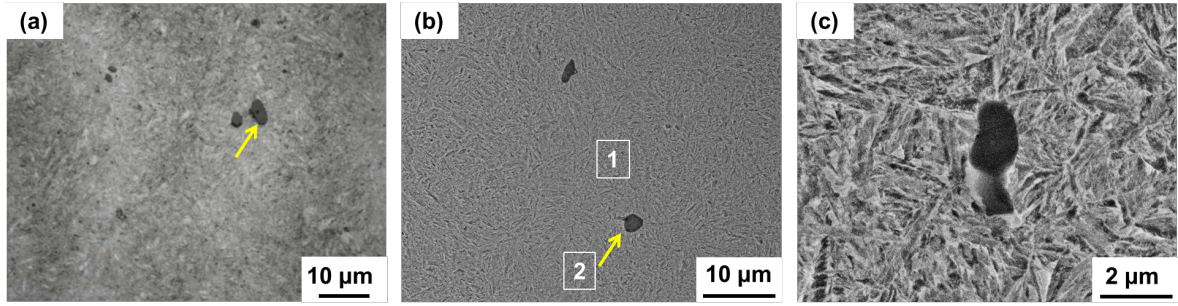


Figure 5.2: (a) Optical micrograph, (b) SEM micrograph, and (c) SEM micrograph with a magnified view of the inclusion, for HS tempered at 250 °C.

Given the complexity of the alloys, these were first characterised by optical microscopy and by SEM, using a MEB Hitachi S-4800 field emission gun operated at 15 keV. Under the optical microscope, several globular structures ranging from 1 to 5 µm in size were observed, as indicated by an arrow in Figure 5.2 (a). Further examination was performed under SEM. EDS scans were carried out on regions 1 and 2 marked on Figure 5.2 (b), where region 2 covers the area within the globular structure. The chemical composition is listed in Table 5.3. Values for carbon have been omitted, as precise carbon contents cannot be resolved using EDS. From the obtained information, the inclusions marked in Figure 5.2 correspond to manganese sulphide, MnS.

Table 5.3: Chemical composition of regions 1 and 2 (in wt.%, Fe to balance).

	Si	Cr	Mn	S
Region 1	2.5	1.1	0.7	trace
Region 2	trace	trace	44	24

The formation of MnS inclusions is unavoidable in industrial processing of steel. The presence of such non-metallic inclusions, are thought to act as the source of crack nucleation in fatigued components [85, 86]. Notice that the chemical composition

measured by EDS gives similar results as the actual chemical composition of the alloy.

5.2.3 Transmission electron microscopy

Figure 5.3 shows low magnification TEM images of the microstructures, highlighting the lath structures. In trying to determine the hypothetical role that individual laths play during work hardening in lath martensite, a similar microstructural analysis as the one carried out for intralath carbides was performed to measure lath width (note that although referred to as lath martensite, from TEM it was observed that the microstructure consisted of mixed lath and plate martensite). 25 measurements per condition were taken, from 2 TEM frames taken at $\times 21k$ magnification. The averages are represented in Figure 5.4.

Given that measurements were taken from random sections, stereological corrections have been applied. For a bainitic microstructure, Chang and Bhadeshia [54] derived the following:

$$\bar{L}_T = \frac{\pi}{2}t, \quad (5.1)$$

where $\bar{L}_T$ is the measured linear intercept in the plane of observation across the lath thickness, and t is the thickness of the plate. Therefore the lath width data have been corrected by a factor of $\frac{\pi}{2}$ [54].

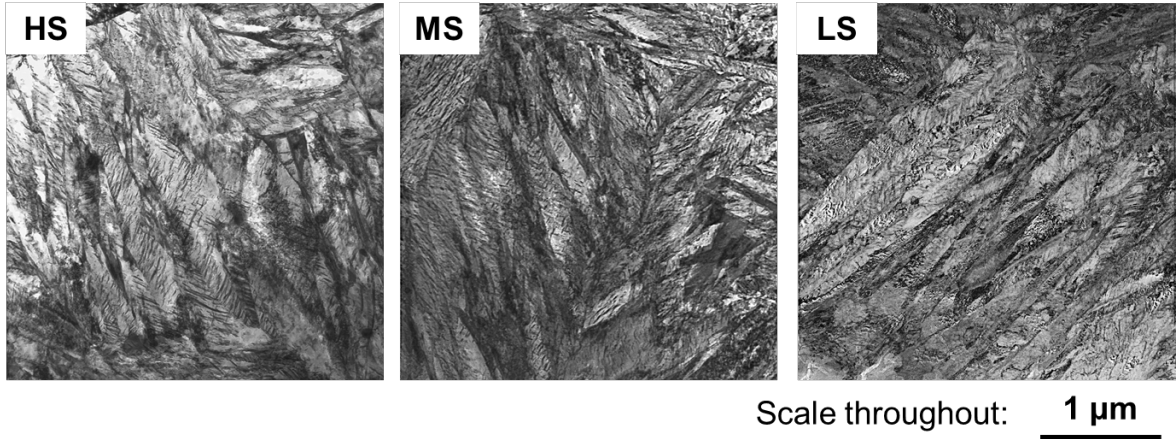


Figure 5.3: Low magnification images showing the lath structures (tempered at 250 $^{\circ}\text{C}$).

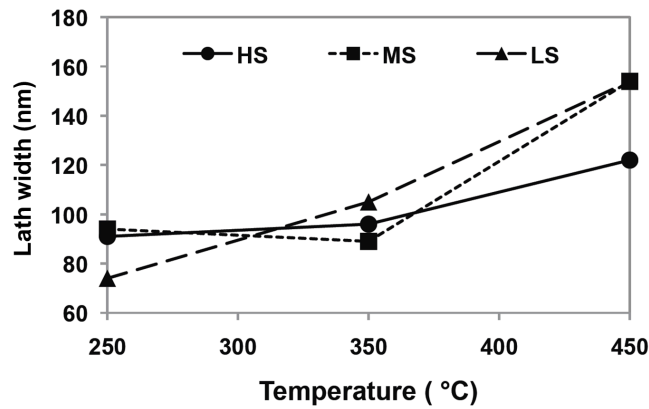


Figure 5.4: Lath width as a function of temperature and silicon content.

Table 5.4 reports the results numerically. Based on the TEM characterisation, it appears that the lath width increases the least for the highest silicon content, HS. In the case of the LS alloy, the increase is twofold.

In tempered martensite, the laths are heavily dislocated. Therefore, given that the lath size and the rate of increase is dependent on silicon content, it suggests that the recovery of martensite is a function of silicon. This point will be revisited when the synchrotron results are presented, where the dislocation density has been measured.

Table 5.4: Lath width (in nm) as a function of temperature and silicon content.

	250 °C	350 °C	450 °C
HS	91 ± 25	96 ± 28	122 ± 41
MS	94 ± 23	89 ± 28	154 ± 46
LS	74 ± 16	105 ± 29	154 ± 63

Microstructural analysis of the intralath carbides was carried out, as shown in Figure 5.5. The extracted equivalent radius and spacing between carbides is summarised in Figure 5.6. No results are available for the 450 °C condition, as the intralath carbides were hardly visible, so this condition was left out.

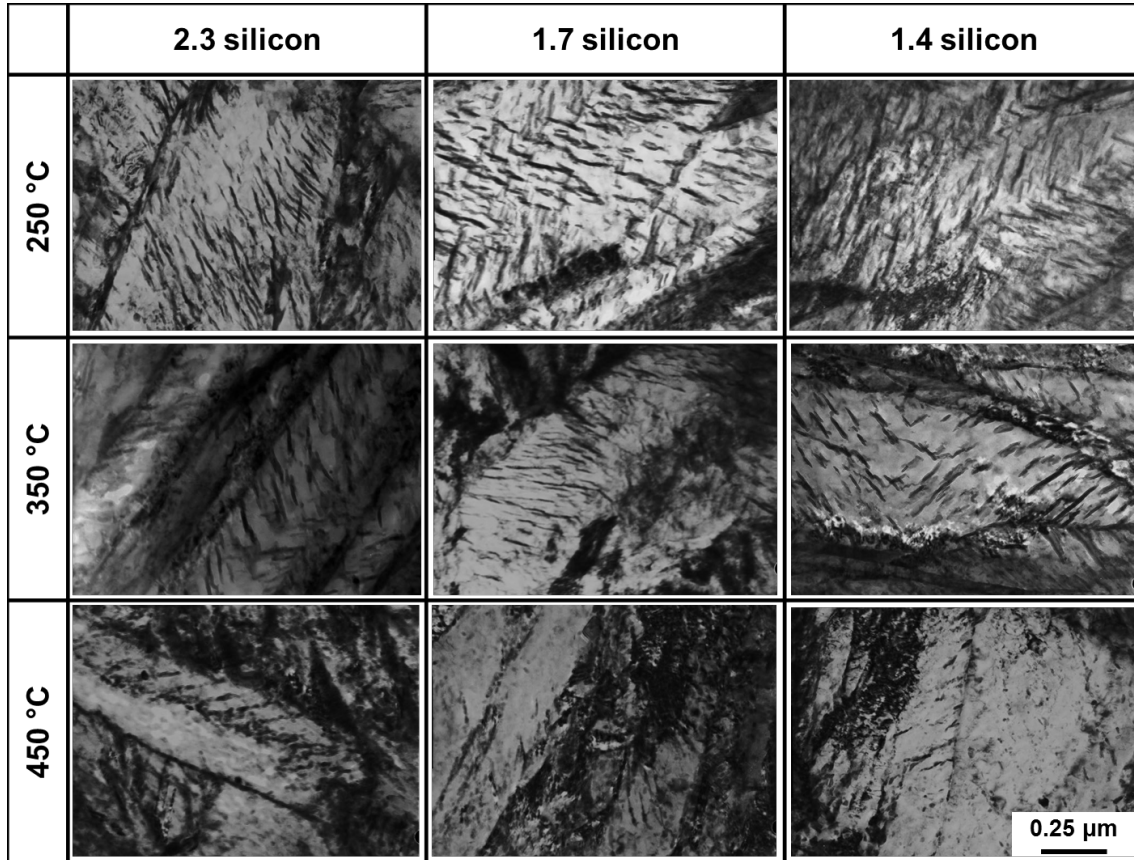


Figure 5.5: Intralath carbides shown for conditions 250, 350 and 450 °C.

Based on the carbide statistics, no obvious trends are seen, since the measurement error overlap between conditions. On the other hand, recalling the results

obtained for Model Alloy (Chapter 4), it was seen that although size did not vary much, the spacing between precipitates increased significantly: from 37.3 nm at 250 °C to 50.3 nm at 400 °C. This is opposite to what is observed in HS, MS and LS. Therefore, it appears that the presence of Mn, Cr, and other alloying elements, stabilises intralath carbides. This has also been observed by Barrow and Rivera-Díaz-del-Castillo [87].

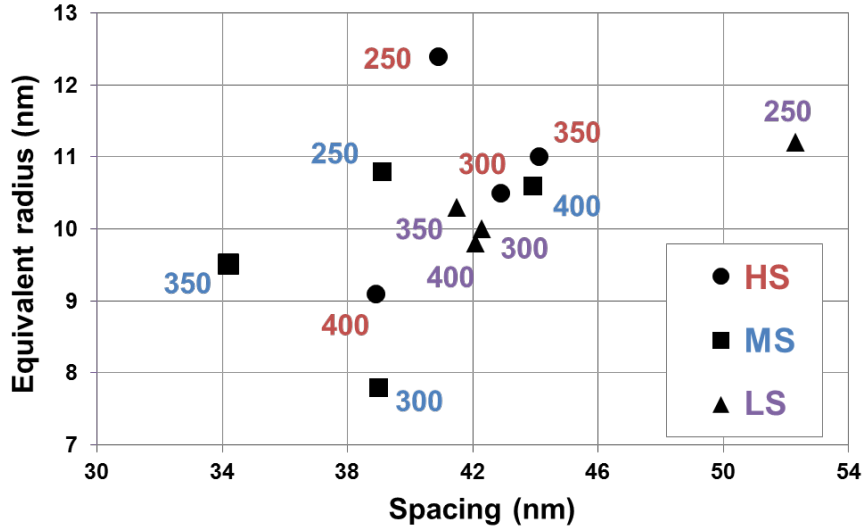


Figure 5.6: Microstructural analysis of intralath carbides.

5.3 The effect of silicon on cementite growth kinetics: *in situ* characterisation using high energy X-rays

Sample preparation

The samples for synchrotron studies were in the form of thin round needles of ~ 0.5 mm diameter and 6 mm length. Initially, the sample consisted of ~ 1.6 mm diameter and 12 mm length. While fixing one end of the sample, sand paper was applied to the other end of the material. Material was successively removed by grinding, until the diameter of the ground section was reduced to 0.5 mm, represented by the

shaded section in Figure 5.7 (a).

Once this form of specimen was obtained, thermocouples were attached to the thicker section, and conditioned in the dilatometer. Once heat treated, the sample was then cut, keeping the thinner cross-section for beamtime.

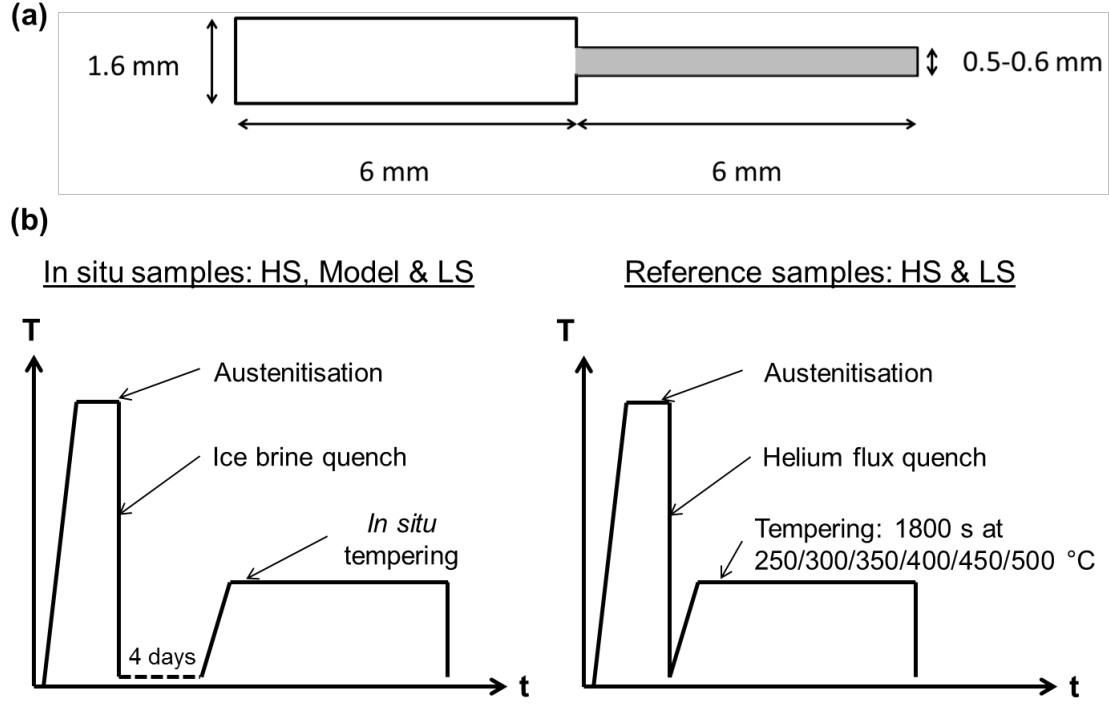


Figure 5.7: (a) Diagram illustrating sample preparation (image courtesy of David San Martín, CENIM), and (b) representation of the two heat treatments followed.

Figure 5.7 (b) shows the two types of heat treatments followed: as-quenched martensite for *in situ* tempering, and reference dilatometry samples. For the *in situ* tempering samples, the needles were austenitised using laboratory furnaces and quenched in ice brine, four days prior beamtime. The reference samples were heat treated in a DT1000 dilatometer.

5.3.1 Preliminary characterisation

In order to ensure that a martensitic microstructure has been obtained during quenching, the as-quenched condition was investigated by means of XRD, hardness and optical microscopy, for alloys HS and LS.

Flat-plate specimens were investigated by conventional XRD methods, which had a surface area of $20 \times 20 \text{ mm}^2$, and a thickness of $\sim 1 \text{ mm}$. A Phillips X'Pert PW3020 model equipped with a copper radiation source ($\lambda \approx 1.540598 \text{ \AA}$) was used for the preliminary characterisation. Scans were taken from 40 to $105^\circ 2\theta$, using a step size of 0.035° and a dwell time of 15 seconds. Diffraction analyses and Rietveld refinement were carried out using HighScore Plus software. The obtained XRD spectra are shown in Figure 5.8 (a).

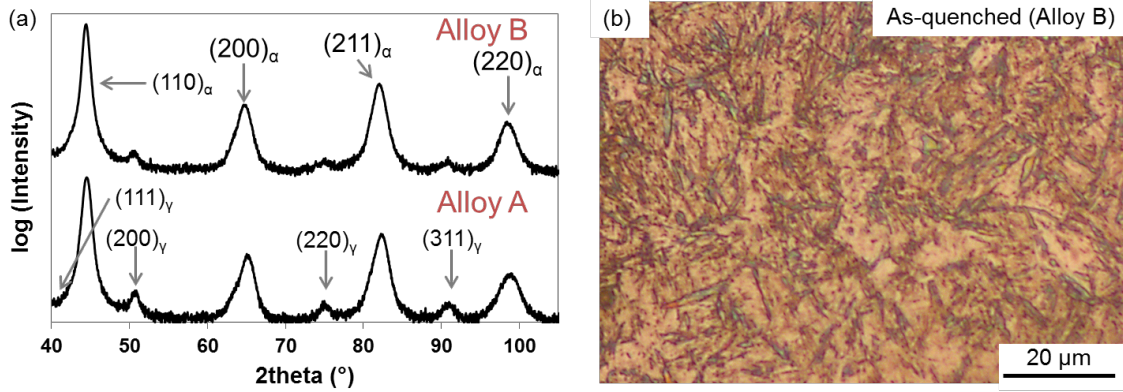


Figure 5.8: (a) As-quenched XRD pattern for flat-plate specimens, and (b) optical microscopy revealing martensitic microstructure for alloy LS needle specimen.

Rietveld refinement was carried out with two phases present: γ -austenite ($\text{Fm}\bar{3}\text{m}$) and α' -martensite (I4/mmm) (Figure 5.8 (a)), and was refined until a good fit was obtained, where $R_{\text{wp}} < 0.15$. R_{wp} is the weighted profile factor, and is thought to be the most meaningful value in following the progress of the refinement. It expresses the agreement between the observed (obs) and the calculated (cal) intensity distributions, which is determined by the following [88]:

$$R_{\text{wp}} = \left(\frac{\sum w_i (y_i(\text{obs}) - y_i(\text{cal}))^2}{\sum w_i (y_i(\text{obs}))^2} \right)^{\frac{1}{2}}, \quad (5.2)$$

where w_i is the observation weight, $y_i(\text{obs})$ and $y_i(\text{cal})$, are the observed and calculated intensity distributions, respectively.

The phase fraction of retained austenite, γ_R , found was 4.9 and 2.5 % for alloys HS and LS, respectively. The lattice parameters were: $a_\gamma = 3.5925$ nm, $a_\alpha = 2.8550$ nm and $c_\alpha = 2.8978$ nm for alloy HS, and $a_\gamma = 3.5870$ nm, $a_\alpha = 2.8666$ nm and $c_\alpha = 2.9003$ nm for alloy LS. The tetragonality of the matrix was 1.015 and 1.012 for alloys HS and LS, respectively.

The needle-shaped specimens were also examined. Etching using 2% nital revealed a martensitic microstructure (Figure 5.8 (b)). Hardness averages for alloys HS and LS were 812 ± 4 and 786 ± 6 HV2, respectively. Therefore it appears that the austenitisation and quenching processes were carried out adequately.

5.3.2 Experimental procedure

In situ synchrotron experiments were carried out at the I11 beamline at the Diamond Light Source, Didcot, UK, under transmission. *In situ* tempering was carried out by heating continuously using the Cyberstar hot-air blower provided by the beamline. The sample was mounted at the tip of a brass holder and fixed with phenol aldehyde epoxy resin. Once the resin was cured, the specimen was then placed horizontally on the spinner, and aligned with the incoming beam using the sample alignment cameras. A 15 keV beam energy ($\lambda \approx 0.827134$ Å) was used for this study. The set-up is shown in Figure 5.9.

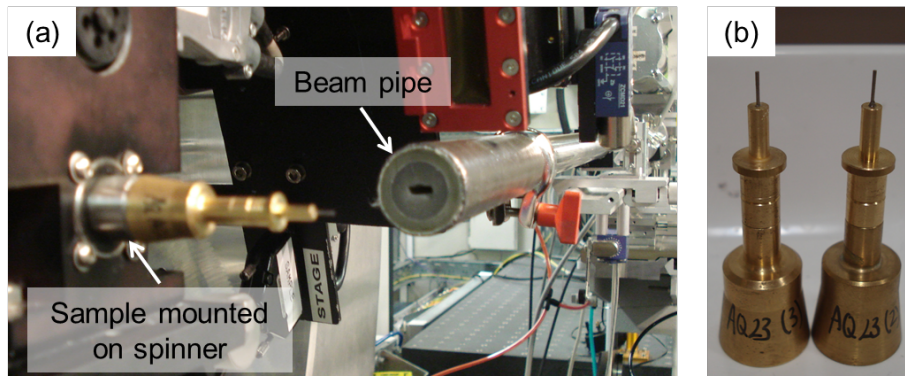


Figure 5.9: (a) Set-up of the beamline, and (b) needle-shaped samples mounted on brass holders.

Test runs were carried out at the start of the beamtime. Due to time constraints, and also because temperature control of the hot-air blower becomes less precise below 250 °C, the heat treatment was carried out starting from 300 °C. Moreover it was also found that a significant temperature gradient existed between the nozzle and the sample. Although it is not possible to state the carbide transition temperature with absolute certainty, the relative transition temperatures can be estimated.

While the furnace was set running at 300 °C, and the sample had been aligned, the hot-air blower was brought to the heating position. To ensure temperature homogeneity, the sample was submitted to isothermal holding for 10 minutes before ramping up the temperature from 300 to 900 °C at a rate of 0.1 °C/s. Due to the nature of this work, the time-resolved PSD detector was used in order to take rapid scans continuously throughout tempering, giving an exposure time of 60 seconds in total for each scan. It is worth noting that between the start and end of one scan, the temperature of the nozzle would have increased by approximately 6 °C.

5.3.3 Temperature calibration

During the preliminary run, it was noticed that a considerable gradient existed between the temperature of the furnace and that of the sample. Given its relatively simple chemical composition, the ternary Model alloy system was first assessed in order to become acquainted with the *in situ* technical aspects.

Figure 5.10 shows the diffraction peaks obtained for Model alloy, where cementite peaks have been indexed.

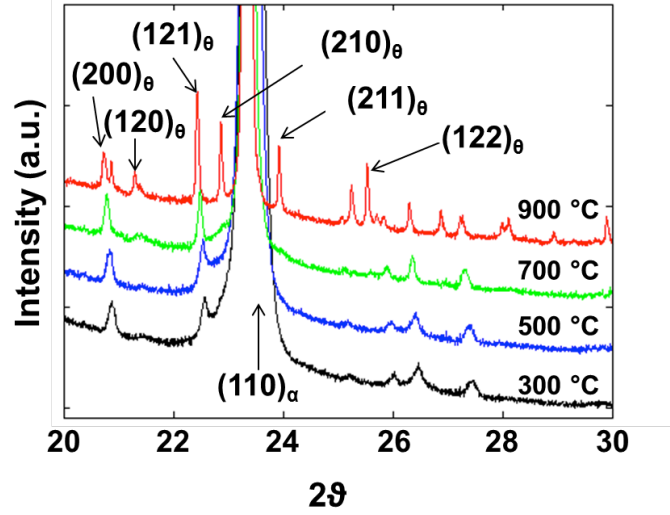


Figure 5.10: Shown $20^\circ < 2\theta < 30^\circ$ for the *in situ* tempering of the Model alloy (NB. Temperature indicated refers to that of the nozzle).

By means of dilatometry, the austenitisation starting temperature of the alloy, A_{c1} , was determined to be $808.3 \pm 2.0^\circ\text{C}$. Although the temperature of the nozzle, $T(\text{nozzle})$, indicated 900°C , there was no evidence of the material undergoing ferrite-austenite phase transformation. Thus confirming a significant thermal gradient between the sample and the nozzle exit.

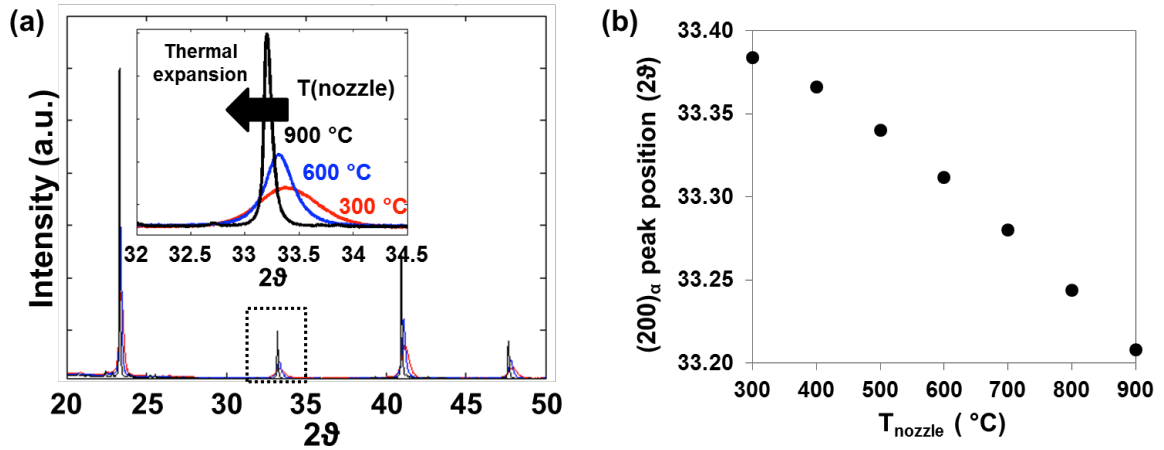


Figure 5.11: (a) Peak shift due to thermal expansion shown for Model alloy where the inset shows a magnified view of the (200) ferrite reflection (NB. Temperature indicated refers to that of the nozzle), and (b) $(200)_\alpha$ peak position at different temperatures.

One way of estimating the thermal gradient is by assuming that the peak shift is caused by thermal expansion of the lattice, as shown in Figure 5.11 (a), and quantified in (b). Hence, given its peak shift, the “true” temperature difference, ΔT_{true} , can be estimated from:

$$\frac{\Delta L}{L} = \alpha_L \Delta T_{\text{true}}, \quad (5.3)$$

where $\Delta L/L$ is the strain caused by lattice expansion, and α_L is $11.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [89]. However, in this case, a slight shift of the ferrite peaks could also be due to a reduction in tetragonality within the matrix phase.

Using Equation (5.3) and the data from Figure 5.11, it is observed that while the nozzle temperature increases from 300 to 900 $^\circ\text{C}$, i.e. temperature increment of 600 $^\circ\text{C}$, the actual temperature increment experienced by the sample is of ~ 447 $^\circ\text{C}$. Hence, the actual tempering would have been carried out until ~ 750 $^\circ\text{C}$ instead of 900 $^\circ\text{C}$. Although this is still an approximation, it provides a more realistic view of the actual tempering conditions. Therefore, from here onwards, this correction factor will be considered.

5.3.4 Reference samples

The diffraction spectra for reference samples prepared by dilatometry are shown in Figure 5.12. The retained austenite seems to be stable even after 1800 s at temperatures up to 400 $^\circ\text{C}$ in the lower silicon alloy, and 450 $^\circ\text{C}$ in the higher silicon contents. This observation is surprising as generally the decomposition of retained austenite (Stage II of tempering) is believed to take place between 200 and 300 $^\circ\text{C}$ [11].

In the case of tempering at 500 $^\circ\text{C}$, carbide peaks in LS alloy are stronger than in the higher silicon alloy (dotted green circles in Figure 5.12).

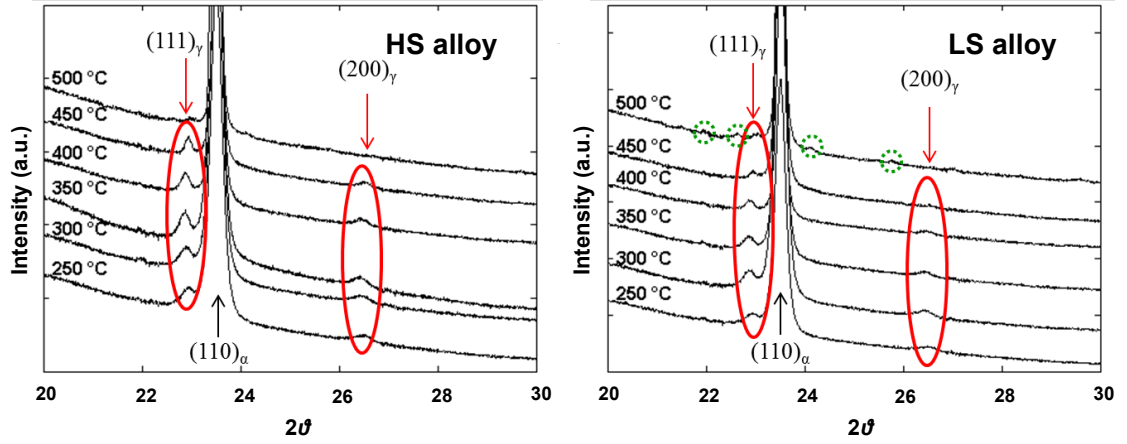


Figure 5.12: XRD spectra shown for the reference samples for alloys HS and LS.

Closer inspection of the $22^\circ < 2\theta < 25^\circ$ region indicates that the $(111)_\gamma$ peak shows higher stability at high silicon content. This observation is consistent with the trend reported in 0.2 wt.%C steels undergoing quenching and partitioning heat treatments, reported by Santofimia *et al.* [90], where by adding 1.5 wt.% silicon, a higher volume fraction of retained austenite was observed when tempered at 350 °C for various time lengths.

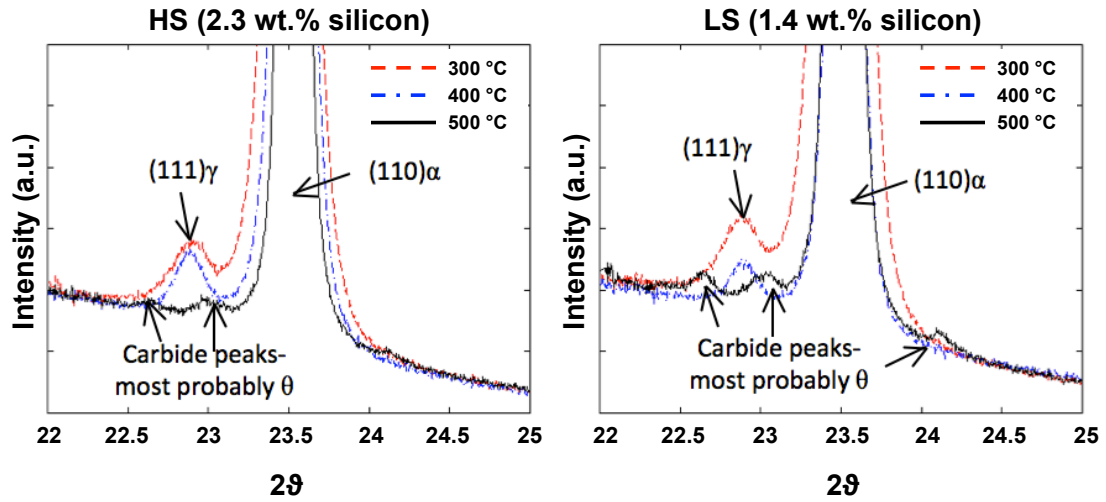


Figure 5.13: Earlier martensite recovery in lower silicon content, as well as higher stability of the retained austenite phase are observed.

Furthermore, it is worth noting that considerable sharpening of the ferrite peaks takes place. Given that peak broadening is attributed to the presence of defects

in the lattice, e.g. dislocations, it is also possible to calculate the evolution in dislocation density during martensite tempering. Moreover, peak sharpening occurs more readily in the lower silicon case, implying a dependency in silicon content for martensite recovery. This will be discussed in §5.4.2.

Absence of ε peaks

Close analysis of the XRD spectra did not show any sign of ε -carbide peaks. One possible explanation is that, owing to its small crystallite size and its low volume fraction, considerable broadening takes place, beyond detection limit. Another possible explanation is that the formation of ε -carbide is suppressed, and instead cementite is directly precipitated. Kalish and Cohen [4] stated that in highly dislocated martensite, carbon preferentially segregates into dislocation cores. As tempering progresses, dislocations lose the ability to retain the carbon and cementite is precipitated, skipping the intermediate ε -phase. Following the work on interrupted ageing (Chapter 3), 4 days of room temperature ageing would have been sufficient for significant microstructural change in the as-quenched state. One further possible explanation is that the sample undergoes $\varepsilon \rightarrow \theta$ during the initial isothermal holding at 300 °C. Although, as seen in Chapter 4, the Model alloy showed that after tempering at 300 °C for 1800 s, ε -carbide was obtained.

5.3.5 *In situ* tempering

Although it has not been possible to follow the early nucleation stage of cementite during synchrotron analysis, the growth stage has been studied. In both HS and LS alloys, similar cementite peaks are already present by the time the first measurement had been taken at 300 °C. Nevertheless, during continuous heating cementite peaks appear much stronger in the lower silicon alloy. The relative intensities for the cementite peaks are much stronger in LS than in HS, implying faster precipitation rates for the lower silicon case during continuous tempering. Since the first obtained

spectra are for $T = 300\text{ }^{\circ}\text{C}$, the inhibiting effect of silicon on the $\varepsilon \rightarrow \theta$ carbide transition remains unproven *in situ* at this moment.

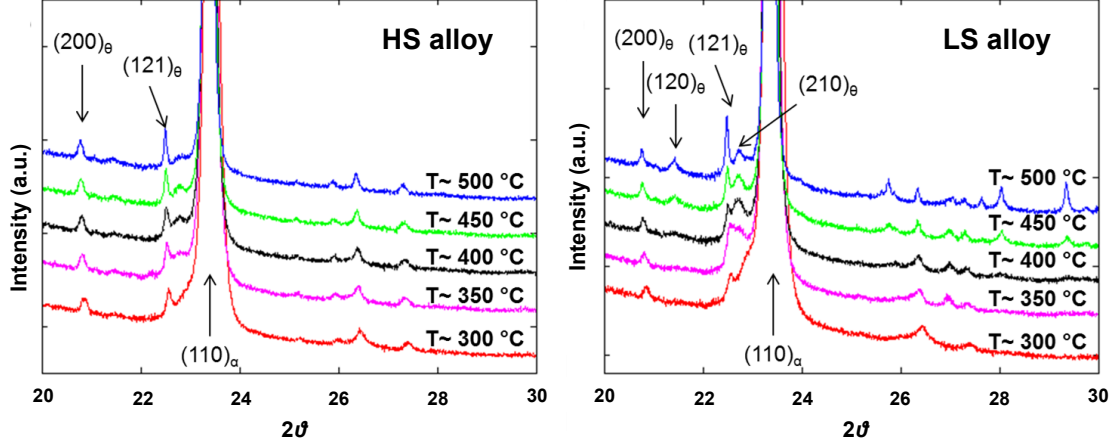


Figure 5.14: *In situ* runs for alloys HS and LS.

5.3.6 Cementite growth kinetics

In the previous chapter, cementite nucleation was modelled under paraequilibrium conditions. Reisdorf [3] showed that, throughout tempering, the silicon content within cementite decreased. This observation was supported by Chang *et al.* [20], where after prolonged tempering, a rich silicon layer was seen to form surrounding the carbide. Based on this, there is a tendency to ascertain that as cementite forms under constrained paraequilibrium conditions; as the conditions become relaxed throughout tempering and orthoequilibrium can be considered, as silicon is eventually rejected from θ .

3D-APT (atom probe tomography) results presented by Caballero *et al.* [27] are charted in Figure 5.15, where it has been observed that the measured silicon content within cementite decreased with increasing tempering temperature.

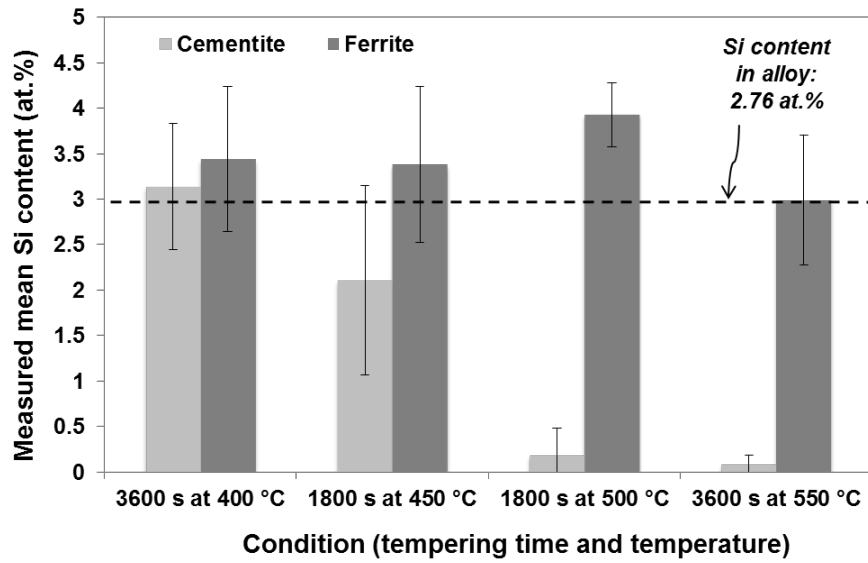


Figure 5.15: Average silicon content in ferrite and cementite for different tempering conditions, from tabulated data in [27].

When considering cementite formation under paraequilibrium conditions at relatively low temperatures, the diffusion of the substitutional elements is negligible. One can assume that, at this stage, only carbon content will vary across the matrix/carbide interface, whereas the content of the rest of the elements remains unchanged. However, under prolonged tempering, the trapped silicon within cementite will begin to diffuse out of the carbide, as the carbide tends to equilibrium. Zhu *et al.* [28] observed that the rejected silicon builds up a Si-rich layer at the interface, as schematically illustrated in Figure 5.16 (a).

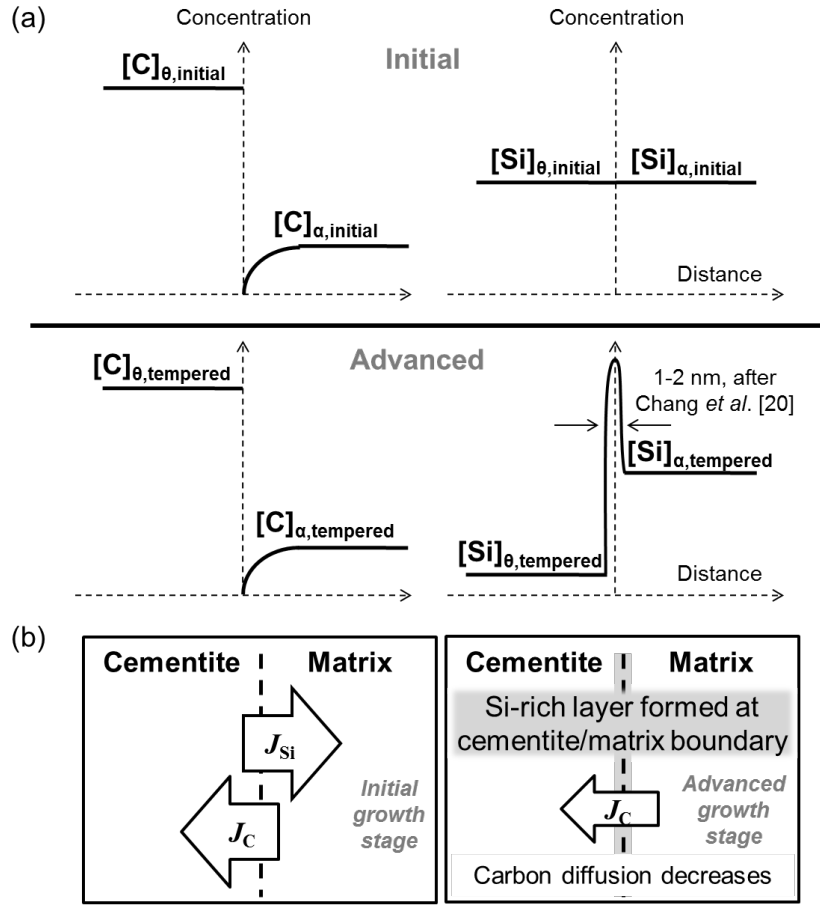


Figure 5.16: (a) Possible growth mechanism for cementite, and (b) silicon and carbon content variation throughout tempering, where J_C and J_{Si} refer to the carbon and silicon flux across the interface.

For continuous carbide growth, further carbon is needed. However, the carbon flux into the carbide across the interface will be reduced due to the Si-rich layer, as illustrated in Figure 5.16 (b). Therefore the diffusion rate of silicon within cementite is likely to be the rate-controlling factor in the growth of carbides. This mechanism has also been hinted by Barrow and Rivera-Díaz-del-Castillo [87]. This view agrees with the carbide growth kinetics seen during *in situ* synchrotron analysis (Figure 5.14).

The slow growth of cementite might also be due to the slow diffusion of carbon through the ferritic matrix. However, it is known that the presence of silicon in α -

ferrite raises the chemical potential of carbon [68]. This causes the carbon to diffuse to more favourable sites within the material, e.g. carbides. This can be interpreted as an additional driving force for the carbon to participate during carbide precipitation. Despite the former, the fact that slower growth kinetics was observed in the higher silicon alloy, hints that the rate is governed by the 1-2 nm Si-rich layer reported by Chang *et al.* [20]. An additional growth rate controlling factor is the partitioning of silicon from the carbide.

5.4 The effect of silicon on martensite recovery

5.4.1 Martensite recovery

Throughout martensite tempering, several changes may occur, which include carbon segregation (Chapter 3), carbide precipitation (Chapter 4), retained austenite decomposition and recovery and recrystallisation of the ferrite matrix [91].

Caron and Krauss [92] observed that during the early stages of tempering there is a significant drop in hardness, as well as in the total grain boundary surface per unit volume. Their method for determining the number of grain boundaries consisted of obtaining micrographs, all of equal dimensions, from different tempering conditions. Concentric circles were drawn on each photograph, where the number of intersections between boundaries and the drawn circles were counted, which gave an indication of the grain boundary content. They observed a reduction in the grain boundary content during prolonged tempering times, which was related to the elimination of low angle boundaries and boundary readjustment.

Recovery is described as the process by which the stored energy in the material is decreased by a change in the dislocation structure. A lower energy configuration is achieved by dislocation motion such as glide, climb and cross-slip. Recovery is known to consist of three components [93]:

- Dislocation annihilation.

- Dislocation rearrangement.
- Subgrain growth.

One characteristic of as-quenched martensite is its very high dislocation density, which can be up to 10^{16} m^{-2} for medium carbon steels. Upon tempering, due to the recovery process, there will be some changes in the microstructures. At this stage, the focus will be on dislocation annihilation and subgrain growth.

Speich and Leslie [94] stated that in Fe-C alloys, recovery becomes an important process at temperatures above 400 °C, whereas recrystallisation generally occurred between 600-700 °C. During recovery, it is believed that the as-quenched lath structure, initially consisting of low angle dislocation cells and high angle lath boundaries, undergoes annihilation of the boundaries and dislocations [94].

In Table 5.4 there already was a hint of recovery manifested in lath thickening as tempering progressed. The thickness increase was lowest for HS, and highest for LS. An initial hypothesis is established: if the apparent change in lath width is to be described as part of the subgrain growth process during recovery, then high silicon content seems to inhibit recovery in martensite.

The effect of silicon in retarding martensite recovery is also hinted in Figure 5.13, where peak sharpening occurs more readily when the silicon content is low. Therefore in order to measure the extent of dislocation annihilation throughout tempering, the dislocation density is measured in the forthcoming section.

5.4.2 Dislocation density throughout tempering

Extensive crystallographic information can be obtained from analysing XRD data.

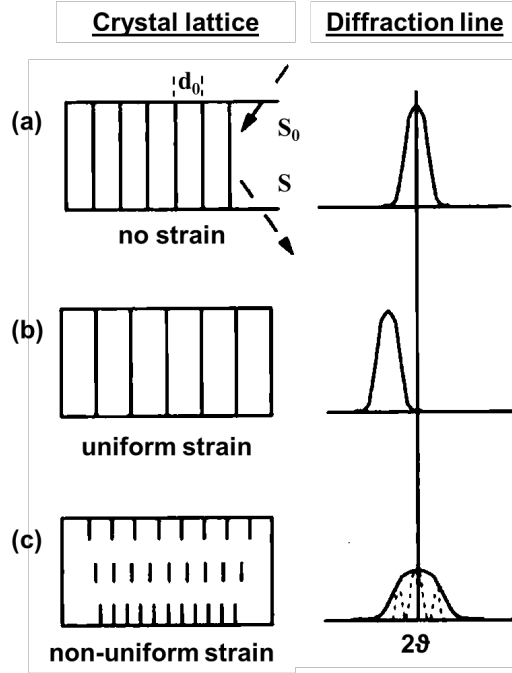


Figure 5.17: Origin of strain in crystals, adapted from Cullity [95].

Figure 5.17 (a) represents a perfect crystal lattice, with no strain present in the material. However, there are various defects that distort the perfect lattice, and influence the peak position and broadening. For instance, (b) shows the case where the presence of alloying elements causes peak shifting due to the dilation in lattice parameters. For example, in ferrite, the presence of silicon would lead to a contraction in the α -Fe lattice, which would shift the peak to the right. On the other hand, the presence of carbon atoms at the interstitial sites, would lead to an expansion in the lattice, shifting the peak to the left. Another cause for uniform strain is the thermal expansion effect experienced at higher temperatures due to a volume expansion of the lattice.

The next phenomenon to consider is peak broadening, Figure 5.17 (c), which is caused by the presence of crystal imperfections such as a small crystallite size, strains and faulting [96, 95]. Quantifying the different effects has been researched extensively, as exemplified by the seminal work by Hall, Williamson and Smallman [97, 98, 99], Warren and Averbach [100, 101] and, later on, further developed by Ungár *et al.* [102, 103]. Many researchers have applied these methods to determine

the dislocation density in ferritic martensite, [104, 105, 106, 107]. Recently, Christien *et al.* have measured *in situ* the dislocation density evolution on a Fe–0.03C–0.3Si–0.8Mn–4.8Ni–15.6Cr–3.1Cu wt.% steel, in both austenite and martensite phases during martensitic transformation by neutron diffraction [108]. It was seen that in both phases the dislocation density increased progressively throughout the austenite to martensite phase transformation, Figure 5.18.

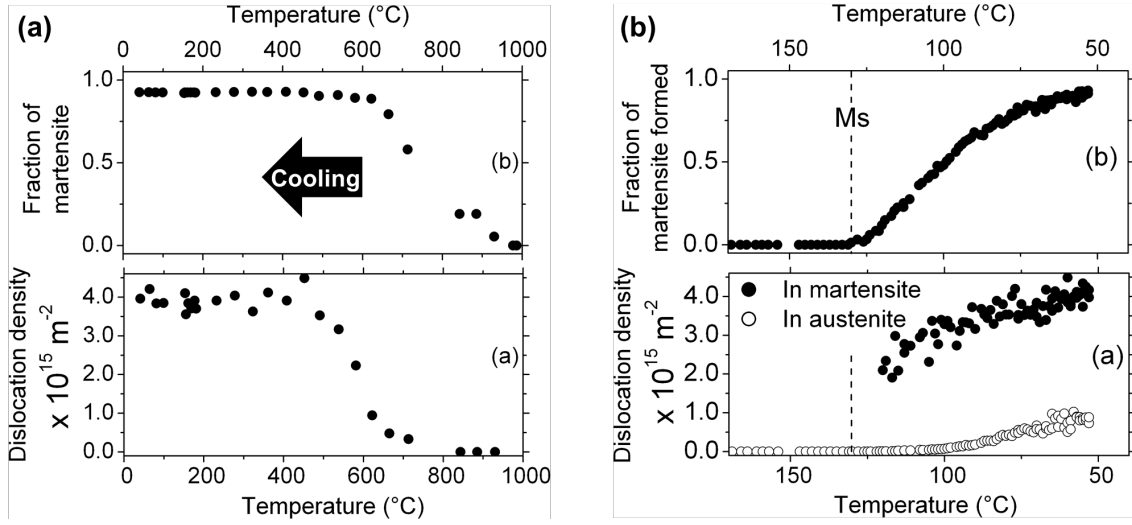


Figure 5.18: Measured dislocation density evolution on a Fe–0.03C–0.3Si–0.8Mn–4.8Ni–15.6Cr–3.1Cu wt.% steel during martensitic transformation (a) during cooling, and (b) near the M_s , adapted from Christien *et al.* [108].

Often in literature, the two methods used for measuring dislocation densities are TEM and XRD. The general agreement is that TEM is suitable for low dislocation densities ($\sim 10^{12} \text{ m}^{-2}$), whereas for high dislocation densities (10^{14} – 10^{15} m^{-2}), XRD methods are preferred. In this work, it was not possible to observe individual dislocations by TEM, perhaps owing to the very high dislocation density in the sample. Therefore XRD methods have been used.

The microstrain resulting from defects within the sample can be obtained by differentiating Bragg's equation at constant λ (NB. $n=1$, where n is the integer

indicating the order of diffraction):

$$\lambda = 2d \sin \vartheta \quad (5.4a)$$

$$\frac{1}{d} = \frac{2 \sin \vartheta}{\lambda} \quad (5.4b)$$

$$-\frac{\Delta d}{d^2} = 2\Delta \vartheta \frac{\cos \vartheta}{\lambda} \quad (5.4c)$$

$$\frac{\Delta d}{d} = 2d\Delta \vartheta \cos \vartheta \frac{-1}{2d \sin \vartheta} \quad (5.4d)$$

$$\frac{\Delta d}{d} = \frac{-\Delta \vartheta}{\tan \vartheta} \quad (5.4e)$$

$\frac{\Delta d}{d}$ term represents the average strain within the material, $\varepsilon_{\text{micro}}$. The broadening due to strain (β_{strain}) is given by the $\Delta \vartheta$ term, which is obtained by the peak's full-width at half maximum (FWHM).

One other factor that contributes to broadening of the diffracted peaks is crystallite size, which can be described by the Scherrer formula [95]:

$$t = \frac{K\lambda}{\beta \cos \vartheta}, \quad (5.5)$$

where t is the crystallite size, K is shape factor, which often is taken to be 1, λ is the X-ray wavelength, β is the line broadening at FWHM, and ϑ is the Bragg angle.

From Equations (5.4e) and (5.5), it can be seen that strain varies with $\tan \vartheta$, whereas crystallite size varies as a function of $1/\cos \vartheta$. The Williamson-Hall method allows the separation of these two properties [109], where the total broadening of the peaks β_{total} is given by the sum of strain and size contributions, β_{strain} and β_{size} , respectively. Instrumental broadening also contributes to β_{total} . Nevertheless, the instrumental broadening at the synchrotron facility on beamline I11, where this work was carried out, is assumed to be negligible. Therefore peak broadening is

given by:

$$\beta_{\text{total}} = \beta_{\text{strain}} + \beta_{\text{size}} \quad (5.6a)$$

$$\beta_{\text{total}} = \varepsilon_{\text{micro}} \tan \vartheta + \frac{k\lambda}{t \cos \vartheta} \quad (5.6b)$$

$$\beta_{\text{total}} \cos \vartheta = \varepsilon_{\text{micro}} \sin \vartheta + \frac{k\lambda}{t} \quad (5.6c)$$

Plotting $(\beta_{\text{total}} \cos \vartheta)$ vs. $\sin \vartheta$ would give a linear plot, where the gradient would give the strain and the intercept would provide information on the crystallite size.

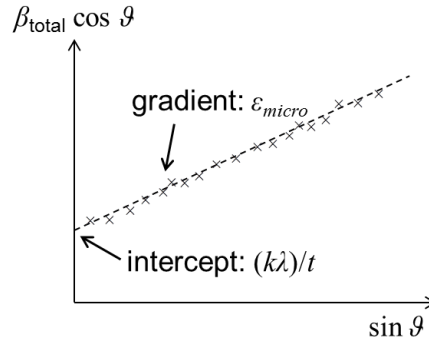


Figure 5.19: Separation of the size and strain effects on a Williamson-Hall plot.

The above remains true only for Lorentzian peaks. For Gaussian peaks, Equation (5.6a) becomes:

$$\beta_{\text{total}}^2 = \beta_{\text{strain}}^2 + \beta_{\text{size}}^2, \quad (5.7)$$

Nevertheless, it is often the case that the curves are best fitted by a Voigt function, which consists of a convolution of Lorentzian and Gaussian. The “double-Voigt” method after Langford [110] models both size- and strain-broadened profile, and has been proven to be more accurate [111].

Based on the strain broadening, Christien *et al.* derived an expression for the dislocation density [108]:

$$\rho = \frac{3E}{\mu b^2(1 + 2\nu^2)} \varepsilon_{\text{micro}}^2, \quad (5.8)$$

where E is the Young’s modulus, μ is the shear modulus, b is the Burgers vector

and ν is the Poisson's ratio.

In this work, Rietveld refinement was performed on the XRD spectra using MAUD software [112], which uses a pseudo-Voigt (PV) function for curve fitting. The microstrain values, $\varepsilon_{\text{micro}}$, were extracted from the refinement and were substituted into Equation 5.8. The values used were as follows: $E = 211$ GPa, $\mu = 80.3$ GPa, $\nu = 0.3$. To determine the value of b , consider the $\frac{1}{2}a\langle 111 \rangle$ Burgers vector in ferrite. This corresponds to a magnitude given by $\frac{\sqrt{3}}{2}a$. Based on the lattice parameters previously extracted from XRD work in §5.3.1, Table 5.5 summarises the Burgers vector for the two alloy systems.

Table 5.5: Burgers vectors for the different alloys.

	a_{α} by XRD (Å)	b (Å)
HS	2.8550	2.473
LS	2.8666	2.483

The microstrain, $\varepsilon_{\text{micro}}$, values obtained from MAUD and the calculated dislocation density values are summarised in Table 5.6. The dislocation density values are summarised in Figure 5.20. It is seen that for all tempering conditions, the dislocation density in HS is higher than in LS, as hinted by Figure 5.13. It is worth noting that instrumental broadening is assumed to be negligible in the current analysis. However, any broadening due to the instrument will overestimate the dislocation density reported in Figure 5.20. Nonetheless the order of magnitude $\sim 10^{15} \text{ m}^{-2}$ corresponds to the typically reported value for martensitic steels [108, 105].

Table 5.6: Summary of the microstrain and dislocation density values obtained.

$T_{\text{tempering}}$ ($^{\circ}\text{C}$)	HS alloy		LS alloy	
	$\varepsilon_{\text{micro}} (\times 10^3)$	$\rho (\times 10^{15} \text{ m}^{-2})$	$\varepsilon_{\text{micro}} (\times 10^3)$	$\rho (\times 10^{15} \text{ m}^{-2})$
250	7.8	6.6	8.0	7.1
300	7.2	5.6	7.4	6.0
350	5.8	3.7	6.4	4.4
400	4.4	2.1	6.0	3.9
450	3.9	1.6	5.9	3.8
500	2.6	7.4	4.1	1.9

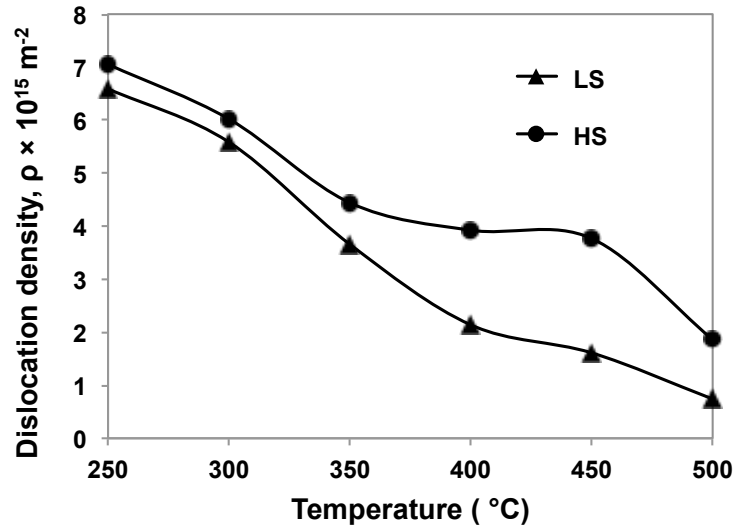


Figure 5.20: Dislocation density evolution with tempering temperature.

Additional XRD was carried out using lab-based samples. These samples, as mentioned in §5.1, were heat treated using lab furnaces. For surface preparation, the samples were polished down to 1 micron using diamond paste, with an OPS colloidal silica finish. The same procedure was used as in §5.3.1, except for the dwell time was decreased to 5 seconds. Results are shown in Figure 5.21.

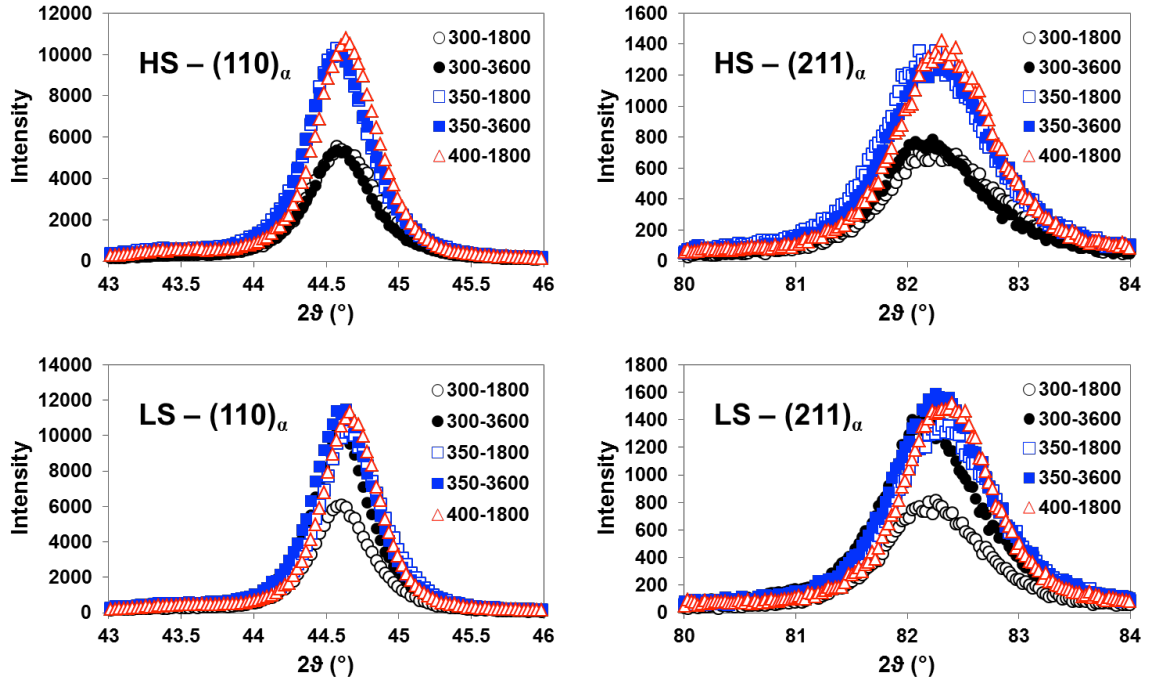


Figure 5.21: Diffraction spectra for the (100) and (211) ferrite peaks. The legend summarises the heat treatment combinations investigated, e.g. 300-1800 means tempered at 300 °C for 1800 seconds.

The first observation that can be made is that, throughout tempering, peak sharpening occurs. This sharpening occurs between 300 and 350 °C for both HS and LS alloys. Nevertheless, based on peak broadening effects, it is observed that in the case of LS, 3600 s tempering at 300 °C has already the same effect as 1800 s tempering at 350 °C for HS. Thus, based on these findings, the kinetics of martensite recovery appears to be influenced by the silicon content.

At this stage, it is not possible to know whether this is a specific property of silicon, or if it is merely due to a solid solution effect in general. Nevertheless, Wittig and Frommeyer [113] reported that the presence of silicon in the bcc-iron lattice caused a reduction in dislocation cross-slip with increasing silicon content. When alloyed with silicon, additional to the Peierls stress from the ferrite lattice, there is a stress increment in moving a dislocation, owing to an increase in the free energy due to the silicon-silicon interaction. Hence, dislocation cross-slip will

be lower in HS than in LS, causing lower recovery kinetics with increasing silicon contents.

5.5 Conclusion

The effect of silicon in martensite tempering has been studied in this chapter. Two main effects have been discussed: its inhibiting effect in cementite growth and its retarding effect in the rate of martensite recovery.

The first mentioned effect has been based on *in situ* synchrotron observations, where initially cementite would nucleate under paraequilibrium conditions, trapping the silicon within. However, during growth, as the system tends to orthoequilibrium, the silicon is rejected from within the carbide. The rejected silicon, as shown by literature, is said to form a Si-rich layer, which inhibits further carbon intake, necessary for continuous carbide growth.

The second effect is related to martensite recovery during the tempering stage. Considerable microstructural changes related to the recovery process were observed. By TEM and XRD methods it was observed how, when silicon content is increased, martensite recovery kinetics is inhibited, as revealed by lath width increase and peak broadening during tempering. This has been related to a reduced cross-slip rate with increasing silicon.

The microstructural features quantified in this chapter will serve as a foundation to the forthcoming chapter, particularly in understanding the plasticity behaviour in medium carbon tempered martensite.

Chapter 6

Plasticity

The characterisation work presented in Chapter 5 identified the several microstructural changes taking place throughout martensite tempering, where the features that most noticeably changed during heat treatments were intralath carbide precipitation, dislocation density and lath width. Literature on plasticity modelling of 0.5–0.6 wt.% carbon martensitic steels is scarce, and it is even a bigger challenge due to the complex microstructures obtained in medium-carbon martensite. A few modifications are introduced into existing plasticity models in order to customise these for the HS, MS and LS alloys.

6.1 Introduction

Strengthening in tempered martensite results from the addition of several contributing effects such as precipitation hardening, solid solution strengthening, forest dislocation hardening and grain size refinement. The aim of the first part of this chapter is to quantitatively determine, with the aid of experimentally determined values, each individual strengthening term, in order to observe how these evolve as a function of both temperature and chemical composition.

The second part deals with reproducing the stress-strain curves that were obtained experimentally. Existing models based on irreversible thermodynamics were

applied, where a few modifications have been incorporated in order to adapt them to medium carbon martensitic steels. Lastly, the third part presents the EBSD work carried out in order to determine the “effective” grain size based on the misorientation between grains.

6.2 Tensile testing

A total of four conditions were tested for all three alloys HS, MS and LS: as-quenched, and tempered 1800 s at 250, 350 and 450 °C. Test specimens were cylindrical, and were heat treated after machining. The tests were performed in accordance with ISO 6892 standard [114]. The machined test samples are shown in Figure 6.1, where L_0 is the original gauge length, L_t is the total length of test piece, S_0 is the original cross-sectional area of the parallel length, L_u is the final gauge length after fracture, and S_u is the minimum cross-sectional area after fracture.

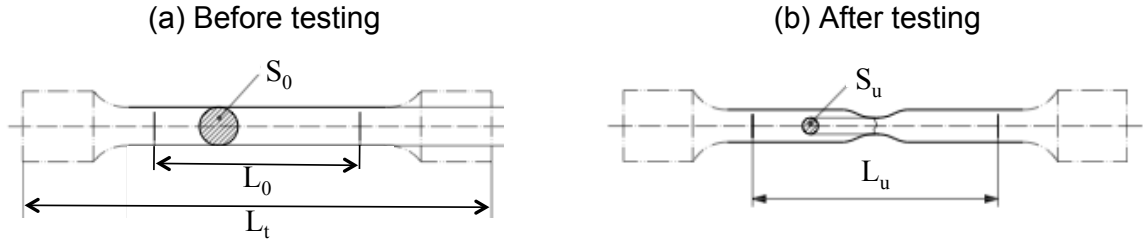


Figure 6.1: Diagrams illustrating tensile specimens (a) before and (b) after failure, adapted from ISO 6892 [114].

Figure 6.2 shows typical stress-strain curves for alloy HS. All as-quenched (AQ) conditions failed before reaching the elastic limit. The other three conditions showed appreciable necking in the region where failure occurred. Two runs per alloy were tested, and the properties are summarised in Table 6.1.

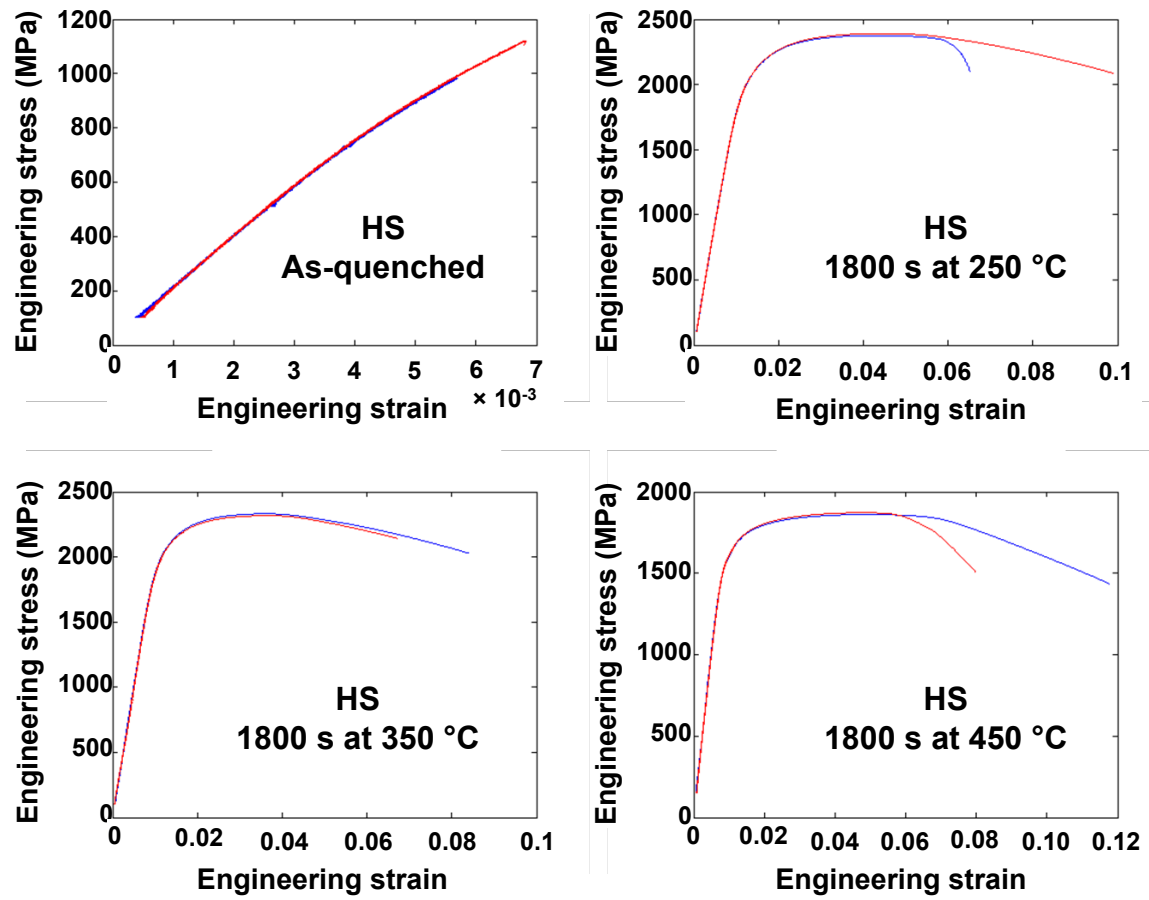


Figure 6.2: HS alloy tensile curves, for the as-quenched condition, and 250, 350, and 450 °C tempering. The two runs per condition are shown in red and blue.

The properties which are usually reported in industrial spring steels specifications are σ_y , σ_{UTS} , A and Z (Chapter 2), where A and Z are the percentage elongation after fracture (Equation (6.1)), and the percentage area reduction (Equation (6.2)), respectively.

$$A = \frac{L_u - L_0}{L_0}, \quad (6.1)$$

$$Z = \frac{S_0 - S_u}{S_0}, \quad (6.2)$$

Although industrially, A and Z are part of the specification, the current project is limited to stress modelling only.

Table 6.1: Summary of tensile properties.

Condition	$\sigma_{y,0.2}$ (MPa)	σ_{UTS} (MPa)	A (%)	Z (%)
HS - 250	2038 ± 2	2382 ± 11	8.8	33
HS - 350	2039 ± 1	2324 ± 10	6.5	22
HS - 450	1602 ± 8	1866 ± 8	9.2	39.8
MS - 250	1991 ± 0.2	2311 ± 7	2.3	16.1
MS - 350	1972 ± 3	2233 ± 6	2	38.4
MS - 450	1550 ± 4	1727 ± 5	3.7	34.5
LS - 250	1936 ± 52	2275 ± 17	2.7	38.0
LS - 350	1916 ± 3	2187 ± 0.2	1.6	19.6
LS - 450	1511 ± 7	1672 ± 10	3.6	35.8

6.3 Fitting σ_y

Morito *et al.* [115] showed that the general equation for estimating the yield stress of lath martensite in 0.2 wt.% C takes the following form:

$$\sigma_y = \sigma_0 + \sigma_p + \sigma_s + \sigma_\rho + k_{HP}d^{-\frac{1}{2}}, \quad (6.3)$$

where σ_0 is the friction stress for pure Fe, an intrinsic property of the material, σ_p is the precipitation hardening contribution, σ_s is the solid solution strengthening factor, σ_ρ is the forest hardening of dislocations effect within the laths and in the low angle boundaries, and $k_{HP}d^{-\frac{1}{2}}$ term is the grain boundary strengthening term, which accounts for the Hall-Petch grain size effect [115].

The biggest challenge is in determining the last term, which accounts for the Hall-Petch effect. In tempered lath martensite, owing to its very complex microstructure,

it becomes difficult to establish the ‘effective’ grain size. Revisiting Figure 2.3, the microstructural features in martensite were: PAG, packet, block, lath; each of them is respectively larger than the following.

While for 0.2 wt.% C, Morito *et al.* [115] have concluded that the block size acts as an ‘effective’ grain size, the literature on medium-C steels is scarce. Figure 5.4 gives some indication on the changes occurring at the microstructural level. During continuous tempering, from the moment the steel is quenched until when it becomes polygonal ferrite, there is a gradual change in the microstructure, where the initially formed martensite laths undergo rearrangement and recombination during recovery and recrystallisation. It is therefore, the starting point of this section to compare existing models with the tensile experiments in §6.2, in order to examine the ‘effective’ grain size term for tempering conditions 250, 350 and 450 °C in HS, MS and LS alloys.

Equation 6.3 is slightly modified, where the $k_{\text{HP}}d^{-\frac{1}{2}}$ term is replaced by a sub-grain strengthening term, σ_{sg} :

$$\sigma_y = \sigma_0 + \sigma_p + \sigma_s + \sigma_\rho + \sigma_{\text{sg}} \quad (6.4)$$

In literature, by experimentally determining σ_y and estimating the σ_0 , σ_p , σ_s and σ_ρ terms, Hutchinson *et al.* [65] calculated the ‘unaccounted strength’, which they found was a function of interstitial carbon content. However, two points should be brought forward related to their method: first, in their calculation of the σ_ρ term, the Taylor factor, M was omitted, and second, their σ_y value was obtained by simply multiplying the Vickers hardness by 3. In Chapter 3, it was shown that in many cases, the actual σ_y value was less than the predicted value from the Tabor relationship. Therefore, the ‘unaccounted strength’ determined by Hutchinson *et al.* clearly is overestimated. Nevertheless, their method of subtraction still remains valid, where if all terms except for one are known; then, by simple subtraction, the

unknown can be determined.

Using the experimentally determined values in Chapter 5, we can estimate σ_0 , σ_p , σ_s and σ_ρ . These values are then to be subtracted from the σ_y values listed in Table 6.1, in order to estimate the σ_{sg} term.

6.3.1 Precipitation hardening, σ_p

Failed tensile specimens were analysed under TEM. The condition HS-250 and 450 were characterised, where two sections were analysed: the region near necking, would have undergone the most plastic deformation, and the region near the gripping ends is where least deformation would have occurred. In Figure 6.3, these are labelled A and B, respectively.

In Figure 6.3 (HS-250), two interesting observations are made from comparing the microstructure from these two regions. The first is that the intralath carbides appear to remain unchanged after failure, implying that precipitation hardening is more probable to follow a by-pass mechanism, rather than particle shearing. The second is that in the microstructure of region A, the laths appear to be both wider in size, and aligned in a particular orientation, whereas region B shows the more customary random orientation of the laths. If the microstructure in B resembles that of packets of martensite, the post-failure microstructure in A appears to have a more defined ‘blocky’ structure.

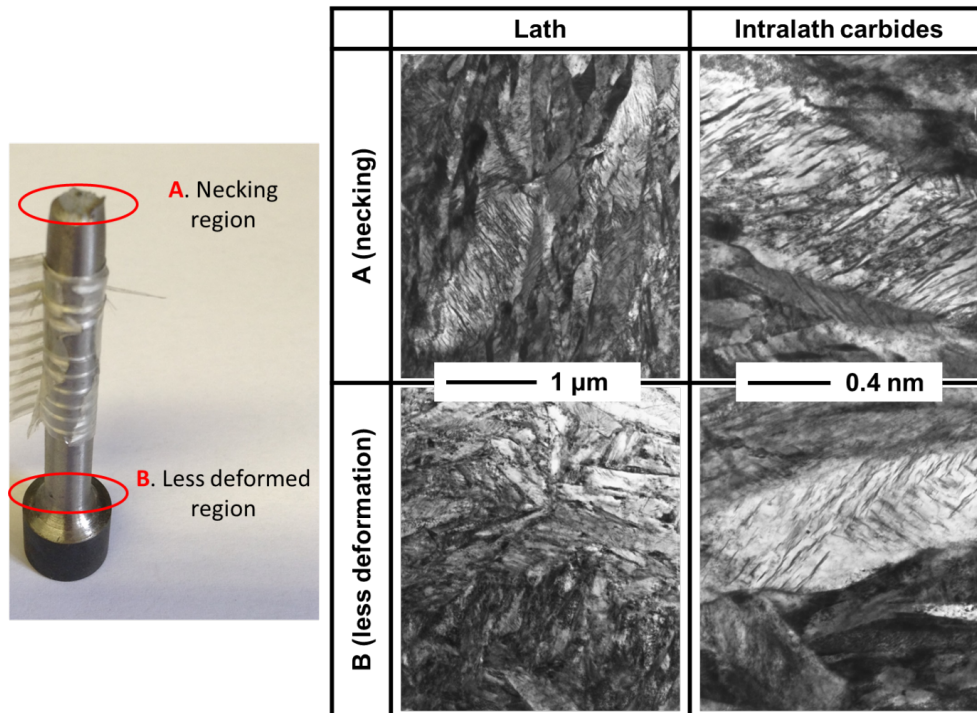


Figure 6.3: TEM micrographs for the HS-250 sample after failure.

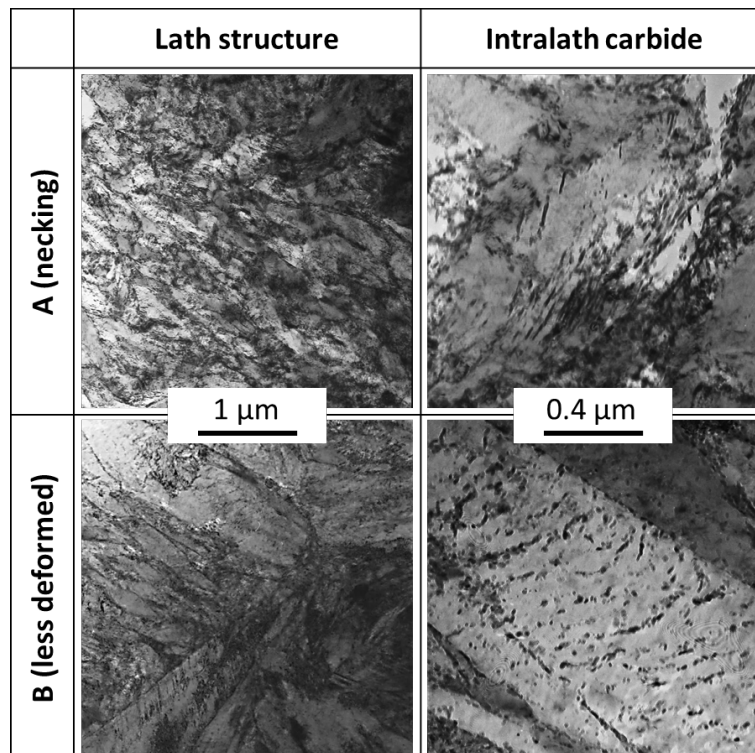


Figure 6.4: TEM micrographs for the HS-450 sample after failure.

The same analysis was carried out for HS-450, shown in Figure 6.4. Quite differ-

ent to the post-failure microstructure pattern observed in HS-250, when tempered at 450 °C, the ferrite laths at the localised necking region tend to form a random structure, with less-defined laths, almost adopting a cellular structure.

It is obvious to see that, despite the same chemical composition, under different tempering conditions a different failure mechanism operates, hinting on the progressive change in the effective grain size throughout tempering. Furthermore, the intralath carbides appear to remain intact during tensile loading; thus, particle by-passing is assumed. The original Orowan equation can be used to describe the degree of precipitation hardening:

$$\Delta\tau_p = 0.6Gb \frac{\sqrt{V_f}}{r}, \quad (6.5)$$

where $\Delta\tau_p$ is the shear strength increment due to precipitation hardening, r is the radius of the particles, and V_f is the volume fraction of the precipitate phase. However, the Orowan equation relies on the assumption that the particles are arranged on a square grid in the slip plane [57]. In order to allow a random dispersion of the particles, the Ashby-Orowan equation (6.6) has been chosen for modelling precipitation hardening, as the original Orowan equation leads to an overestimate of the hardening term, especially for small particle size [57]. This is illustrated in Figure 6.5.

$$\Delta\sigma_p = \left(\frac{0.538Gb\sqrt{V_f}}{X} \right) \ln \left(\frac{X}{2b} \right), \quad (6.6)$$

where X is the diameter of the particle, taken to be the equivalent spherical diameter of the rod-shaped intralath carbides.

Based on the information presented in §5.2.3, and using Equation (6.6), Table 6.2 summarises values for X and V_f , and the corresponding σ_p values for all conditions. Given the absence of data for the 450 °C condition, those for 400 °C are used, and instead a lower volume fraction is input.

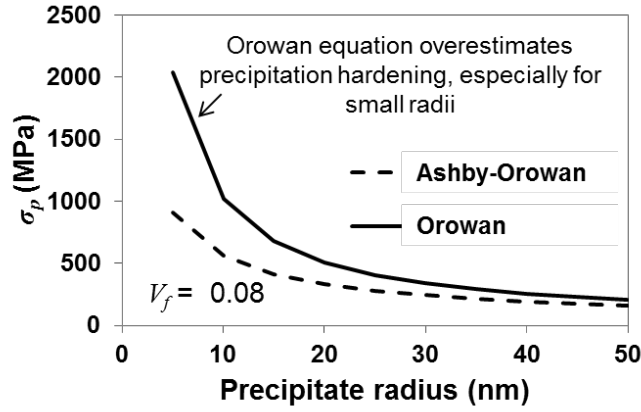


Figure 6.5: Comparison of the Orowan vs. Ashby-Orowan equations for precipitation hardening.

The values used for b were 2.483, 2.480 and 2.473 nm for alloys LS, MS and HS, respectively (Table 5.5). In the case of the shear modulus, Ghosh and Olson reported that in the case of lath microstructure, the high dislocation density decreases the shear modulus by $\sim 5\%$ compared to the cubic ferrite counterpart, thus $\mu_{\text{ferrite}} = 80$ GPa corresponds to $\mu_{\text{lath}} = 76$ GPa [116].

6.3.2 Solid solution strengthening, σ_s

Given the chemical composition of an alloy, the solid solution strengthening term can be obtained by empirical means [117]. The values obtained for HS, MS and LS are summarised in Table 6.3, where only the elements for which data are available are considered. Notice that the interstitial carbon content has a drastic effect on σ_s . For the sake of simplicity, the tetragonality is assumed to be 1, as most carbon would have precipitated during the 1800 s tempering. Attention is drawn to chromium. In literature, its effect in solid solution is still not clear, where some have reported contradictory effects [118, 119]. Kelley and Stoloff [119] have concluded that between 147 and 300 K, up to 10 wt.% Cr in high-purity iron has little effect on the yield strength, given the small atomic misfit between Cr and Fe, and their same bcc crystal structure. Therefore the effect of Cr has been omitted.

Table 6.2: Estimating precipitation hardening.

Condition	X ($2 \times r_{\text{equiv}}$) (mm)	V_f	$\Delta\sigma_p$ (MPa)
HS - 250	1.58×10^{-5}	0.08	628
HS - 350	1.40×10^{-5}	0.08	683
HS - 450	1.43×10^{-5}	0.05	540
MS - 250	1.38×10^{-5}	0.08	693
MS - 350	1.21×10^{-5}	0.08	757
MS - 450	1.35×10^{-5}	0.05	555
LS - 250	1.43×10^{-5}	0.08	676
LS - 350	1.31×10^{-5}	0.08	717
LS - 450	1.25×10^{-5}	0.05	586

Table 6.3: Estimating solid solution strengthening contribution [117].

Element i	$\Delta\sigma$ per 1 wt.% of i (MPa)	i wt. % in alloy	$\Delta\sigma_{s,i}$ (MPa)
C	5544	-	-
Si	83	2.3/1.7/1.4	190.9/141.1/116.2
Mn	32	0.7	22.4
Cr	-31	0.9	-27.9
Cu	39	0.15	5.85
Ni	0	0.2	0

6.3.3 Forest dislocation hardening, σ_ρ

The hardening contribution from dislocations can be estimated by the following:

$$\Delta\sigma_\rho = M\alpha Gb\sqrt{\rho}, \quad (6.7)$$

where M is the Taylor factor, taken to be 3, $\alpha = 0.25$, and ρ is the initial dislocation density following heat treatment. During the synchrotron measurements, only alloys HS and LS were characterised (Figure 5.20). The dislocation density for the MS is interpolated from the previous two values. Table 6.4 provides a summary of ρ and $\Delta\sigma_\rho$.

Table 6.4: Estimating forest dislocation hardening.

Condition	$\rho \times 10^{15} \text{ m}^{-2}$	$\Delta\sigma_\rho$ (MPa)
HS - 250	7.1	1184
HS - 350	4.4	939
HS - 450	3.8	866
MS - 250	6.8	1161
MS - 350	3.9	885
MS - 450	2.2	682
LS - 250	6.6	1150
LS - 350	3.7	856
LS - 450	1.6	568

6.3.4 Grain size effect

Substituting the numerical values into (6.4), the grain size effect contribution can be worked out by simple subtraction, as summarised in Table 6.5.

Table 6.5: Unaccounted stress: grain size effect.

Condition	σ_y (MPa)	σ_0 (MPa)	σ_p (MPa)	σ_s (MPa)	σ_ρ (MPa)	σ_{sg} (MPa)
HS - 250	2038 ± 2	54	628	219	1184	(46)
HS - 350	2039 ± 1	54	683	219	939	144
HS - 450	1602 ± 8	54	540	219	866	(77)
MS - 250	1991 ± 0.2	54	693	169	1161	(87)
MS - 350	1972 ± 3	54	757	169	885	106
MS - 450	1550 ± 4	54	555	169	682	89
LS - 250	1936 ± 52	54	676	144	1150	(88)
LS - 350	1916 ± 3	54	717	144	856	145
LS - 450	1511 ± 7	54	568	144	568	158

On Table 6.5, the values within brackets on the σ_{sg} represent negative values. Given that it has no physical meaning to have a negative stress contribution, an alternative σ_y expression is employed. Often, in plasticity modelling, the flow stress is given by [120]:

$$\tau = \tau_0 + \tau_s + \tau_b + \sqrt{\tau_{in}^2 + \tau_p^2}, \quad (6.8)$$

where τ is the shear stress, and the subscripts ‘b’ and ‘in’ refer to the kinematic and isotropic hardening, respectively. The former represents the long range back stress due to the pile-up of dislocations at the grain boundary, shown in Equation (6.9), where n is the number of pile-up dislocations and D is the ‘effective’ grain size; whereas, the latter is the contribution due to the dislocations in the grain interior, equivalent to the previously defined σ_ρ term, shown in Equation (6.10) [121, 122].

$$\tau_b = \frac{Gb}{D}n, \quad (6.9)$$

$$\tau_{in} = \alpha Gb\sqrt{\rho_{initial}}, \quad (6.10)$$

Therefore, an alternative expression for σ_y is:

$$\sigma_y = \sigma_0 + \sigma_s + \sigma_{sg} + \sqrt{\sigma_\rho^2 + \sigma_p^2}, \quad (6.11)$$

This form of expression, which relies in a quadratic mixture law, is also consistent with the observations made by Queyreau *et al.* [123], where they have evaluated both the individual and the superposed contribution of these two mechanisms. It is thought that these dislocations impinge on each other, while the rest of the terms remain additive. Applying (6.11), a new set of σ_{sg} values are obtained, summarised in Table 6.6 and illustrated in Figure 6.6.

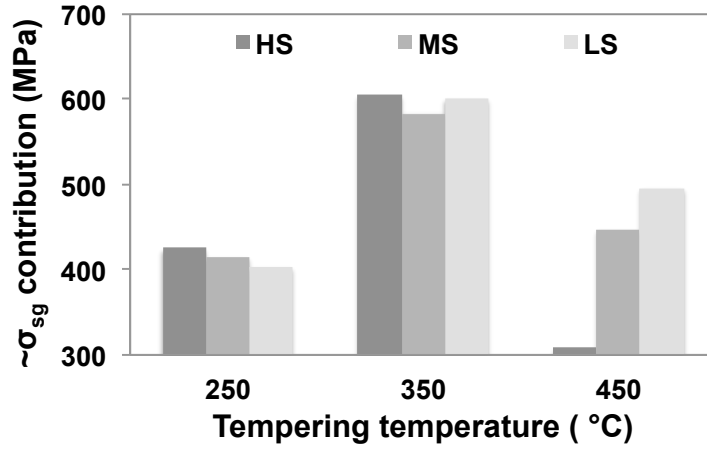


Figure 6.6: Estimated contribution of the σ_{sg} term throughout tempering.

Table 6.6: Unaccounted stress: grain size effect.

Condition	σ_y (MPa)	$\sigma_0 + \sigma_s + \sqrt{\sigma_p^2 + \sigma_{\rho}^2}$ (MPa)	σ_{sg} (MPa)
HS - 250	2038	1585	425
HS - 350	2039	1406	605
HS - 450	1602	1265	309
MS - 250	1991	1548	415
MS - 350	1972	1360	584
MS - 450	1550	868	447
LS - 250	1936	1504	404
LS - 350	1916	1287	601
LS - 450	1511	987	496

The following section looks into the grain size effect, in order to understand the trends observed in Figure 6.6.

Carbon in solid solution

Given the strong effect that carbon has on solid solution strengthening (Table 6.3), it deserves further attention. During the XRD peak analysis of the model alloy which contained the same carbon content (Fe-0.55C-2.0Si wt.%), it showed that after 1800 s tempering at 250 °C, the ferritic phase remained tetragonal ($c/a = 1.005$), while at 300 °C and higher tempering conditions, the tetragonality reduced to 1.

From Equation 4.12, it can be estimated that a tetragonality of 1.005 corresponds to 0.11 wt.% C in solid solution. Substituting this value into Table 6.3, the strength increment corresponding to the carbon alone would be of 610 MPa. This value appears to be rather high, as it would account for almost 30 % of the experimental σ_y . Furthermore, taking HS-250 as an example, incorporating the effect of the carbon in solid solution in Equations (6.4) and (6.11) would give $\sigma_{sg} = -656$ and -185 MPa, respectively.

It is also possible that the reported value of 5544 MPa per 1 wt.% C is an overestimate. Capturing the effects of carbon in ferrite is challenging, as finding the isolated solid solution effect without interference from neighbouring carbides, grain boundaries and dislocation will be difficult. Therefore, although modelling the strengthening effect of carbon in solid solution is crucial, currently, challenges remain in determining the exact carbon concentration in pure solid solution, as well as determining an accurate value of $\Delta\sigma$ per 1 wt.% C.

Expressions for grain size effect

The widely-accepted Hall-Petch effect shows that the increase in strength is inversely proportional to the square root of the grain size, d :

$$\Delta\sigma_y \propto \frac{1}{\sqrt{d}}, \quad (6.12)$$

However, in lath martensitic steels containing 9–12% Cr, Ghassemi-Armaki *et al.* [124] have made use of the following expression for subgrain boundary hardening:

$$\sigma_{\text{sg}} = \frac{10Gb}{\lambda_{\text{lath}}}, \quad (6.13)$$

where λ_{lath} is the width of the elongated subgrains, referring to individual laths, typically reported to be 0.3–0.5 μm in this family of steels. Applying (6.13), a value for σ_{sg} in the range of 530–320 MPa was obtained. Based on this, they had concluded that the contribution from the lath boundaries was predominant in martensite, even over the precipitation hardening term.

Daigne *et al.* [125] based their work in a much simplified version of Equation (6.4), where the σ_ρ term was omitted. Basing their work on a Fe–0.4C–0.2Si–0.9Mn–0.1Ni–0.2Cr wt.% alloy, their proposed expression for the σ_y (MPa) was:

$$\sigma_y = 290 + \frac{116}{w_{\text{lath}}} + \frac{61}{L}, \quad (6.14)$$

where w_{lath} is the lath width (μm) and L is the average distance between a precipitate and its near neighbours, which according to Kocks's [126] formulation, is determined by:

$$L = 1.18r \left(\frac{2\pi}{3V_f} \right)^{\frac{1}{2}}, \quad (6.15)$$

where r and V_f are the radius and volume fraction, respectively, of precipitates.

What becomes obvious is that grain size hardening is inversely proportional to grain size. In Chapter 5, it was observed that the average lath width increased with increasing tempering temperature. This was explained in terms of the martensite recovery process. Observing the changes from 250 to 350 °C in Figure 6.6, despite the apparent increase in the lath width observed in TEM with increasing temperature, rather counterintuitively, the grain size effect contribution also increases, albeit the decrease in the overall σ_y . This is worth further consideration.

For better visualisation, the percentage strengthening contributions from each of the terms are summarised in Figure 6.7. As tempering temperature increases, there appears to be a net decrease in the combined effect of forest dislocation and precipitation hardening, and consequently, the grain size effect gains importance.

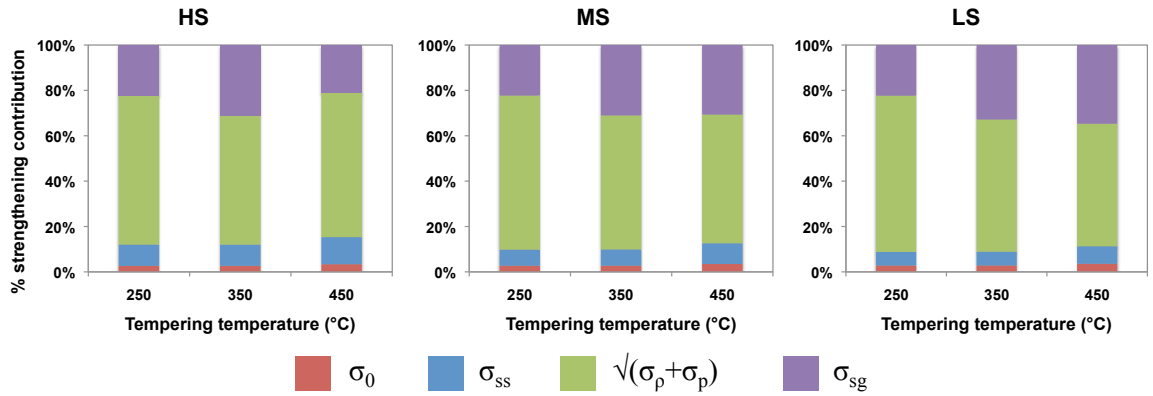


Figure 6.7: Percent strengthening contribution as a function of tempering temperature and silicon content.

If one were to suppose that the width of individual martensitic laths acts as the ‘effective’ grain size, then it will fail to explain the increasing grain size effect

with tempering temperature between 250 and 350 °C. Given that usually the grain size strengthening effect is inversely proportional to the grain size, the increase in lath width observed experimentally will not explain the simultaneous increase in the grain size effect.

When increasing the tempering temperature from 350 to 450 °C, there is a reduction in the σ_{sg} term. The decrease in strength can be explained by the increasing lath size, which is the case as observed by TEM. However, the increase in σ_{sg} contribution from 250 to 350 °C cannot be explained by the present TEM results.

In understanding the σ_{sg} contribution, one approach is by characterising the nature of the grain boundaries within the material. EBSD would be a suitable technique, as the characterisation and location of high and low angle boundaries, based on the misorientation angle between adjacent grains, could provide some clues. Generally, it is thought that low angle boundaries are considered to be transparent to dislocation motion, whereas high angle boundaries tend to hinder dislocation motion. By using a specific misorientation angle as the criterion for the ‘effective’ grain boundary, it would be possible to determine the effective grain size.

Now that most of the strengthening contributions have been determined, the second part of this chapter aims at reproducing the stress-strain curves that were obtained experimentally.

6.4 Brief introduction to plasticity theory

Considerable amount of work on plasticity modelling can be found in literature. For instance, Fribourg *et al.* developed a model for precipitation hardening in aluminium alloys, where they have modelled Orowan loop storage in precipitates [127].

For ultrafine grains, Huang *et al.* [122] have developed a model based on irreversible thermodynamics. For the detailed specifics, their original work is referred. Previously, it was defined that the yield strength of the alloy can be expressed in

terms of additive terms. In determining the flow stress, Huang *et al.* modelled the evolution of the terms n and ρ in Equations (6.9) and (6.10), respectively, during plastic deformation.

6.4.1 Kinematic hardening

During plastic deformation, as dislocations pile-up at the boundary, the value of n in the kinematic hardening expression in Equation (6.9) is bound to change. The evolution of n with respect to the applied plastic shear strain, γ_p , is given by:

$$\frac{dn}{d\gamma_p} = \frac{\lambda_{\text{slip}}}{b} \left(1 - \frac{n}{n^*} \right), \quad (6.16)$$

where λ_{slip} is the mean spacing between slip planes at the grain boundaries, and n^* is the maximum number of dislocations that can pile up at the grain boundary on a given slip plane. Beyond this number, the accumulated stress is large enough for climb or cross-slip to occur. N.B. in order to distinguish the austenite phase, γ , used in earlier chapters with the shear strain, the latter is accompanied by a subscript ‘p’.

By combining Equations (6.9) and (6.16) and integrating whilst assuming $n=0$ when $\gamma_p=0$, the kinematic hardening term becomes:

$$\tau_b = \frac{Gb}{D} n^* \left[1 - \exp \left(- \frac{\lambda_{\text{slip}}}{bn^*} \gamma_p \right) \right], \quad (6.17)$$

The correct use of n^* value is crucial. In interstitial free steels, this value was between 3 and 4 [122], although in precipitation-hardened aluminium steels, this value was found to be 9 and 60 for the 7xxx and 6xxx alloys, respectively [127, 128].

In order to obtain an estimate value for D , Equation (6.13) can be applied using σ_{sg} values. Most values lie within the 309–605 MPa range, which would correspond to an average value of $D \approx 0.4 \mu\text{m}$. Although this is a crude approximation, it serves as a starting point in obtaining the right order of magnitude.

6.4.2 Isotropic hardening

Much work has been carried out in defining the evolution of the dislocation density with shear strain, $\frac{d\rho}{d\gamma_p}$, mostly originally based on the Kocks-Mecking approach:

$$\frac{d\rho}{d\gamma_p} = \frac{k_1}{b} \sqrt{\rho} - k_2 \rho, \quad (6.18)$$

where k_1 is the storage coefficient and f is the dynamic recovery term.

During plastic deformation, the following cases must be considered regarding dislocations: generation, glide along slip systems and annihilation. The change in entropy due to these processes is given by:

$$d_i S = \frac{dW_{ge}}{T} + \frac{dW_{gl}}{T} + \frac{dW_{an}}{T}, \quad (6.19)$$

where dW_{ge} , dW_{gl} and dW_{an} are the energies dissipated due to the processes of dislocation generation, glide and annihilation, respectively.

Based on the theory of irreversible thermodynamics, Huang *et al.* [122] derived an expression for the change in entropy during plastic deformation in terms of dislocation density:

$$dS = \frac{1}{T} \left[\mu b^2 + \frac{\tau b}{(\rho_{in})^{1/2}} \right] d\rho_{in} + \frac{1}{T} \left[\mu b^2 + \frac{\tau b}{(\rho_{in})^{1/2}} \right] \frac{\nu_0}{\dot{\gamma}_p} \exp\left(-\frac{\Delta G}{k_B T}\right) d\rho_{in} d\gamma - \frac{1}{T} (\tau d\gamma), \quad (6.20)$$

where ν_0 is the atomic vibration frequency, ΔG is the effective activation energy for dislocation annihilation.

Rivera-Díaz-del-Castillo and Huang [129] showed that the entropy is related to the shear stress by a proportionality constant C :

$$dS = \left(\frac{C}{T}\right) \left(\frac{b}{l}\right) d\tau_{in}, \quad (6.21)$$

where l is the average distance between dislocations. Thus Equation (6.21) becomes:

$$dS = \frac{Cb}{T} \rho_{\text{in}}^{1/2} d\tau_{\text{in}}, \quad (6.22)$$

From the Taylor relation (Equation (6.10)), the evolution of τ_{in} with shear strain can be written with constant α as $\frac{d\tau_{\text{in}}}{d\gamma} = \left(\frac{\alpha\mu b}{2\rho_{\text{in}}^{1/2}}\right) \left(\frac{d\rho_{\text{in}}}{d\gamma}\right)$, an expression for the evolution of ρ is obtained, where the effects of precipitation hardening has also been incorporated [120]:

$$\frac{d\rho}{d\gamma_p} = \frac{1}{1 + \left(\frac{\tau}{Gb\sqrt{\rho}}\right) - \frac{1}{2}C\alpha_c} \left[\frac{\sqrt{\tau_{\text{in}}^2 + \tau_p^2}}{Gb^2} - \left(1 + \frac{\tau_b}{Gb\sqrt{\rho}}\right) \frac{\nu_0}{\dot{\gamma}_p} \exp\left(-\frac{\Delta G}{k_B T}\right) \right] \rho, \quad (6.23)$$

where C and α_c are material constants, which were taken from the literature to be -100 and 0.25 , respectively, and ΔG is the effective activation energy for dislocation annihilation accounting for the average of the activation energies for dislocation climb or cross-slip, which was taken to be 0.766 eV [122]. k and T are the Boltzmann constant and the absolute temperature, respectively, and $\dot{\gamma}$ is the shear strain rate, taken to be 0.002 s^{-1} for the following set of calculations.

6.4.3 Example 1: HS-250 condition

The first step, was to convert the engineering stress-strain values obtained from the tensile tests into true stress-strain values. As this model is only concerned with the plastic behaviour of steels, it was necessary to modify the kinematic strengthening term in Equation (6.17). The reason being that at the beginning of the plastic deformation, i.e. when $\gamma_p = 0$, this would give $\tau_b = 0$. However, up to the yielding point, there is already some contribution from the ‘effective’ grain size, which was determined by σ_{sg} in §6.3.4 earlier on. Therefore in order to carry this term forward,

the following is proposed:

$$\tau_b = \tau_{b,0} + \frac{Gb}{D} n^* \left[1 - \exp \left(- \frac{\lambda}{bn^*} \gamma_s \right) \right], \quad (6.24)$$

where $\tau_{b,0}$ would be the equivalent shear stress for the σ_{sg} obtained previously, and has been treated as a constant.

Considère's criterion: necking

It is a widely established concept that the onset for necking begins when the following condition is achieved, which is known as the Considère's criterion:

$$\sigma = \frac{d\sigma}{d\epsilon}, \quad (6.25)$$

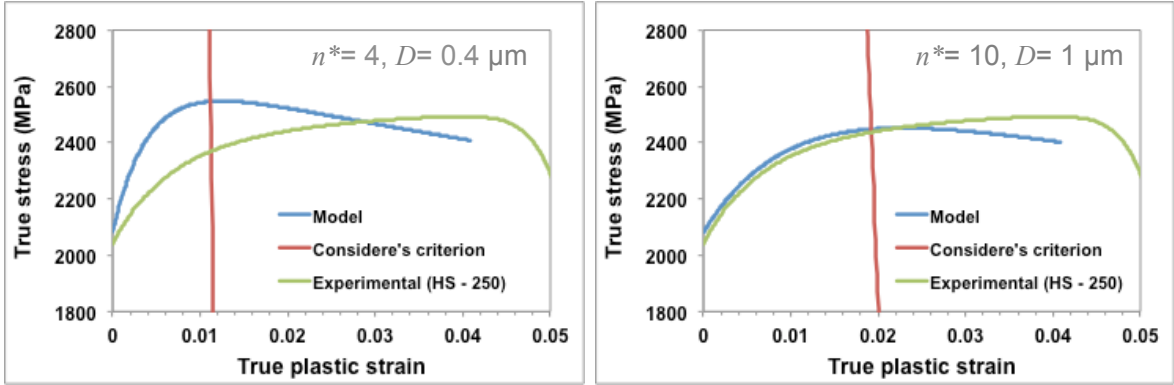


Figure 6.8: Modelling plasticity for the HS-250 condition, where different parameters have been used.

All the parameters that were obtained experimentally have been used as input to the model. Figure 6.8 shows preliminary fittings made for the HS-250 condition. On the left panel, the initial values of $n^* = 4$ and $D = 0.4 \mu\text{m}$ were used. However, the shape of the tensile curves do not match. Furthermore, Considère's criterion predicts very early necking. These two parameters were changed, as shown on the right panel, to $n^* = 10$ and $D = 1 \mu\text{m}$, and a better fitting was obtained. D appears to be rather high, thus EBSD would be a very useful technique in evaluating the 'effective' grain size. Nevertheless, a better fit with respect to the experimental data

is obtained.

The failed region (that underwent necking) was observed for this particular condition, using an F20 Tecnai FEG-TEM (a higher resolution TEM), operated at 200 kV, under STEM mode. Zoomed regions are shown in Figure 6.9. The light region represents an individual lath, where piled-up dislocations are clearly visible at the lath boundary.

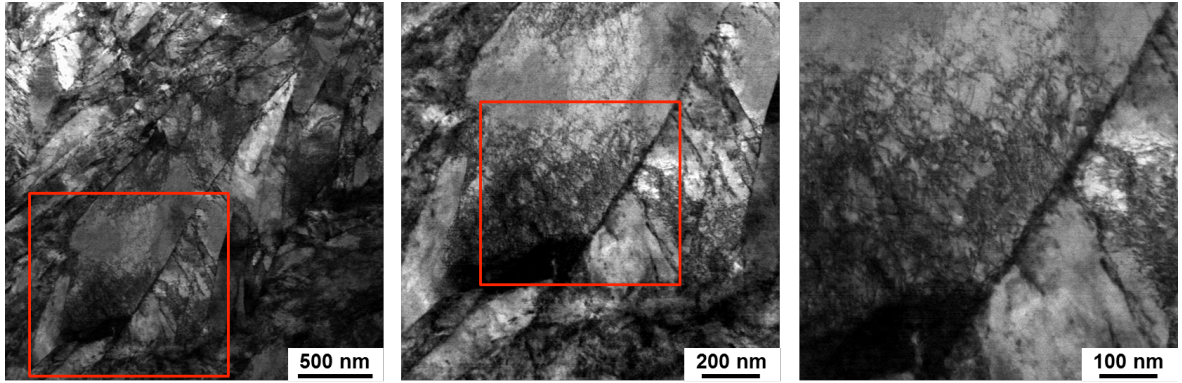


Figure 6.9: HRTEM images showing piled-up dislocations at lath boundaries on a sample failed by necking.

6.4.4 Example 2: HS-450 condition

The same parameters as in Figure 6.8 were applied to the HS-450 condition, as shown in Figure 6.10. The first set of results were obtained using $n^* = 10$ and $D = 1 \mu\text{m}$. However, the model overestimated the strengthening, therefore a larger grain size was used, $D = 1.5 \mu\text{m}$. Although a better fit was obtained, when Considère's criterion was applied, early necking was predicted. By increasing n^* to 12, the fit was improved.

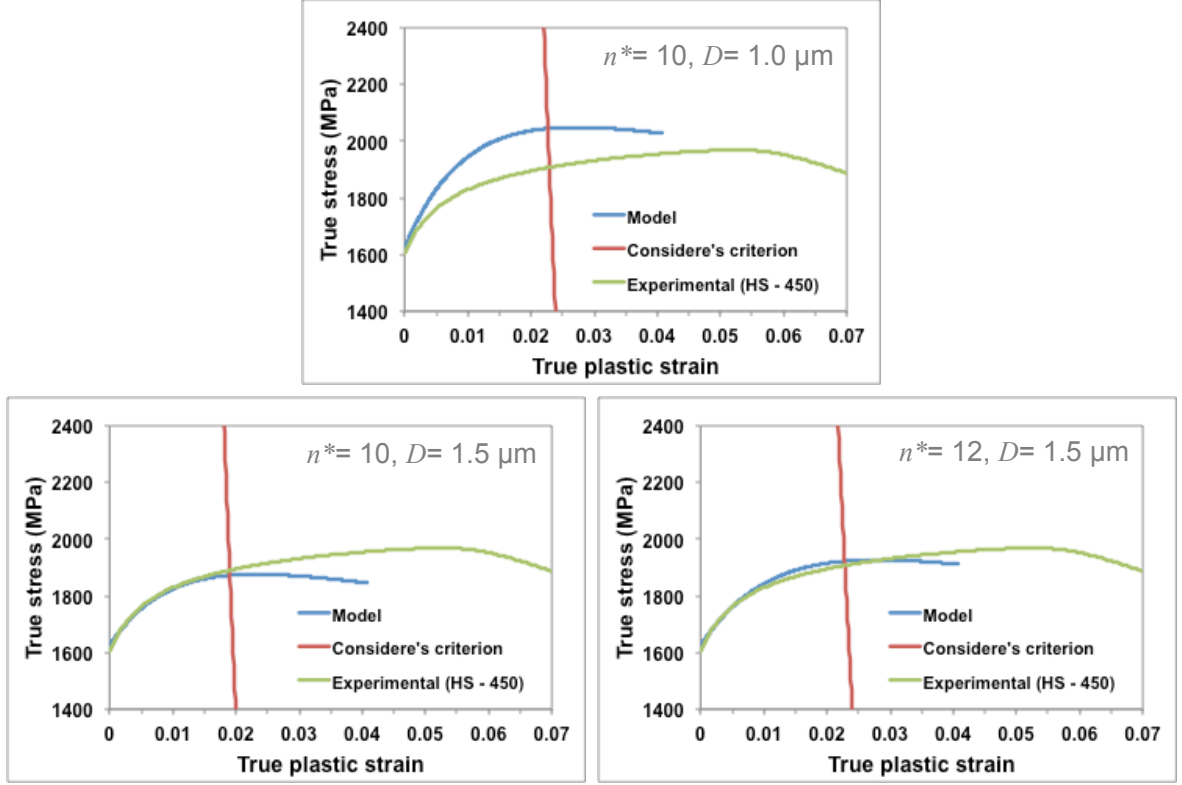


Figure 6.10: Modelling plasticity for the HS - 450 condition.

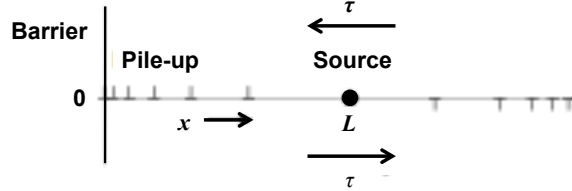


Figure 6.11: Illustration of dislocations pile-up against barriers, after Hull and Bacon, [130].

During plastic deformation, as dislocations are generated from sources within grains (Figure 6.11), the number of dislocation pile-ups is given by [130]:

$$n = \frac{L\tau}{A}, \quad (6.26)$$

where L is the distance between the source and the boundary, and the x in the diagram defines the pile-up spreading region, $0 \leq x \leq L$. A is $\frac{Gb}{\pi}$ or $\frac{Gb}{\pi(1-\nu)}$ for screw and edge dislocations, respectively.

If the assumption is made that the dislocation generation source is located in the middle of the grain, then it might be possible to state that for a bigger grain size, i.e. a larger L value, the higher the n is. In other words, larger grains might be able to retain more dislocations, increasing the value of n^* . Therefore, it appears that n^* increases with increasing D .

6.4.5 Example 3: LS alloy

The model was also applied to the lower silicon alloy. The values for n^* and D were adjusted until a reasonable fit was obtained.

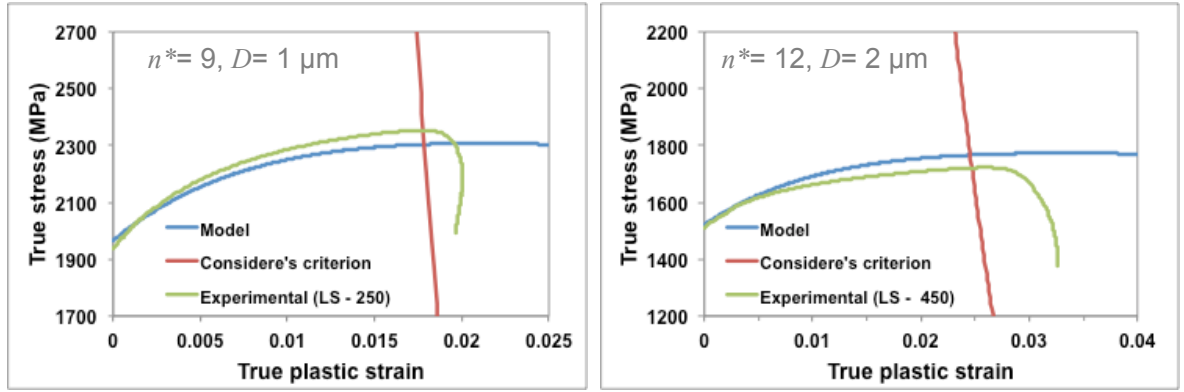


Figure 6.12: Model applied to LS alloys.

For the LS-250 condition, $n^*=9$ and $D=1 \mu\text{m}$, while these values increased to 12 and $2 \mu\text{m}$, respectively, for the LS-450 condition.

If a comparative study is made between HS and LS for the different tempering conditions, it appears that the increase in the ‘effective’ grain size, D , is bigger in the LS than in the HS alloy case. Relating this observation back to the findings in Chapter 5, this could be explained in terms of the recovery process being slowed down in the presence of silicon.

Although this model still remains at a preliminary stage, where there are still other refinable values that need to be adjusted, such as λ_{slip} and ΔG as a function of chemical composition, for instance, the plasticity model reinforces the effect of silicon on the different strengthening contributions in tempered martensite.

6.5 Grain size study by EBSD

Hutchinson *et al.* carried out a grain size study for as-quenched martensite using EBSD techniques [65]. Figure 6.13 (a) shows EBSD maps for four different steels, where the black continuous lines represent the PAG boundary (defined by a misorientation angle of 45°). The misorientation distributions of grain boundaries for all steels are summarised in Figure 6.13 (b).

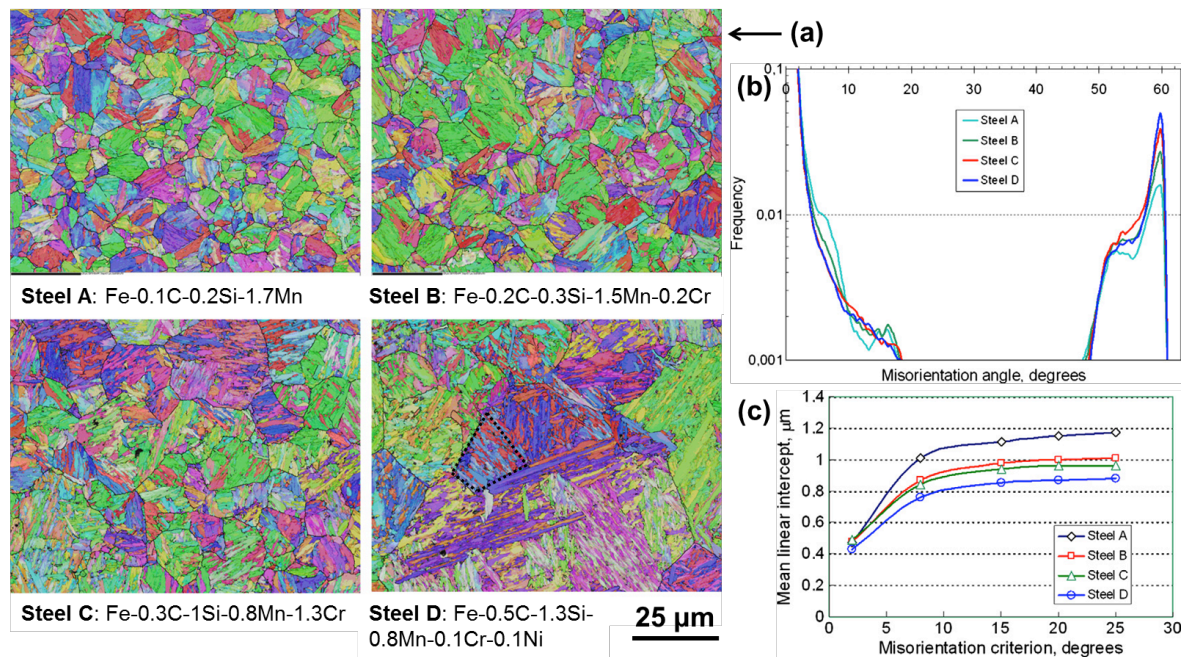


Figure 6.13: Misorientation angles in as-quenched martensite for four different chemical composition steels, after Hutchinson *et al.* [65].

On their analysis, Hutchinson *et al.* showed that ‘block’ structure formation becomes more prominent with increasing carbon content, as shown in Figure 6.13 (a). Based on their description, a packet structure has been highlighted by the black dotted line in Figure 6.13 for steel D, which consists of several blocks of alternating colours.

The increasing complexity of the lath martensite microstructure with increasing carbon content poses a challenge in determining the grain size needed for predicting

mechanical behaviour. One way of estimating the grain size is by considering the misorientation angle between adjacent grains, as generally, the high angle boundaries are likely to inhibit dislocation motion, while low angle boundaries remain transparent to dislocations.

Figure 6.13 (c) shows the variation in the grain size as a function of the misorientation angle, which has been used as a criterion for defining grain boundaries. According to this figure, for an as-quenched medium carbon steel the grain size is likely to be between 0.4 and 1 μm . However, as tempering progresses, and recovery of the matrix phase takes place, these values will change.

EBSD has proven to be a powerful analytical technique, as it allows mapping of the misorientation angles between grains. The grain boundary angle can then be used to estimate the effective grain size. Therefore, the aim of the EBSD work was to measure the grain size evolution throughout martensite tempering under the influence of silicon. Previously, in Chapter 5, the individual laths were found to be in the range of $\sim 0.1 \mu\text{m}$. However, given the nature of martensite microstructure, it is unlikely that the individual laths contribute significantly to grain boundary strengthening. Thus, using the misorientation angle as a criterion, ‘larger’ microstructural units will be considered.

6.5.1 Experimental procedure¹

The samples that were previously used for lab-based XRD in Chapter 5, were cut into four square sections of $10 \times 10 \times 1 \text{ mm}^3$. The samples analysed were: HS-250, HS-450, LS-250 and LS-450. Samples HS-250, HS-450 and LS-250 were prepared to an OPS colloidal silica finish, whereas another sample of LS-250 and LS-450 were electrolytically etched (40 V for 12 s).

¹This work has been carried out in collaboration with Elodie Boucard and Nathalie Gey (Université de Lorraine), and Thomas Sourmail (ASCOMetal).

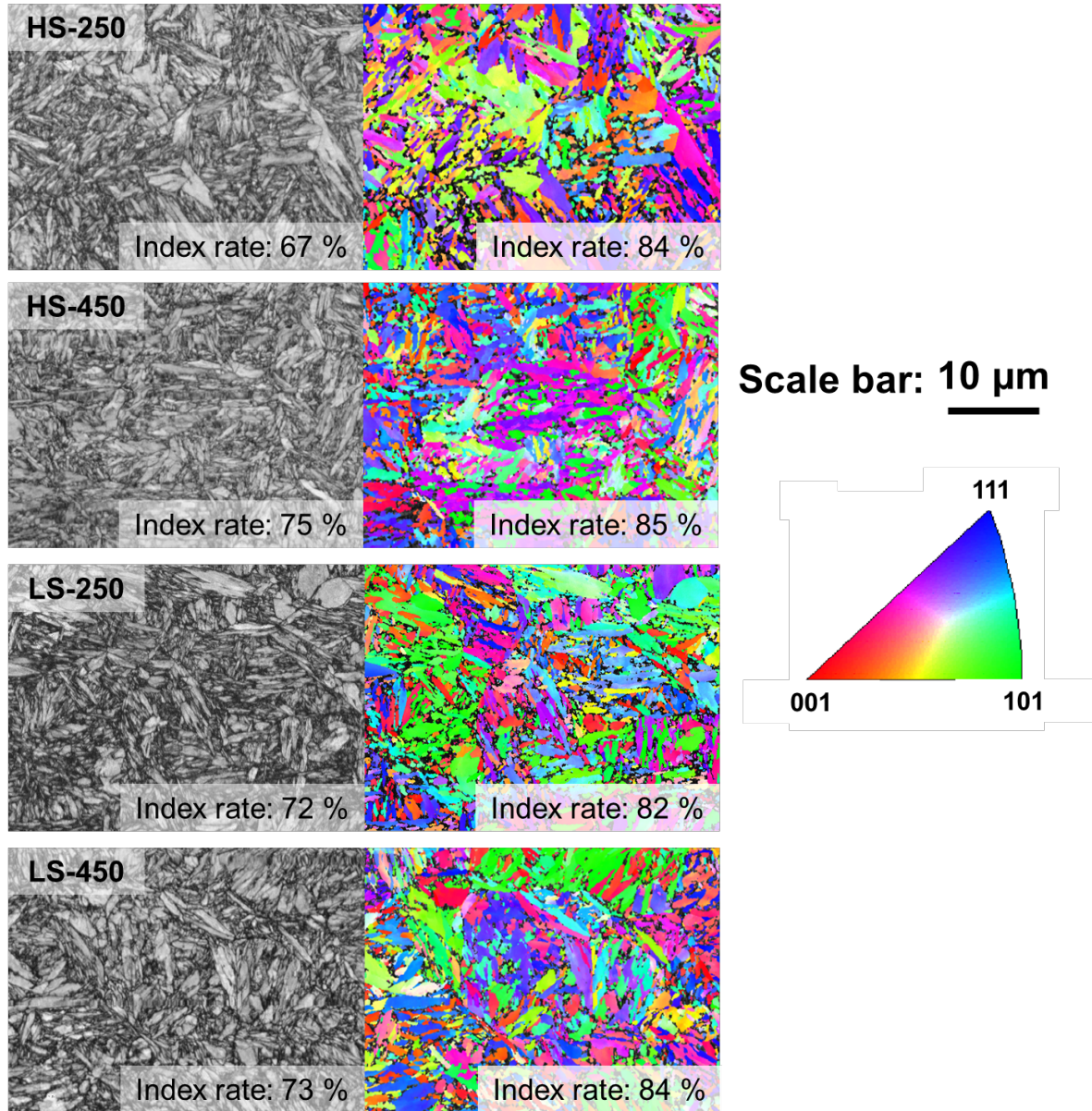


Figure 6.14: IQ and IPF images (after some cleaning) for all samples.

The EBSD patterns were acquired using a Zeiss SUPRA40 SEM. All measurements were done with the Channel 5 system (Oxford Instrument), operated at an accelerating voltage of 20 kV. The step size used varied between 50 and 75 nm. The image quality (IQ), or band contrast (BC), maps are shown in Figure 6.14, where the initial index rate at the moment of acquisition is shown for each sample (NB. LS-250 prepared by electropolishing gave a poor index rate of 47%, therefore the sample prepared using OPS is considered from here onwards). The inverse pole

figure (IPF) maps are also shown after some cleaning. Cleaning is a noise reduction process, where non-indexed regions are assigned a crystallographic orientation based on that of their neighbouring grains, hence artificially increasing the index rate. Some non-indexed regions still remain, shown as black regions on the IPF maps.

6.5.2 Grain size determination based on misorientation angle

Post-processing of the data has been carried out in Tango (HKL Channel 5). Using the software, a histogram plot of the misorientation angle, φ , can be obtained. The histograms for all samples are shown in Figure 6.15 (this histogram has been obtained after a first correction has been applied). The results follow the same trend as those reported by Hutchinson *et al.* where most angles are in the range of 5–15°, and in the range of $\varphi > 45^\circ$. The peaks in the region of 54–60° is characteristic of certain orientation relationships between austenite and martensite, such as Nishiyama-Wassermann and Kurdjumov-Sachs [10, 65].

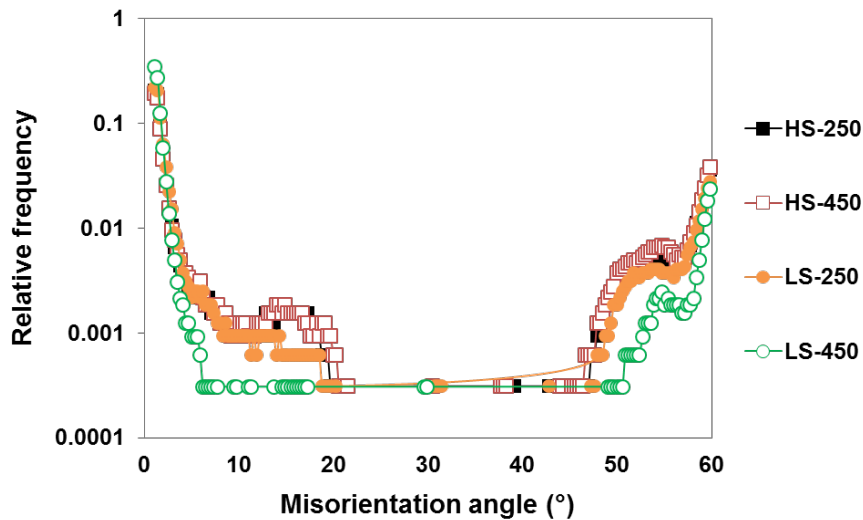


Figure 6.15: Histogram plotting frequency of misorientation angle

It is worth noting that HS-250 and HS-450 overlap at all angles. When comparing

HS-250 and LS-250, the main difference is observed in the range of $20 < \varphi < 30^\circ$. In the case of LS-450, most angles are either $5 < \varphi < 10^\circ$, and at $\varphi > 50^\circ$. Most angles are found at $\varphi < 10^\circ$ and $\varphi > 50^\circ$, with almost no misorientation angles in the middle. This gives further supporting evidence on the retarding effect silicon plays during martensite recovery.

There are two methods of measuring grain size: linear intercept and grain area. Before taking size measurements, the first step was to define the criterion for a grain boundary based on the misorientation between two adjacent grains. Morito *et al.* showed that lath boundaries have a misorientation angle, φ of $2.8\text{--}2.9^\circ$, whereas sub-blocks boundaries had a characteristic value of 6° [10]. Given that the EBSD resolution limit is of 5° , this technique is not ideal for characterising individual laths. However, it is a useful technique for determining other structures in martensite.

Having defined the criterion for a grain boundary based on the misorientation, the second step was to correct for noise reduction, artificially increasing the index rate. This was done iteratively, until the index rate approached $\sim 100\%$. This was a necessary step, since the non-indexed regions would be interpreted as an intercept and count as a separate grain. Therefore in order to overcome with this problem, the index rate was artificially increased to $\sim 100\%$, as shown in Figure 6.16.

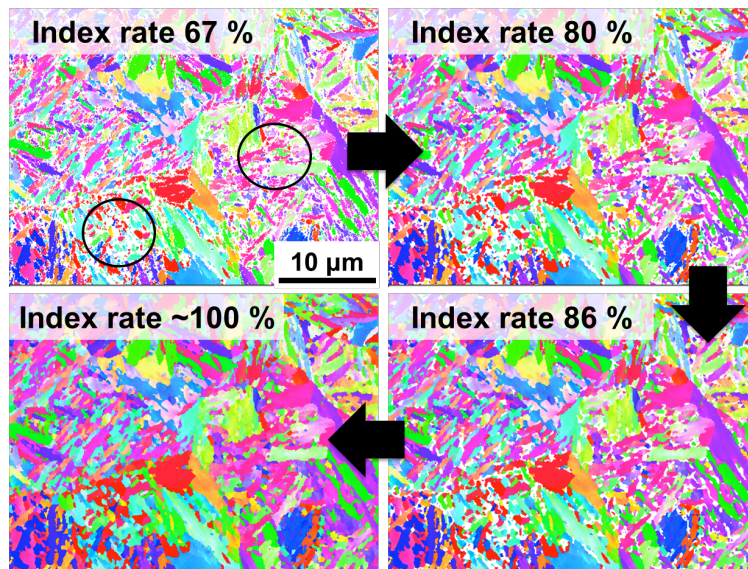


Figure 6.16: Sequence of noise reduction.

Linear intercept method

This particular method has its drawback, as it is sensitive to how the measurements are taken. For instance, the grain size results are dependent on the number of intercept lines drawn and their orientation. Table 6.7 summarises the differences observed in the average grain size for HS-250.

Table 6.7: Disparity in mean grain size ($\varphi = 5^\circ$, index rate 67 %).

	No. of lines= 6	No. of lines= 10
Horizontal lines	0.72 μm	0.69 μm
Vertical lines	0.79 μm	0.77 μm

Values can fluctuate $\sim 0.1 \mu\text{m}$ when using the linear intercept method, perhaps due to the highly irregular shapes. Nevertheless, in order to obtain approximate values, the average grain size is summarised in Figure 6.17, where 10 horizontal lines were drawn, on IPF maps with index rate $\sim 100 \%$.

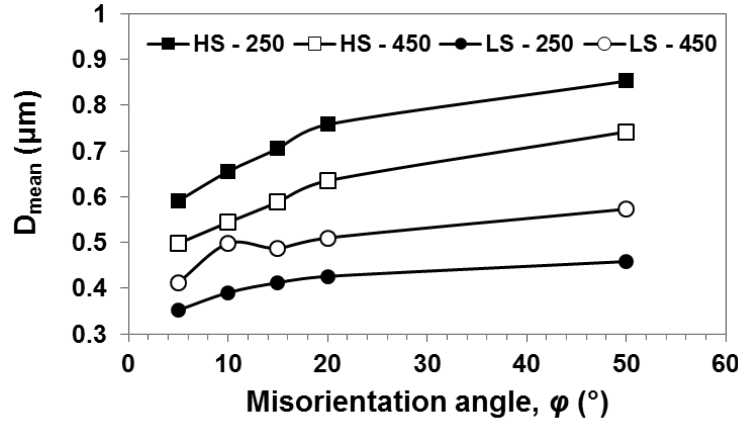


Figure 6.17: Average grain size based on φ using the linear intercept method.

Notice that the trend observed in Figure 6.17 contradict the trends observed by TEM and plasticity modelling. Throughout tempering, as martensite recovery takes place, a larger grain size is expected at higher tempering conditions. Furthermore, this increase is expected to be less with increasing silicon content. However, the

results in Figure 6.17 showed smaller grain sizes for LS than for HS.

The values of D_{mean} between $\varphi = 20$ and 50° are smaller than expected, especially when considering that $\varphi = 45^\circ$ corresponds to prior austenite grain boundaries [65], which are likely to be one order of magnitude greater than the value predicted by the linear intercept method.

Grain area method

An alternative method of measuring grain size in Tango is by the ‘detect grain’ function. The equivalent grain diameter is extracted from the measured area. Figure 6.16 showed that, as image correction is applied, grain size overestimation occurs. Bearing this in mind, two sets of measurements have been taken: before correction and after correction (index rate $\sim 100\%$). The former, is taken to be the lower limit, whereas the latter would represent the upper limit; the actual value being within these limits.

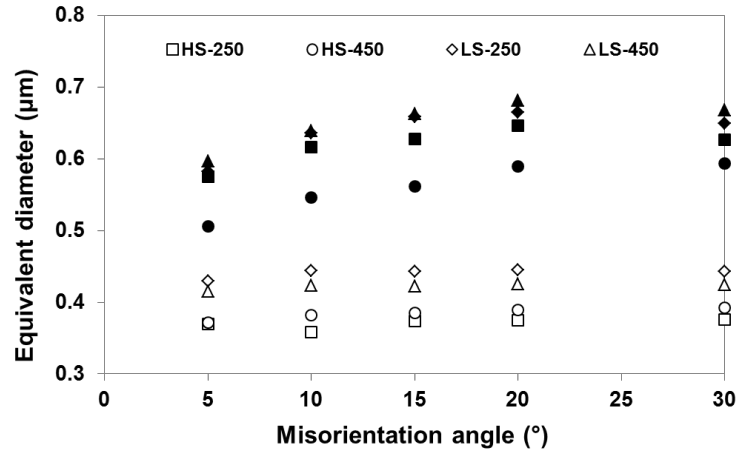


Figure 6.18: Grain size measurement by ‘detect grain’ method in Tango, where the filled markers represent the upper boundary and the open markers show the lower boundary for grain size measurements.

From Figure 6.18, it appears that for HS, the grain size actually decreases with increasing tempering temperature, and that for LS, grain size does not vary much throughout tempering. These are in contradiction with the trend observed from

plasticity modelling. The two methods for measuring grain size are compared in Table 6.8 for $\varphi > 15^\circ$. It is reported in the literature that the transition between low to high angle boundary is in the region of $10\text{--}20^\circ$, with 15° being generally accepted as the threshold [131, 132].

Table 6.8: Differences observed in grain size ($\varphi > 15^\circ$).

	Grain area method	Linear intercept method
HS-250	$0.37 - 0.58 \text{ }\mu\text{m}$	$0.71 \text{ }\mu\text{m}$
HS-450	$0.38 - 0.56 \text{ }\mu\text{m}$	$0.59 \text{ }\mu\text{m}$
LS-250	$0.44 - 0.66 \text{ }\mu\text{m}$	$0.41 \text{ }\mu\text{m}$
LS-450	$0.42 - 0.66 \text{ }\mu\text{m}$	$0.49 \text{ }\mu\text{m}$

Except for HS-250, the values obtained from the linear intercept method fall close to the range obtained by the grain area method. Also, notice that in all cases, the average grain size is below the $1 \text{ }\mu\text{m}$ value predicted by the plasticity model. A possible reason for the significantly smaller grain size measured by EBSD is the irregularity of the shapes observed in 2D. The results presented here are average values, and the presence of numerous smaller grains will substantially decrease the average value.

D and n^*

Having determined D from the EBSD measurements, the values were plotted back into the plasticity model, where only the value of n^* was adjusted. The values obtained by the linear intercept method were used from Table 6.8. The plots are summarised in Figure 6.19. Compared to the previous Figures 6.8, 6.10 and 6.12, the fitting between the model and the experimental curve is not improved by using the D values obtained from EBSD.

The slight disagreement observed between the EBSD values and the model will be commented. Although questions remain on the validity of the parameters used in the

model (§6.4.5), the EBSD results are counterintuitive. In the HS alloys, as tempering temperature increases, one would expect an increase in grain size. Nevertheless, D was seen to drop from 0.71 to 0.59 μm when the temperature increased from 250 to 450 $^{\circ}\text{C}$. Furthermore, as explored in Chapter 5, silicon is thought to decrease the rate of recovery, thus a bigger grain size is expected in the LS alloy.

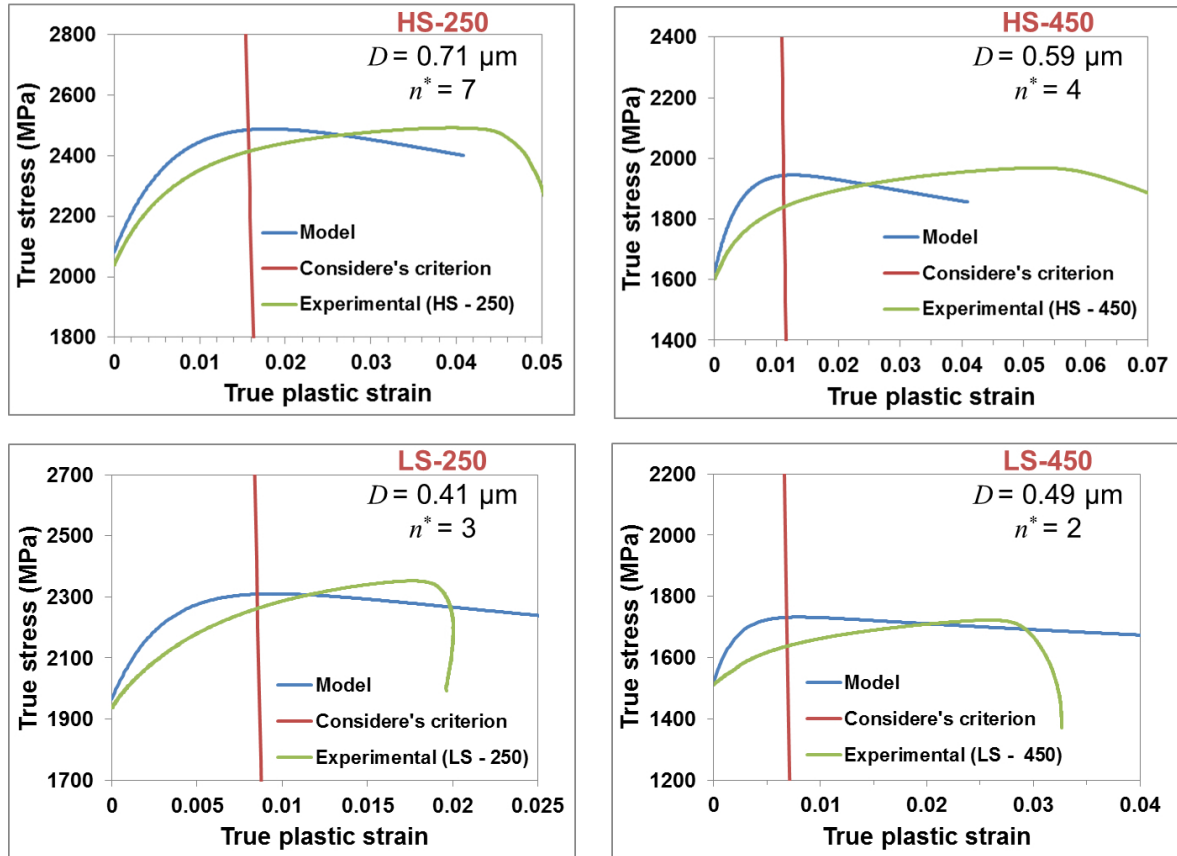


Figure 6.19: PAG boundaries revealed by thermal etching.

Prior austenite grain size

Using the same procedure as in Chapter 3, the prior austenite grain (PAG) size was revealed by the method of thermal etching. Figure 6.20 shows representative micrographs obtained for all three alloys.

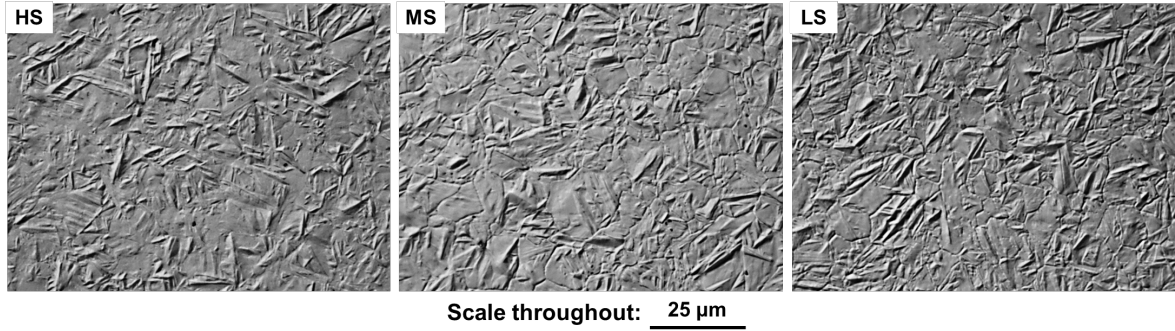


Figure 6.20: PAG boundaries revealed by thermal etching.

Notice that the PAG boundaries could not be revealed for the HS alloy. The mean PAG size was found to be 11.4 ± 1.1 and 12.3 ± 1.1 μm for MS and LS, respectively. These values are comparable with those that can be obtained by EBSD. Hutchinson *et al.* showed that prior austenite grains can be revealed by high angle boundaries $\sim 45^\circ$. In Figure 6.21, a prior austenite grain is highlighted, where the thick dotted lines have been drawn in order to highlight the boundaries.

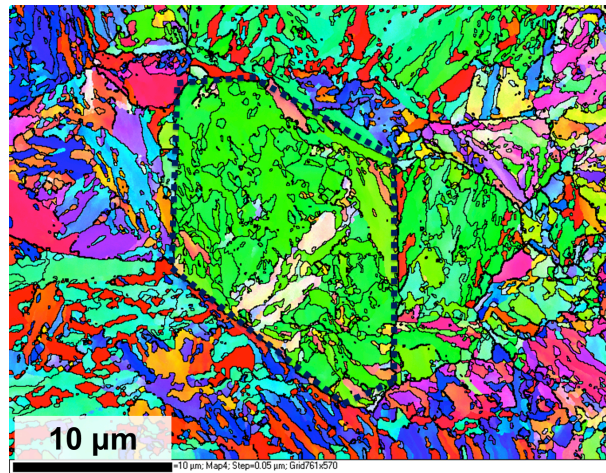


Figure 6.21: PAG visible for condition LS-450.

From Figure 6.21, the PAG appears to be ~ 15 μm, which agrees with the value found by thermal etching.

6.6 Discussion

It becomes clear that martensite possesses a very complex microstructure, which makes it challenging for mechanical properties modelling. Based on the analysis carried out, Figure 6.22 gives an idea of the dimensions of the substructures involved in martensite.

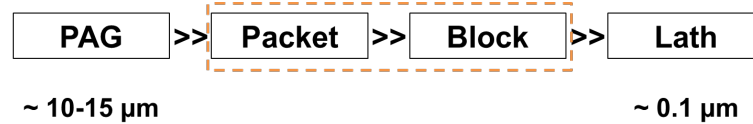


Figure 6.22: Representation of the dimensions of the hierarchical structures within martensite.

Determining the ‘effective’ grain size still remains a challenge. Conventionally, it is thought that only high angle boundaries contribute to the strengthening effect. Nonetheless, Figure 6.9 shows a network of ‘tangled’ dislocations built-up at the lath boundary, for a HS-250 sample that failed by necking. It might be the case that at the early tempering stage, there has not been sufficient time for dislocations to rearrange, and so even individual lath units that are heavily dislocated, might add to the strengthening effect.

6.7 Conclusions

Using the experimental results obtained in Chapter 5, the key microstructural parameters contributing to strengthening in 0.55 wt.% steels have been unveiled. The high dislocation density in these steels contribute significantly to the ultra-high strength. An attempt has been made in revealing the ‘effective’ grain size using different methods.

The method of determining the grain size based on plasticity modelling supported the idea presented in Chapter 5, where silicon inhibits the recovery process of martensite. Since grain growth is impeded under the influence of silicon, this

resulted in finer sub-units as the silicon content increased within the alloy. The predicted grain size for LS was bigger than HS.

The misorientation angle histogram plots obtained from EBSD also confirm the effect of silicon in martensite recovery. Nevertheless, obtaining a suitable grain size using EBSD remains a challenge.

The strengthening contribution due to sub-grain boundary hardening, σ_{sg} , was also computed. From the post-fracture TEM analysis of sample HS-250, it appears that at low tempering temperatures, given the very high dislocation density, even the low angle lath boundaries can contribute to strengthening. In order to successfully model the grain size effect, a more exhaustive study of the kinetics of martensite recovery is needed.

Chapter 7

General conclusions and scope for future work

7.1 Conclusion

In developing new grades of martensitic steels, the microstructure-property relationship must be understood. This is a challenging study, owing to the complex microstructure of martensite, especially with increasing carbon content, and the numerous processes occurring. At the temperature range where industrial processes usually occur, the changes taking place are carbon segregation, carbide precipitation and recovery of the ferrite matrix. Each of these phenomena was studied in detail.

Interrupted ageing

Grades used for spring steels contain a significant amount of carbon. Due to its interstitial nature, it undergoes immediate reactions as it tends to precipitate as carbides. Controlling carbon-related reactions from the start of a heat treatment is crucial, as this will have a marked effect on the final properties.

This has been the starting point for the work in understanding the effect of interrupted ageing (IA). By incorporating an intermediate stage between quench-

ing and tempering, where quenched martensite is left to age at room temperature, changes in the precipitation process were observed, causing a response in the hardness properties. Generally an increase of $\sim 10\%$ in Vickers hardness was seen via interrupted ageing. Thermoelectric power was used to model carbon segregation to dislocations, where it was postulated that room temperature ageing increased the number of effective nucleation sites for the subsequent tempering stage, reflected in a more stable microstructure and the formation of finer precipitates.

Therefore, the incorporation of interrupted ageing (IA) during the heat treatment is a process that can potentially be implemented in industry. In applications where high hardness is the priority, the process of IA offers microstructural and dimensional stability and an increase of $\sim 10\%$ HV over conventional quenching and heat treatment. Nonetheless, a restriction on the component size applies, given the relatively high quenching rates required in order to control carbon segregation.

Furthermore, building upon existing models and techniques, an understanding of the time-temperature aspects of the segregation/nucleation has been gained. Placing the conventional heat treatment as a reference, the effects on carbide precipitation of the duration of the IA time, and the time and temperature of the subsequent tempering stage, was quantified. The incorporation of IA resulted in a finer microstructure, where the duration of the IA influenced the spacing between intralath carbides.

The effect of silicon during martensite tempering

The effect of silicon has been a major point of interest shared by industrial and academic researchers. The presence of silicon as an alloying element has led to improvements in mechanical properties. Despite decades of research, there have been unanswered questions that require further exploration. In this work, the effect of silicon has been studied from the microstructural (carbide precipitation) and mechanical property points of view.

The effect of silicon in carbide precipitation was examined. By observing the evolution of carbide peaks *in situ* using high-energy X-rays, it was seen how the presence of silicon inhibited the growth of cementite. Due to technical difficulties it was not possible to characterise the early nucleation stage. Nevertheless, based on the classical nucleation theory, where cementite formation was modelled under paraequilibrium conditions, higher silicon content was predicted to retard nucleation.

Although precipitation hardening plays a major role in the properties of martensitic steels, there are other contributing factors that need to be considered, such as solid solution strengthening, forest dislocation hardening and grain boundary strengthening. Based on the microstructural analysis by TEM and line broadening by XRD methods, the strengthening contributions of several features were determined. Owing to the high dislocation density in martensitic steels, the forest dislocation hardening term was seen to be the primary contributor, followed by precipitation hardening.

As a result of dislocation density measurements, there have also been indications on the possible role of silicon in retarding martensite recovery during tempering. This point is also reinforced by TEM analysis. It was observed that the width of the individual lath units increased during tempering. However, this increase was least for high contents of silicon.

Modelling strengthening effects

In order to successfully model plasticity, it is important to determine the grain size effect. This is a particular challenge in tempered martensite, due to the complex microstructure. The microstructural subunits within martensite have been studied extensively, especially for carbon contents up to 0.2 wt.%. However for higher contents, such as 0.5–0.6 wt.% C, the literature on these alloys is scarce. During tensile loading, the matrix phase participates actively in the kinematic hardening. There-

fore, it becomes necessary to characterise the boundaries present within martensite. Generally, it is believed that high angle boundaries arrest dislocation motion, while low angle boundaries remain transparent to them. In order to study the grain boundaries, a few selected conditions were studied using EBSD techniques. Assuming that the transition from low to high angle boundary is defined by a critical misorientation angle of 15° , this boundary condition was set in defining the grain size. Grain size measurements gave an equivalent diameter value in the range of 0.4–0.6 μm .

By the method of thermal etching, the prior austenite grain (PAG) size was measured to be in the order of 10 μm , while by low magnification TEM, the individual lath sizes were seen to be $\sim 0.1 \mu\text{m}$. Given that the building units in martensite consist of PAG > packet > block > lath, considering the order of magnitude, it is likely that the grain boundary contributing to strengthening correspond to that of block and/or packet structures.

Using a plasticity model based on irreversible thermodynamics, the tensile curves obtained for different tempering conditions were reproduced for a corresponding grain size. The value was in the order of 1–2 μm , which is slightly higher than the ones found by EBSD.

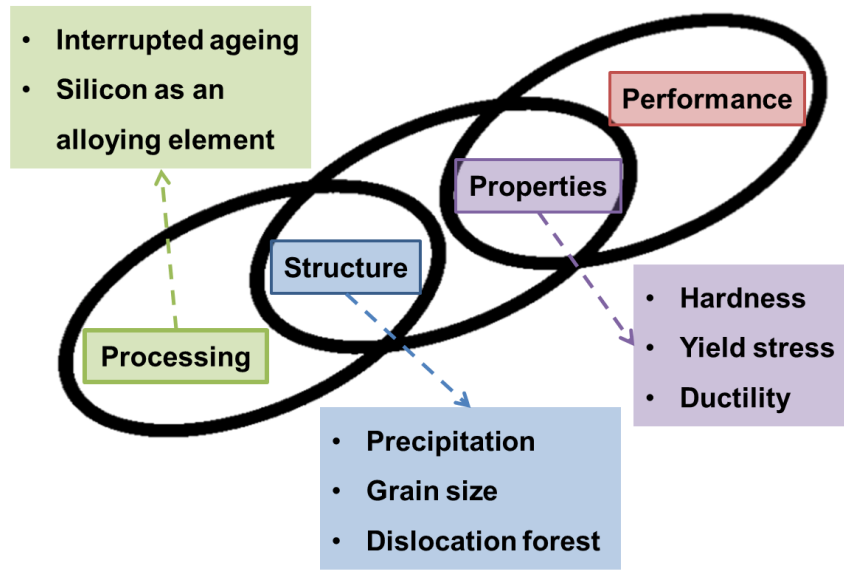


Figure 7.1: Main ideas and contributions represented on the chain model, and applied in this thesis.

Figure 7.1 summarises the findings in this work, which can be interlinked at the processing, microstructural and properties levels. As a consequence of the various studies presented in this thesis, a better understanding of medium (0.5 wt.%) carbon tempered martensite has been gained. This will serve as a strong foundation and potentially become a powerful tool in assisting the design of new martensitic alloys for the industry, where depending on the desired property that needs to be optimised, a specific set of microstructural features can be targeted and tailored through processing.

7.2 Scope for future work

Based on the present work, there are several interesting points that deserve further investigation:

- During mechanical modelling, the main focus has been on optimising the tensile properties. However, grades used for spring steel applications also have

a minimum impact energy requirement. During the interrupted ageing work, conditions undergoing interrupted ageing displayed relatively poor ductility, hinting the following: (a) a possible relationship between carbon content in ‘true’ solid solution and brittleness, or (b) unfavourable carbon atom configuration as a consequence of the atmosphere formations around dislocations during IA, that may dramatically reduce dislocation motion. However, very little improvements were observed on σ_y and σ_{UTS} during tensile loading. This is counterintuitive, as one would assume an increase in σ when the dislocation motion is hindered, and given the significant hardness improvement.

- A further in-depth EBSD study of the steels would be extremely valuable, in order to develop a firm understanding of the microstructure and the various sub-units involved. Carrying out a study of how each building unit evolves during tempering, understanding the nature of the boundaries involved, and relating this to martensite recovery is key to an accurate plasticity model.
- The significance of the retained austenite phase during martensite tempering is worth exploring. Given that the volume fraction of retained austenite in this family of steels is under 10%, its presence has been neglected so far. Nevertheless, owing to its relative carbon enrichment, the decomposition of the metastable phase could lead to further carbide precipitation, or solid solution hardening.
- One aspect of the carbide precipitation that needs further clarification is the role of silicon in the $\varepsilon \rightarrow \theta$ carbide transition. Given the technical difficulties experienced during synchrotron heat treatments *in situ*, it would be advisable to perform *ex situ* a series of different time-temperature combinations and carry them out as room temperature measurements.
- The process of martensite recovery is worth further exploration. In this work, it was suggested that silicon plays a role in the recovery of martensite. In order

to confirm that the retarding effect is specific to silicon rather than a general observation due to the presence of alloying elements in the ferrite lattice, silicon could be substituted by another alloying element. A comparative study, where by measuring the same properties, such as dislocation density and sub-units size, would clarify this issue.

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