



UNIVERSITY OF
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Hydrogen trapping in bearing steels: mechanisms and alloy design

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To Amin Maalouf

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. P. E. J. Rivera-Díaz-del-Castillo in the Department of Materials Science and Metallurgy, University of Cambridge, between October 2009 and September 2012.

This work is to the best of my knowledge original, except where acknowledgement and references are made to previous work. Neither this, nor any substantially similar dissertation has been or is being submitted for any degree, diploma or other qualification at any other university or institution. This dissertation does not exceed the word limit of 60,000 words.

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ABSTRACT

Hydrogen embrittlement is a problem that offers challenges both to technology and to the theory of metallurgy. In the presence of a hydrogen rich environment, applications such as rolling bearings display a significant decrease in alloy strength and accelerated failure due to rolling contact fatigue. In spite of these problems being well recognised, there is little understanding as to which mechanisms are present in hydrogen induced bearing failure.

The objective of this thesis are twofold. First, a novel alloy combining the excellent hardness of bearing steels, and resistance to hydrogen embrittlement, is proposed. Second, a new technique to identify the nature of hydrogen embrittlement in bearing steels is suggested. The new alloy was a successful result of computer aided alloy design; thermodynamic and kinetic modelling were employed to design a composition and heat treatment combining (1) fine cementite providing a strong and ductile microstructure, and (2) nano-sized vanadium carbide precipitates acting as hydrogen traps. A novel technique is proposed to visualise the migration of hydrogen to indentation-induced cracks. The observations employing this technique strongly suggest that hydrogen enhanced localised plasticity prevails in bearing steels. While proposing a hydrogen tolerant bearing steel grade, and a new technique to visualize hydrogen damage, this thesis is expected to aid in increasing the reliability of bearings operating in hydrogen rich environments.

Nomenclature

$V_{\alpha'}$	martensite content after quenching from austenitisation temperature
$\bar{x}$	mean diffusion distance
β^*	atomic attachment rate taking into account long-range diffusive transport of atoms in the nucleation rate equation
ΔG_s	misfit strain energy
ΔG_{vol}	volume free energy change
ΔG_V	chemical free energy change per unit volume
J	nucleation rate
P	pressure
a_1	reliability constant in bearing life equation
a_2	material fatigue properties constant in bearing life equations
a_3	lubricant constant in bearing life equation
c	maximum load carried in bearing life equation
L_{10}	life corresponding to 10% of bearing failures
p	bearing load in bearing life equation
μ_A	mean free energy of A in ferrite

ν	Poisson constant
D_H	hydrogen diffusion constant
σ	interfacial energy per unit area
σ_E	effective interfacial energy
τ	incubation time
ε	linear misfit strain
A_{e3}	temperature separating the ferrite + the austenite and austenite phase field
D_C	diffusion coefficient of carbon in austenite
D_V	diffusion coefficient of vanadium in austenite
E	Young's modulus
G^*	activation energy for nucleation
G^α	Ferrite Gibbs free energy
$G^{T,P}$	molar Gibbs energy at (T, P)
h	Planck constant
H^{SER}	enthalpy in the reference state at 298.15 K
k	Boltzmann constant
M_S	martensite start temperature
N_0	total number of potential nucleation sites in the nucleation rate equation
N_A	Avogadro's number
Q^*	activation energy for the transfer of atoms across the interface

R_0	radius of a precipitate
t_M	time for a precipitate dissolution
V_{mol}^M	molar volumes of the matrix
V_{mol}^P	molar volumes of the precipitate
$v^{P,T}$	atomic volume at (T, P)
Z	Zeldovich factor in the nucleation rate equation
B_S	Bainite start temperature

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Chapter 1

Introduction

Hydrogen embrittlement in ultra-strong steels is a widespread phenomenon, but the exact role that hydrogen plays in that process is not well understood. Embrittlement is believed to start with hydrogen atoms diffusing into a steel component often unintentionally exposed to a hydrogen-rich environment. Hydrogen ingress to bearing steels is frequently caused by lubricant decomposition [1]. There are many other possible ways of hydrogen entry as described in Section 2.1.

One of the most important properties of bearings is resistance to rolling contact fatigue. Therefore, considerable attention has been paid to the influence of hydrogen on the premature failure of components subjected to rolling contact. As shown in Figure 1.1, bearing life decreases dramatically with increasing the amount of hydrogen.

A few parts per million of atomic hydrogen might cause a decrease in bearing fatigue life by a factor of 100 [2]. It is generally held that the presence of hydrogen accelerates the usual fatigue damage which occurs at lower stresses. For instance, the typical contact pressure for bearings is up to about 3 GPa, and early hydrogen related failures usually occur at low to moderate contact pressures (1 to 2 GPa).

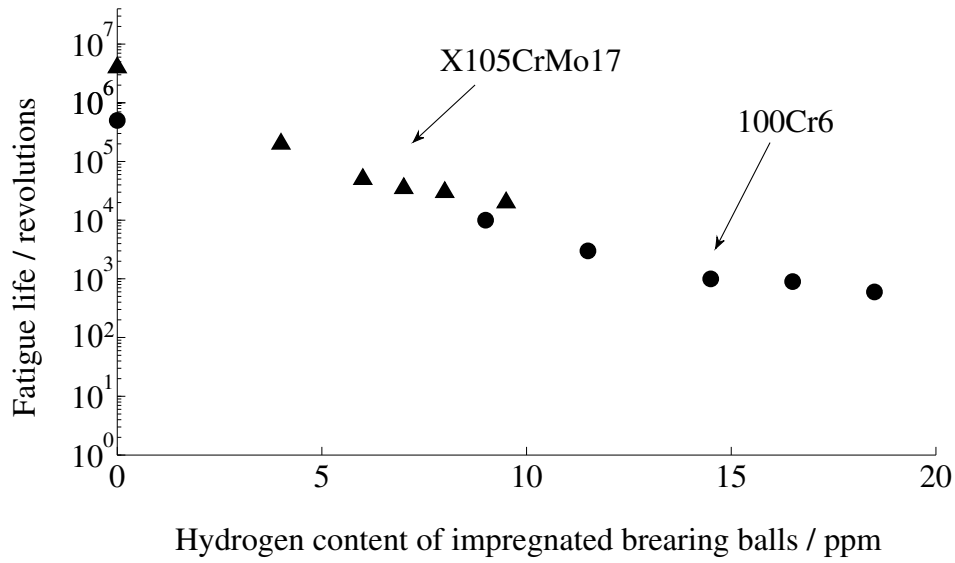


Figure 1.1: The influence of hydrogen on fatigue life of X105CrMo17 and 100Cr6 bearing balls, adapted from Ciruna [2].

Figure 1.2 shows a typical form of damage leading to failure: flaking on a bearing inner raceway ring [3].

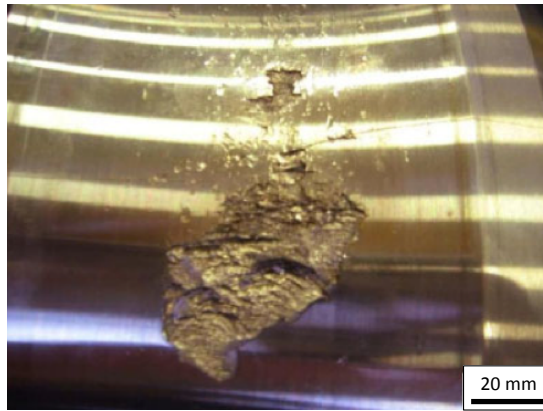


Figure 1.2: An example of material removal by white structure flaking on wind turbine bearing inner ring [3].

This type of failure demands complete replacement of the bearing. In addition, monitoring the development of damage is difficult when it starts under the surface, so it is hardly detected before serious or total damage of the component. At the microstructural level, cracks are frequently accompanied by white etching areas which are sometimes preceded by dark etching regions [4]. Rolling contact pressure causes a dark etching sub-surface region ~ 0.3 mm under the contact surface when an etched specimen is observed

by optical microscopy.

Kino [1] reports that white etching areas can both be oriented perpendicular or parallel to the rolling direction, and have a negative impact on rolling contact fatigue life. This negative influence is greater for the latter orientation, which shortens the fatigue life notably. His results clearly show that a short life flaking mode, believed to be induced by hydrogen, is preceded by microstructural changes such as the appearance of white etching areas. Apart from white etching areas, the microstructure of bearing steels might often develop cracks growing around inclusions, voids, pores and carbides, which resemble a butterfly wing [5], and are commonly referred to as 'butterflies'. An example of a butterfly is shown in Figure 1.3.

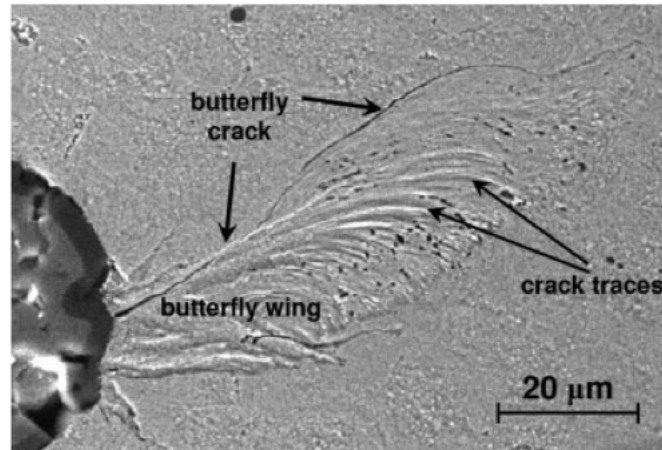


Figure 1.3: Scanning electron microscopy image of a butterfly wing parallel to the rolling direction, from left to right, in 100Cr6 steel. After Grabulov [5].

Hydrogen diffusion into steel may cause premature cracking in various components such as tempered martensitic and bainitic bearing parts, pearlitic and bainitic rail tracks, gear boxes, wind turbines, aerospace and marine engine parts. The damage caused by hydrogen is similar in all mentioned parts. However, their microstructures might be very different and the crack initiation and propagation variable. In this thesis more attention is devoted to studying and understanding the hydrogen influence on martensitic and bainitic microstructures, since these are common in bearings. The studies include modelling the microstructure development of hydrogen resistant martensitic bearing steels, the experi-

mental verification of achieved microstructures, and mechanical testing both in hydrogen free and rich environments. However, as hydrogen can influence the performance of large size bearings and these are usually bainitic, the research incorporates some superbainitic microstructures. All designed and tested steels were compared with 100Cr6 bearing steel.

Because of the significant amount of evidence showing that hydrogen alters the fatigue crack propagation kinetics and the mechanical properties of bearing steels, shortening bearing life, many attempts have been made to quantify the role played by hydrogen. One of the objectives of this work was to design a hydrogen resistant steel via immobilising it once it diffuses into the microstructure. To face this challenge, a detailed literature review is first needed. A review on the possible ways of hydrogen diffusion into steel, hydrogen embrittlement mechanisms, hydrogen trapping strategies, requirements to be met by hydrogen embrittlement resistant steels, possible alloy design strategies and hydrogen trapping verification are presented in Chapter 2. Modelling strategies are described in Chapter 3, which also presents the chosen modelling methodology, results, as well as an analysis of the results while suggesting the chemical compositions of novel hydrogen embrittlement resistant steels along with example heat treatments.

To stop the deleterious influence of hydrogen there have been many attempts to trap hydrogen in steels, for example via controlling the amount of retained austenite, grain boundaries and fine precipitates. Some of those attempts have been successful, for example via designing a vanadium carbide nanostructures to trap hydrogen [6]. Existing steel grades, which are resistant to hydrogen embrittlement are not appropriate for bearing applications due to their low carbon content leading to reduced hardness, a property crucial for ensuring resistance to rolling contact fatigue.

When studying hydrogen behaviour in steels not only alloy design, steel making and heat treatment processes are important, but also the experimental methods for hydrogen charging and detection. Since, hydrogen concentration in steel is much smaller and its diffusion coefficient is several orders of magnitude higher than other elements, it is difficult to indicate where it is located in the microstructure. Several detection techniques are

reviewed in Chapter 4. This chapter also reports both hydrogen charging and the analysis of experiments performed on the designed steel and the reference 100Cr6 martensitic steel. The experiments were extended to hydrogen-charged superbainite samples transformed at 200 °C and 300 °C as well as to pure iron for estimating the degrees of mobile hydrogen. Two techniques such as melt extraction and hydrogen desorption analysis were applied with their results being described in Chapter 4. The former technique provides information on the total hydrogen content, while the later quantifies the amount of hydrogen trapped at certain trapping sites and it helps to identify their type.

One of the designed alloys is characterised in Chapter 5. The new grade was cast and thereafter, heat treated both in a dilatometer for thermal desorption analysis and dilatometry studies, and in salt bath furnaces for mechanical testing. Microstructural observations and the measured mechanical properties are summarised in Chapter 5.

Chapter 6 is the conclusions, and Chapter 7 includes propositions for future work with regard to hydrogen trapping strategies, mechanisms, possible techniques for hydrogen detection and useful experiments.

Chapter 2

Literature review

2.1 Hydrogen intake and microstructural alterations

Hydrogen can cause damage in alloys via different mechanisms. Degradation always starts with the decomposition of molecules into hydrogen at the surface followed by its diffusion into the bulk. It has been claimed that hydrogen diffusion occurs along Fe(110) or Fe(100) low-index crystallographic planes [7]. The solubility of hydrogen is very low but its mobility is high; additionally, a high probability of trapping at defect sites at low temperature limit the evidence for the site occupancy. Some of the reference diffusivities in austenitic and ferritic stainless steels are listed in Table 2.1 [8].

Table 2.1: Hydrogen diffusivity in austenitic and ferritic stainless steels at 50 °C [8].

Steel	Diffusivity / $\text{m}^2 \text{s}^{-1}$
405 (ferrite)	2.8×10^{-12}
304 (austenite)	1.1×10^{-15}
316 (austenite)	2.0×10^{-15}
316L (austenite)	2.4×10^{-16}

Hydrogen diffusivity is temperature dependent and can be easily estimated assuming it follows a random walk

$$\bar{x} = \sqrt{2D_H t}, \quad (2.1)$$

where $\bar{x}$ is the mean distance that a hydrogen atom can diffuse during time t , and D_H is hydrogen diffusion coefficient. When using Equation 2.1, the time for hydrogen to diffuse 1 mm in steel at different temperatures might be calculated; the approximate time is listed in Table 2.2.

Table 2.2: Approximate time for hydrogen to diffuse 1 mm.

Temperature	Time
+ 150 °C	3 min
+ 25 °C	12 h
- 18 °C	24 days
- 79 °C	330 years

When hydrogen dissolves in steel it can either become trapped or freely move through interstitial sites [9]. It is generally accepted that mobile rather than trapped hydrogen causes damage [10], since it might interact with various defects present in the steel microstructure, but the main damage mechanism has not been identified yet. There are many theories aiming to explain the mechanisms leading to damage, some of these theories are described next. However, as mobile hydrogen becomes trapped, its deleterious influence can be minimised. The literature studies show that the mechanical properties of steels with the engineered hydrogen trapping sites may not be decreased by the presence of trapped hydrogen [6, 11, 12].

Hydrogen may be admitted into the microstructure from various sources, these typically include its absorption during processing steps such as heat treatment or surface treatment, and during service, for example from water electrolysis or lubricant decomposition. High strength steels used in nuclear and power applications are highly susceptible to hydrogen embrittlement, sometimes the failure can take place just after assembling the equipment. It is claimed that this happens because of hydrogen absorption after surface

treatment like pickling and electroplating [13]. Heating components up to $200\text{ }^{\circ}\text{C s}^{-1}$ is often used to decrease hydrogen content, but this practice was reported to cause problems in some applications [14]. Pérez-Escobar *et al.* found the hydrogen desorption peak at $500\text{ }^{\circ}\text{C}$ in an undeformed and uncharged 0.17-1.6Mn-0.4Si-2.0Al steel, claiming that hydrogen was introduced to the material during processing [15].

Oil and grease are popular lubricants commonly used in bearings. It prevents metal-to-metal contact between rolling contact elements. However, oil properties usually change during operation and oil may become a strong source of hydrogen, which in most cases diffuses into the bulk. The presence of hydrogen is usually the result of lubricant decomposition during repeated stresses, and the heat caused by rolling conditions. Hydrogen atoms and ions might be generated and accumulated at grain boundaries and, when reaching a critical amount, can cause hydrogen embrittlement flaking. Research on Japanese SUJ2 (1C–1.5Cr) steel shows that hydrogen may diffuse from a lubricant, which upon decomposition evokes hydrogen embrittlement flaking by exceeding a hydrogen content beyond a critical amount, about 1 ppm (Figure 2.1).

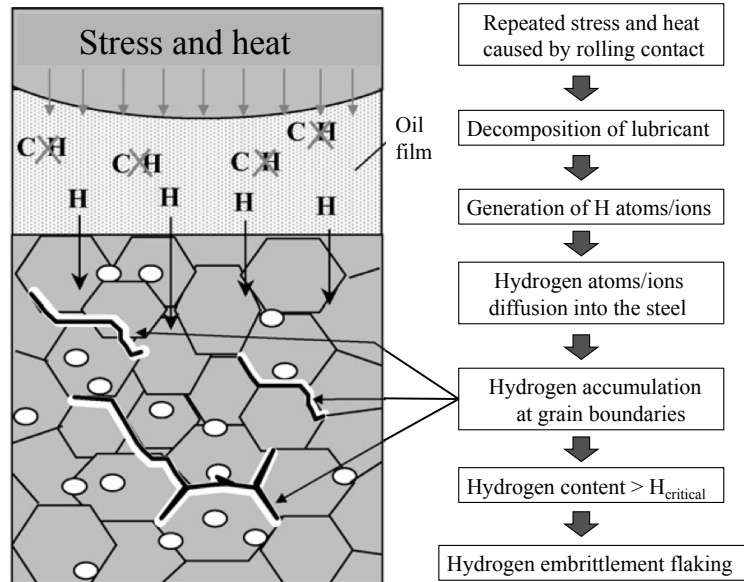


Figure 2.1: Hydrogen diffusion into the steel microstructure from lubricant decomposition [1].

Embrittlement caused by hydrogen entering the steel from oil was reported also in an oil-hydraulic unit [16], and the feeding line of an oil refinery [17]. The results show that hydrogen diffusion in these applications caused failures making the steels brittle and susceptible to cracking.

It was reported that MAC oil (synthetic multialkylated cyclopentanes) decomposition results in the formation of products such as H_2^+ , CH_3^+ or $C_2H_5^+$ [18], which further interact with the metal surface and leading to hydrogen embrittlement [19]. The nascent surface results from the removal of oxides or adsorbed layers, this may be due to friction, electric current break through or vibrations [20]. Lu *et al.* has examined oil decomposition and its influence on the nascent surface of a 100Cr6 bearing steel, and demonstrated the occurrence of hydrogen diffusion into the bulk due to hydrocarbon oil decomposition [18]. The oil decomposition mechanism is illustrated in Figure 2.2.

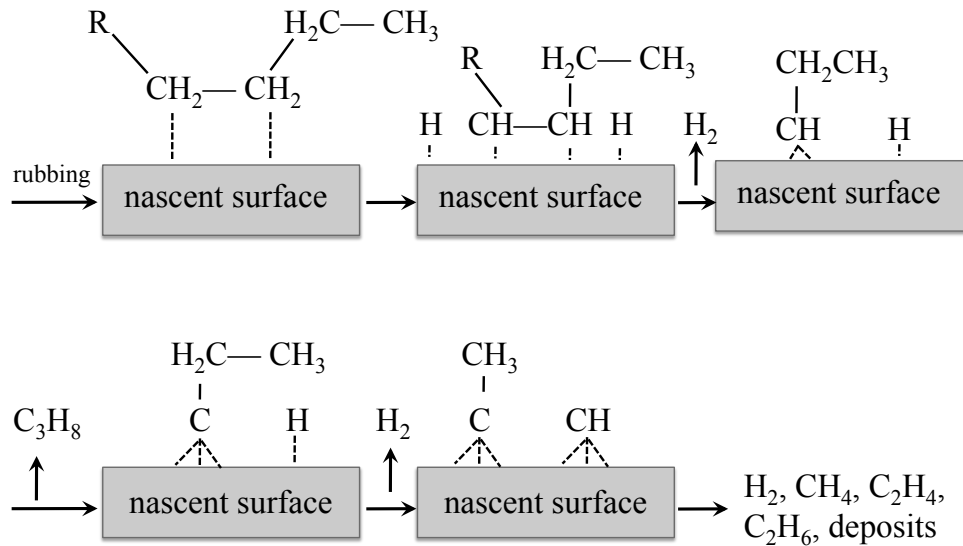


Figure 2.2: Mechanism of hydrocarbon oil decomposition on the nascent steel surface [18].

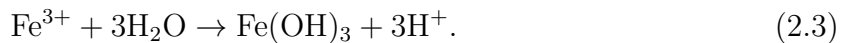
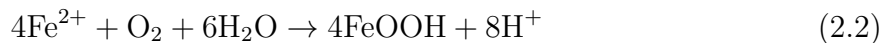
Water present in the lubricant is believed to be another source of hydrogen; water can react with the exposed metal surface in the bearing contact zone. It was shown by

Grunberg and Scott that lubricant containing water decreases bearing fatigue life dramatically [21]. Humid environments have been associated with hydrogen-induced cracking in pearlitic rails, showing frequent failure during service. These cracks have been reported to originate at the subsurface making difficult to predict damage [22].

Hydrogen can be introduced to steel even via atmospheric corrosion, as it has been shown in high-strength bolts, where hydrogen ions are liberated at the microcathode section in electrochemical corrosion with hydrogen depolarization. It was concluded that, as hydrogen ions saturate bulk, brittle failure appears [23].

In the case of wind turbine gearboxes, which are often exposed to standstill and idling operations, hydrogen was proven to enter the steel due to salt water and salt contamination from the offshore environment [3]. These results in static and fretting corrosion. Certain types of movements (e.g. vibrations) between the raceway with respect to other components can remove the passivation film, and expose the metal surface to atmospheric corrosion [3].

The formation of rust has been associated with hydrogen entry in structural steels. Hydrogen ions are formed and can diffuse into the bulk due to pH drop (H^+ formation) by formation of initial rust on weathering [24]. This situation can be summarised by the reactions



Hydrogen has been reported to occur on welding; cracking commonly takes place after a short time after welding. The moisture contained in the flux as well as the coating of manual metal arc electrodes determines the amount of hydrogen present. The type and cleanliness of the electrode are highly important, as well as the oil and grease, rust, paint and cleaning fluids on the welded surfaces [25].

Hydrogen permeated into the bulk reacts with carbon at temperatures higher than 200 °C, forming methane as prescribed by



This phenomenon is often referred to as internal decarburization, resulting in methane accumulation in voids in the matrix. The gas pressure in these voids can generate an internal stress leading to the formation of cavities, blistering and internal cracks due to weakening at the grain boundaries [9]. Hydrogen pressure in cavities has been reported to approach 109 MPa depending on the cavity size [26]. Hydrogen reacts with cementite and precipitates such as vanadium and titanium carbides but the later carbides are stable in the presence of hydrogen. The interactions between hydrogen and cementite can be described by



As it can be seen from reactions 2.4 and 2.5, there is a decrease in the number of gas molecules, altering their associated volume causing a pressure increase in the system. Furthermore, at higher temperatures hydrogen can react with oxides such FeO causing water formation. Water molecules are big in comparison to the lattice dimensions and display limited mobility what might lead to increased internal stresses [27].

The various mechanisms described above indicate that, when exposed to certain environments and loading conditions, hydrogen ingress in mechanical components can hardly be prevented. Once present in the matrix beyond a critical concentration, various forms of damage may occur. This, however, requires hydrogen to diffuse throughout the matrix. Therefore, a good way to deal with it would be to immobilise it, as this would minimise the deleterious effect associated to it.

2.2 Hydrogen embrittlement and delayed brittle fracture mechanisms

There have been many attempts to explain the nature of hydrogen embrittlement in steel. To understand such phenomenon we need to study the behaviour of hydrogen in the microstructure. Hydrogen embrittlement can be divided in two types: environmental embrittlement and internal embrittlement. The type of hydrogen embrittlement is determined by the hydrogen source. Hydrogen can be absorbed from the environment via dissociation of gaseous H_2 , or other chemical reactions between the steel surface and water, lubricant or other possible sources. This is commonly referred to as hydrogen environmental embrittlement [28]. Conversely, hydrogen that is present in the steel before loading, such as hydrogen from heat treatment, surface treatment or joining, is referred to as internal embrittlement. There is a difference in the hydrogen embrittlement rate between the two processes. In the case of hydrogen environmental embrittlement, hydrogen adsorption and diffusion to the zone ahead of the crack tip are detrimental, whereas in internal hydrogen embrittlement diffusion controls the process rate. To date, however, there is no single theory that satisfactorily explains all the possible mechanisms of hydrogen-induced mechanical properties degradation in a single framework. The most popular mechanisms are Hydrogen Enhanced Localised Plasticity (HELP), Hydrogen Enhanced Decohesion (HEDE) and Hydrogen Enhanced Strain Induced Vacancy formation (HESIV), which are described in the following subsections. In the case of delayed brittle failure, two conditions need to occur: a critical local hydrogen concentration ahead of the crack tip and a large stress concentration [29]. In general, in the literature the occurrence of delayed brittle failure is considered to be caused by the same mechanisms as for hydrogen embrittlement [12, 29].

2.2.1 Hydrogen Enhanced Localised Plasticity (HELP)

Hydrogen Enhanced Localised Plasticity (HELP) postulates that hydrogen increases the stacking fault energy enhancing dislocation mobility in the vicinity of the crack tip; this stems from the tendency for hydrogen to diffuse to the damaged zone, and accumulate at the crack tip [30]. Hydrogen is assumed to decrease the repulsive forces between two edge dislocations, leading to a reduction in the equilibrium distance between them in a pile-up process. This phenomenon was observed in hydrogenised stainless steel, where dislocations moved closer both to the obstacles and to each other [31]. Hydrogen atoms become attracted to lattice strains surrounding dislocations and form Cottrell-type atmospheres; however, instead of increasing the yield stress as carbon does, they lower it [32]. Transmission electron microscopy shows that, when stressing a hydrogen-charged 310S stainless steel thin foil (Figure 2.3), two phenomena are observed: the dislocation velocity increases and the distance between dislocations is reduced as they pile-up [31].

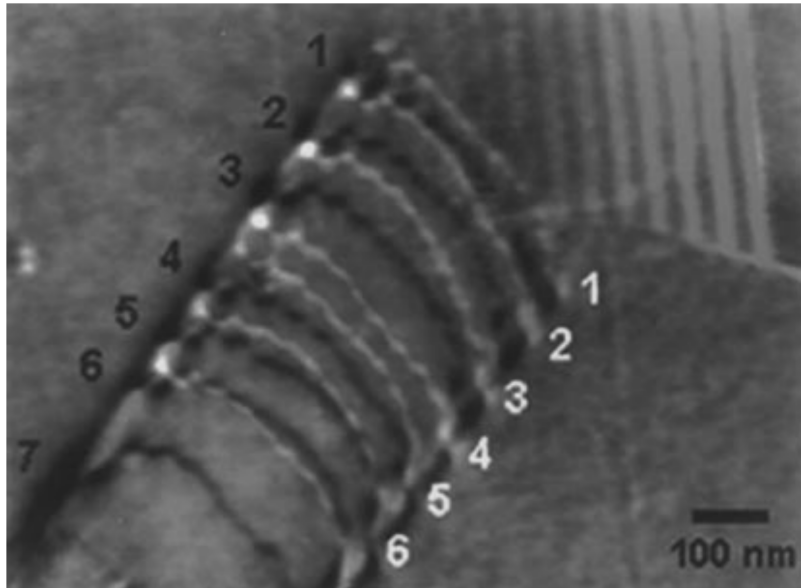


Figure 2.3: A comparison of two transmission electron microscope images showing a pile-up of dislocations against a grain boundary in vacuum (black numbers and dislocation lines) and an image taken from the same pile-up at constant stress, after introduction of 95 torr of hydrogen gas in the environmental cell (white numbers and dislocation lines). This comparison image has been created by superimposing a negative image of the final configuration of the dislocations in 95 torr of hydrogen gas on the initial configuration of the dislocations in vacuum [31].

This result is consistent with the experimental observations by Jagodzinski and Hanninen in pure iron (Figure 2.4), where they claim that hydrogen “affects the current dynamic equilibrium of the dislocation pile-ups decreasing the stress required to provide the given plastic strain. In other words, hydrogen shielded pile-ups require lower stresses to maintain their configuration, which is experimentally observed as the softening effect” [33].

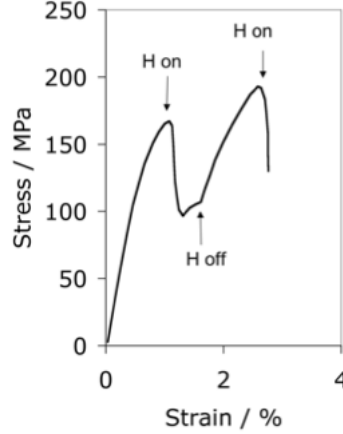


Figure 2.4: Tensile test results conducted on pure iron showing changes in flow stress while the hydrogen charging is switched on or off [33]. The experiment was conducted at a strain rate of $8 \times 10^{-5} \text{ s}^{-1}$.

In agreement with the experimental observations, molecular dynamics simulations employing semi-empirical potentials [34] indicate that hydrogen can weaken the strain-mediated interactions among dislocations and between precipitates, a phenomenon Myers *et al.* have referred to as “reduced interactive pinning” [35]. All in all, experiment and simulation point in the direction of hydrogen enhanced localised plasticity as a key softening mechanism; consequently it has occupied a prominent place in the literature [31, 32, 36, 33, 37, 38]. HELP mechanism is illustrated in Figure 2.5.

It has been assumed that HELP softening promotes the development of white etching areas, the formation of shallow but numerous voids that lead to further macroscopic brittle failure [4]. This increases deformation at the localised region adjacent to the crack surface leading to fracture. Failure appears due to exhaustion of the plastic strain capacity of the material, or due to dislocation pile-ups that nucleate cracks. The fracture caused by HELP mechanism can be either intergranular or transgranular. The intergranular fracture

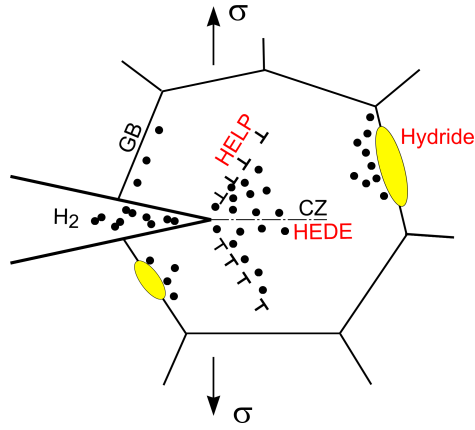


Figure 2.5: Schematic drawing illustrating hydrogen embrittlement mechanisms. HELP: Hydrogen Enhanced Localized Plasticity, HEDE: Hydrogen Enhanced Decohesion; and Hydride formation and embrittlement [39].

occurs when the concentration of hydrogen is greater at grain boundaries rather than in the grains themselves, resulting in deformation and fracture in their vicinity, this type of fracture occurs at lower stresses. The fractured surface displays small and shallow dimples, as illustrated in Figure 2.6 for 0.28C–0.40Si–1.70Ni–0.71Cr–0.73Mn–0.31Mo steel.

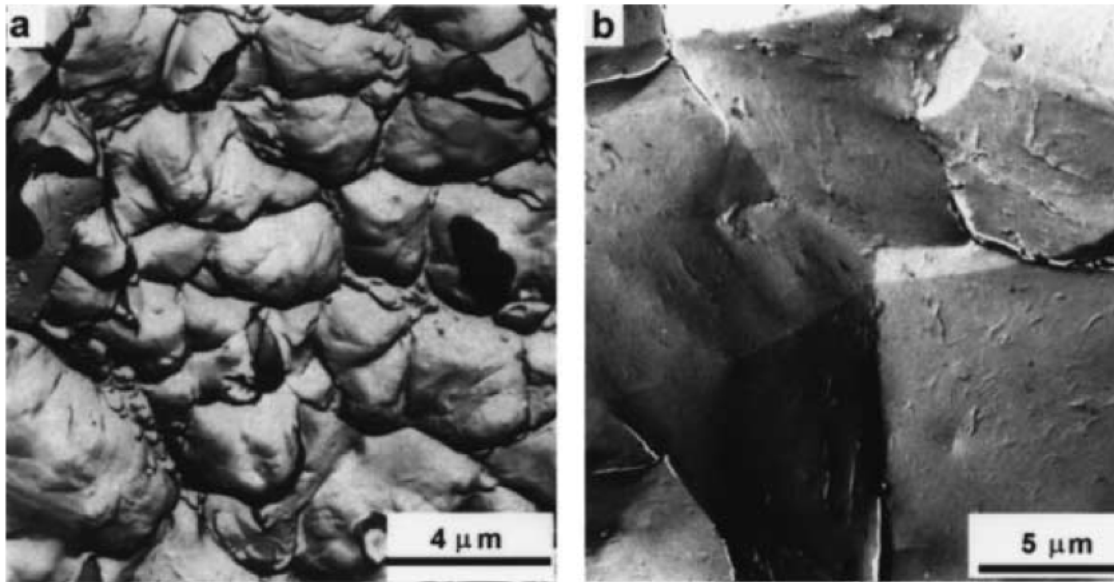


Figure 2.6: Replicas showing: (a) tear ridges and (b) dimples on a fracture surface of hydrogen embrittled steels. Adapted from [38].

Fracture progressing through grains is called transgranular. Given the dissimilar crystallographic orientations among the grains, the crack changes direction as it progresses

through the bulk. As a case in point, transgranular fracture has been observed on a SAE 1050 cold-rolled carbon steel shaft failed during operation with no evidence of fatigue cracking [40]. Hydrogen was claimed to be absorbed during welding process. A transgranular fracture microphotograph of the carrier shaft can be observed in Figure 2.7.

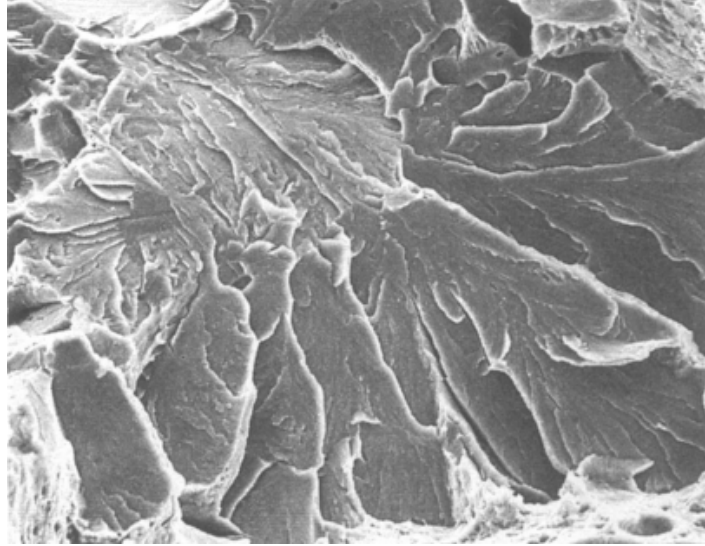


Figure 2.7: Transgranular fracture taken from carrier shaft broken during operation [40].

The HELP mechanism assumes that hydrogen embrittlement occurs due to the increased dislocation mobility in the presence of hydrogen. However, this is inconsistent with the common understanding of a metal becoming more ductile as the dislocations are able to move more rapidly. Although, the effect of hydrogen on the stacking fault energy has been considered by HELP, the influence on the strain field surrounding dislocations seems to be neglected though the distance between the dislocations observed by TEM was reported to decrease.

2.2.2 Hydrogen Enhanced Decohesion (HEDE)

HEDE is based on the assumption that the presence of hydrogen decreases the lattice strength [41]; this occurs because hydrogen diffuses and accumulates in regions of high stress (including the crack neighbourhood) locally decreasing the cohesive bonding energy, as illustrated in Figure 2.5. It follows that the stress needed for crack initiation as

well as propagation is decreased, and cleavage failure is encouraged [42]. The relationship between hydrogen content and cleavage toughness were investigated and experimentally correlated [43, 44]. Fracture surfaces associated with HEDE lack on ductile failure markings. HEDE was related to experiments showing that the crack tip opening angle decreases notably with increasing hydrogen pressure in stressed Fe-3Si (wt%), and in nickel single crystals (Figure 2.8).

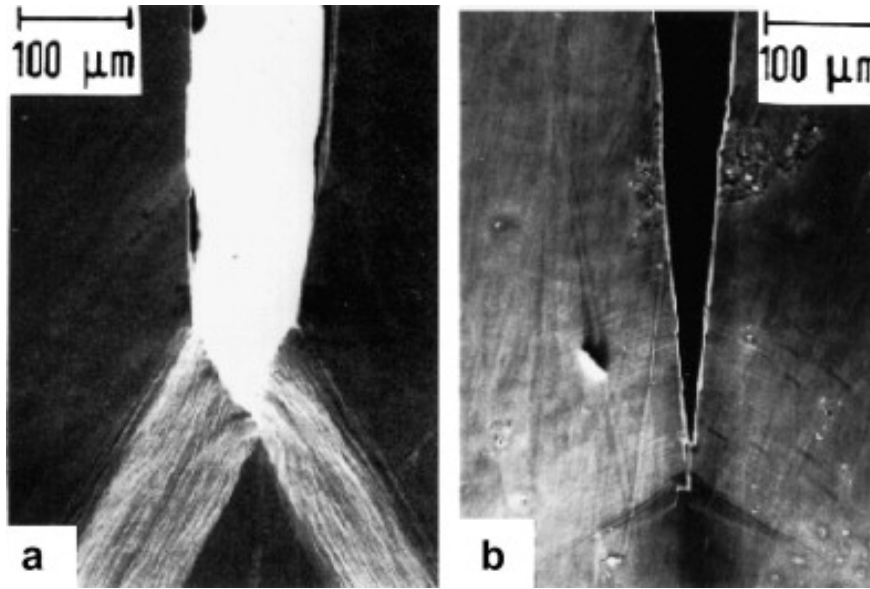


Figure 2.8: Influence of hydrogen on the crack tip opening angle a) in vacuum and b) in hydrogen atmosphere [45].

These results were explained by a mixture of slip and bond breaking, through which bond breaking prevails. When considering the mechanical response in the presence of hydrogen, it was shown that this reduces the shear modulus and the stacking fault energy in nickel [46].

Nevertheless the HEDE mechanism is based on the assumption that the decohesion occurs due to the reduction in the bonding between the atoms by hydrogen, there have are no experimental results that support this hypothesis.

2.2.3 Hydrogen Enhanced Strain Induced Vacancy (HESIV)

HESIV mechanism postulates that the formation of vacancies is enhanced under strain and the presence of hydrogen, leading to ductile crack growth by slip localisation [12]. This is a direct consequence of what is presented in section 2.1. Thermal desorption studies show that the susceptibility of a material to hydrogen embrittlement depends on the presence of vacancies. Vacancies can be caused by deformation, and are stabilized by hydrogen, that results in enhanced plasticity or ductile fracture [12]. The fracture process starts with the initiation of microcracks and microvoids followed by coarsening and coalescence, finally causing fracture. This process can be observed during crack extension resistance curve analysis (R-curve), that shows the correlation between ductile crack growth resistance with creation of point defects [47]. It has been assumed in many studies that not only ductile crack growth but also fracture toughness is related to the density of strain-induced vacancies in the presence of hydrogen [12, 48, 49]. The hydrogen related failure was observed in Inconel 625 and iron investigated by tensile testing (Figure 2.9); the results prove the important role of vacancies formed due to the hydrogen rather than just the presence hydrogen itself [48, 49].

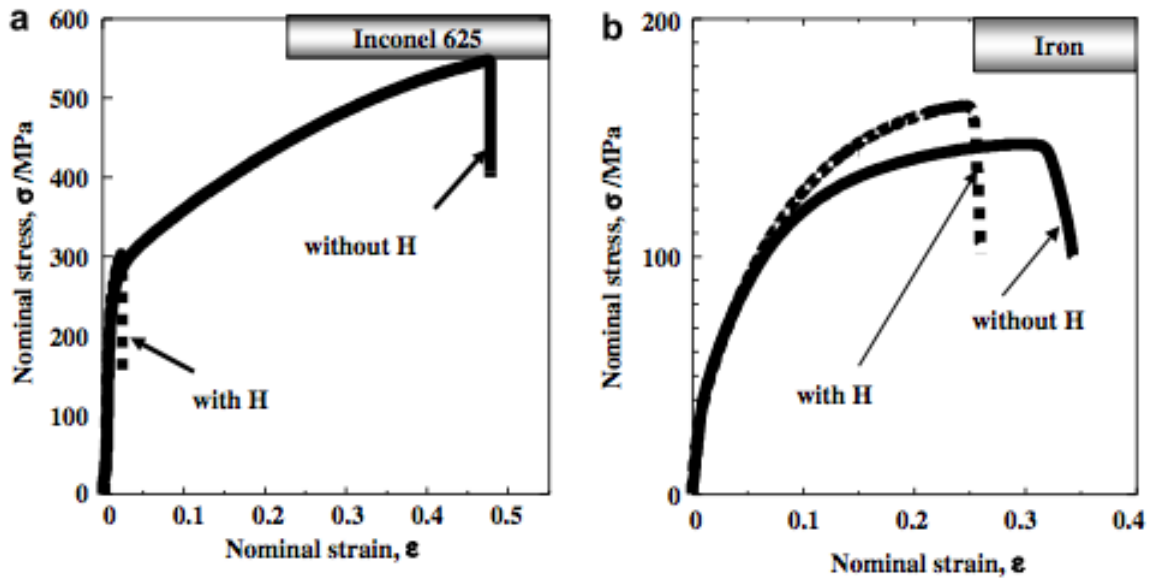


Figure 2.9: Tensile curves of a) Inconel 625 and b) iron with and without H-charging [48].

The influence of hydrogen on crack nucleation and growth in fatigued specimens was

investigated by Nagumo [50] showing that hydrogen dramatically decreases fatigue life. The defect density in the fractured samples after hydrogen charging was found to be greater than for the samples fractured after a similar number of cycles but without hydrogen charging [50]. The fracture of hydrogenised samples was smooth with no signs of cleavage-like fractures [50]. Fracture microphotographs on 0.57C-1.42Si-0.65Mn-0.67Cr steel after fatigue test are shown in Figure 2.10. There are many investigations showing that vacancies play an important role in ductile crack growth, however, the exact role of hydrogen on vacancy formation is still not understood.

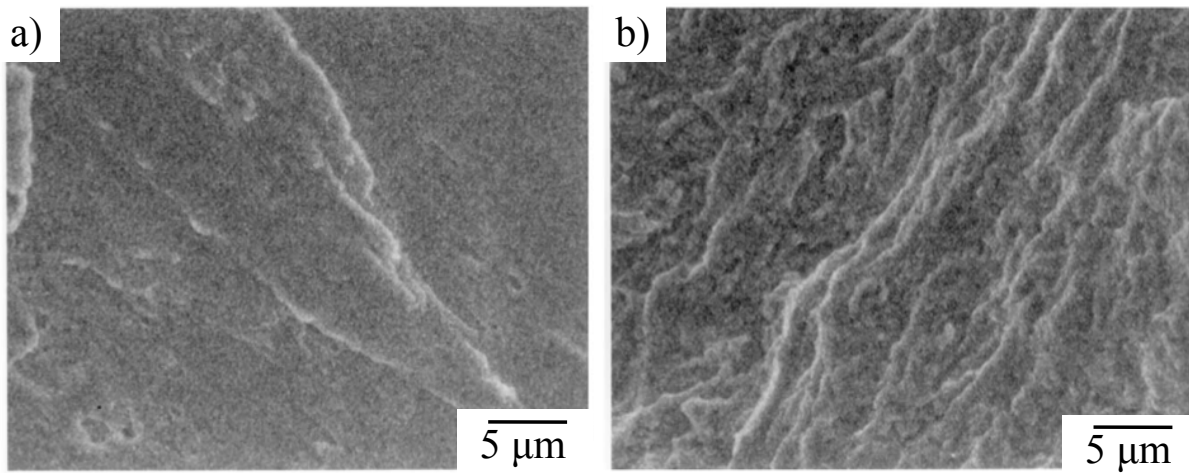


Figure 2.10: Microphotographs of fracture in 0.57C-1.42Si-0.65Mn-0.67Cr steel samples subjected to a fatigue test at the stress amplitude of 610 MPa a) with and b) without hydrogen precharging [50].

2.3 Trapping strategies

As discussed in Section 2.2, mobile hydrogen accelerates and fosters hydrogen embrittlement in many materials. Numerous attempts for stopping or trapping diffusible hydrogen have been reported in the literature employing a variety of mechanisms. Some of the microstructural features and lattice defects used for trapping include: dislocations and microvoids [51], cementite-ferrite interfaces [52], boron atoms [25] [51], TiC [53], V_4C_3 [6], MnS-ferrite interface [51], vacancies [54] and grain boundaries [55]. By binding with microstructural traps, hydrogen atoms locally decrease the free energy becoming trapped

around room temperature; such binding energy was suggested to be in the range of 0.03–1.3 eV. When considering the spatial distribution of hydrogen in steel, it was reported that hydrogen tends to accumulate at trapping sites [56]. Free energy levels of a trapping site with respect to the rest of the microstructure is illustrated in Figure 2.11.

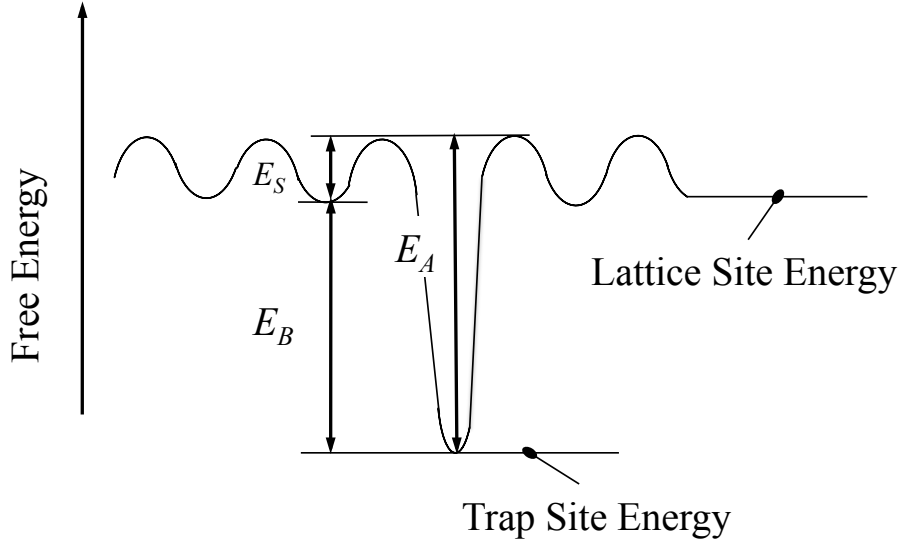


Figure 2.11: Free energy levels of normal and trapping lattice sites, where E_B is the binding energy, E_S is the saddle energy and E_A is trap activation energy for hydrogen to be released from a trap site. $E_A = E_B + E_S$. Adapted from [52].

Microstructural traps have been classified according to their activation energy for trapping. Pressouyre [57] considered the traps to be attractive, physical, or a mixture of the two. In the case of attractive traps, hydrogen atoms are attracted by forces due to electric fields, stress fields or temperature gradients. An electrical field example is an electronegative impurity atom, which electron deficiency attracts mobile hydrogen. Stress fields are introduced to the microstructure by defects such as coherent and semicoherent grain boundaries, particles and dislocations. These types of defects are also considered to be reversible, since they can trap or release hydrogen. Their desorption temperatures (T_E) and characteristic trap activation energy (E_A) are relatively low. A reversible trap is considered as such if its activation energy is less than ~ 50 kJ/mol [58]. Typical activation energies and temperature peaks for reversible traps are listed in the Table 2.3.

Physical traps are those in which diffusible hydrogen falls as a result of a random

Table 2.3: Types of reversible and irreversible hydrogen traps.

Type of trap	Peak Temperature °C	Activation energy kJ/mol	Material	Reference
Reversible hydrogen traps:				
Grain boundaries	112	17.2	Pure iron	[51]
Dislocations	215	26.8	Pure iron	[51]
Microvoids	305	35.2	Pure iron	[51]
V ₄ C ₃ (coherent)	~220	30	Low carbon steel	[6]
TiC (semi-coherent)	~230	-	Low carbon steel	[11, 59]
Ferrite/Fe ₃ C interface	~120	18.4	Medium carbon steel	[60, 61]
Dislocations	205	-	Medium carbon steel	[60]
Retained austenite	310	45	High carbon steel	[62]
Irreversible hydrogen traps:				
TiC (incoherent)	~710	86.9	Medium carbon steel	[63]
MnS	~495	72.3	Low alloy steel	[63]
Fe ₃ C (incoherent)	-	84	Medium carbon steel	[52]
Retained austenite	~600	55	Dual Phase Steel	[52, 64]

walk. This group includes irreversible traps that capture hydrogen until their saturation, and which further release becomes very difficult or in most cases impossible [58]. Some traps belonging to this group are high angle grain boundaries, incoherent particle–matrix interfaces and voids. In most cases, the microstructure contains a mixture of traps, which act both as attractive and physical, and only the dominant character of one over the other defines the nature of the microstructure. It is difficult to judge which traps are better for structural steels, but in the case of bearing steels irreversible traps are considered to be not beneficial, since they are incoherent and big, which would have a negative influence on rolling contact fatigue [65].

There are therefore many possible sites that attract hydrogen in the microstructure, some are stronger than the rest. In this section we focus on the most common trapping strategies: precipitates, retained austenite, dislocations and other crystal defects.

2.3.1 Trapping on precipitates

Hydrogen trapping can be observed on nano-sized as well as bigger precipitates. As the precipitates coarsen, their coherency and trapping nature change from reversible to irreversible. The differences between these two types of trapping are described above. Bigger precipitates were reported to trap hydrogen irreversibly at their interface. Nano-

sized TiC shows reversible trapping [11]; however, as its size increases, the character on its interface with the matrix changes to semicoherent, and then incoherent leading to irreversible hydrogen trapping [66], [63]. A popular precipitate that either reversibly or irreversibly traps hydrogen is cementite. Trapping on cementite also depends on its size, and therefore its trapping activation can vary from 18.4 [67] to 84 kJ/mol [68].

Fine precipitate particles have been selected as hydrogen traps in these studies since they display a high number density they may also increase tensile strength via precipitation hardening [57]. Moreover, it is more difficult to examine where hydrogen atoms are lodged around fine particles, whether the trapping occurs on particle-matrix interfaces, strain fields in the vicinity of coherent precipitates, or at the precipitates themselves. These difficulties are caused by the high spatial resolution required and the high diffusivity of hydrogen in steel. By using three-dimensional atom probe with a heavy hydrogen (deuterium) charging cell, the sites of hydrogen accumulation can be determined [11]. The results of this analysis show that trapping associated to fine TiC is at the interface between matrix and TiC, and not to the TiC strain field in the matrix. Three dimensional atom probe maps of deuterium charged and uncharged samples with tiny TiC precipitates are shown in Figure 2.12.

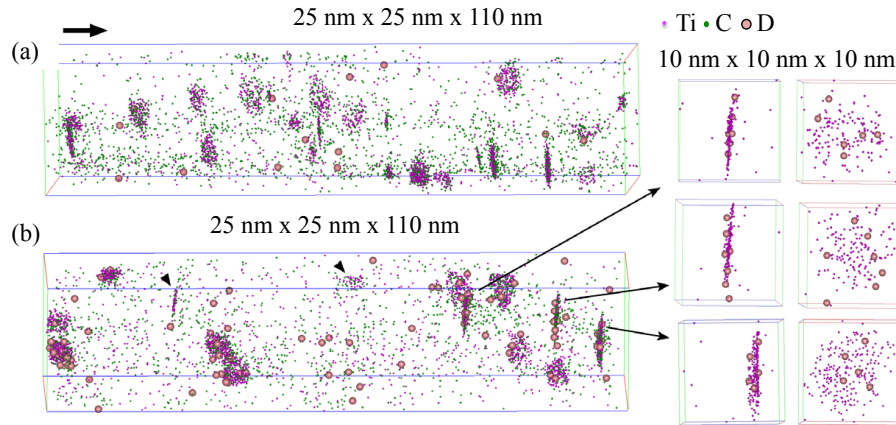


Figure 2.12: Three dimensional maps of steel containing nano-sized TiC precipitates a) without deuterium charging and b) after deuterium (D) charging [11]. The arrow shows the direction of the analysis.

Although the coherency strain is claimed not to be responsible for trapping on TiC,

such is assumed cause trapping on V_4C_3 [6] and NbC [59]. Matrix lattice strains are induced due to the matrix/precipitate coherency. Both V_4C_3 and NbC have a Baker and Nutting orientation relationship $\{100\}_{V_4C_3} \parallel \{110\}_\alpha$, which in the early stages of precipitation, the particles are coherent with the matrix, shows $\sim 3\%$ misfit between the ferrite matrix $\langle 010 \rangle_\alpha$ and $\langle 110 \rangle_{V_4C_3}$ precipitate [69]. Yamasaki and Bhadeshia showed that the state of coherency of the carbide can change with molybdenum addition [6]. Their research shows that a steel displays greatest trapping capacity for higher amount of molybdenum, see Figure 2.13.

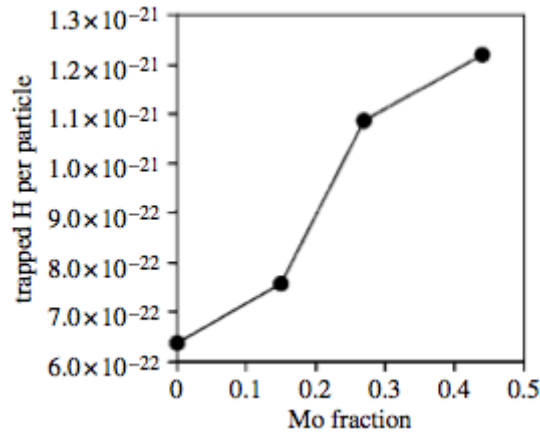


Figure 2.13: Influence of Mo in $(V,Mo)_4C_3$ carbide on hydrogen trapping capacity [6].

2.3.2 Trapping on retained austenite

Thermal desorption analysis shows that a maximum desorption temperature peak might vary noticeably from 600 °C, with trap activation energy $E_A = 55$ kJ/mol in supper duplex stainless steel, to 310 °C in ferritic welds [64, 68] ($E_A = 45$ kJ/mol) in 0.82C-0.17Si-0.48Mn-0.02Cr (wt%) steel [62]. Those studies show that retained austenite can be trapped either reversibly or irreversibly (Table 2.3). Thermal desorption analysis spectra show that hydrogen trapped in retained austenite decreases its amount significantly after a week from hydrogen charging, but remains stable even up to four weeks after charging (Figure 2.14) [62].

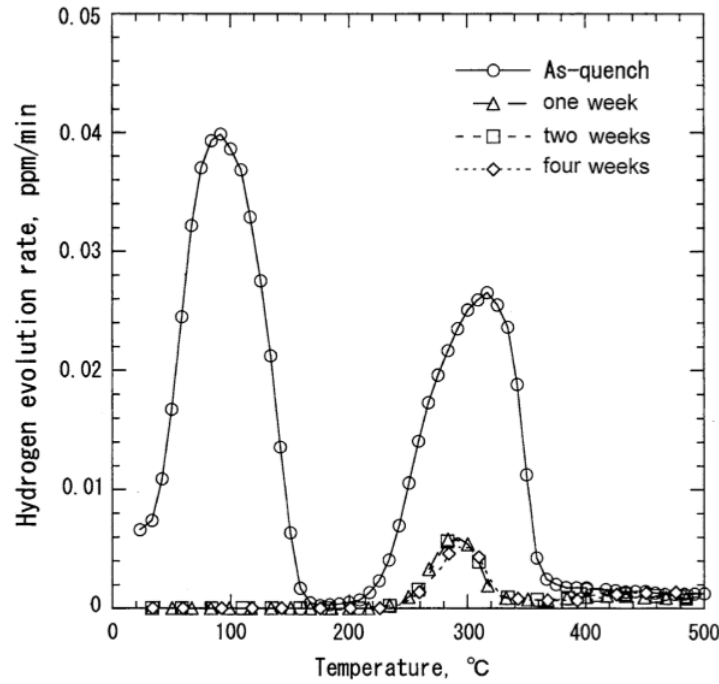


Figure 2.14: Thermal desorption analysis of 0.82C-0.17Si-0.48Mn steel after 1 h hydrogen charging at 950 °C and exposing at room temperature for varying times. Heating rate 100 °C h⁻¹ [62].

Pérez-Escobar *et al.* investigated hydrogen desorption from retained austenite at 500 °C in undeformed and uncharged 0.17-1.6Mn-0.4Si-2.0Al steel, claiming that the hydrogen was introduced to the material during steel processing [15]. Pérez-Escobar's assumptions are similar to Scott's, who claims that hydrogen absorption is caused by surface treatment like pickling and electroplating [13]. It is believed that even outgassing is not able to eliminate hydrogen from islands of retained austenite, since they act as a reservoir, but as the material works under high mechanical stresses, the stored hydrogen can be released to ferrite and cause catastrophic fracture [70]. Similar concerns were shared by Andreone and Murut [70]. Their research on 0.42C-0.78Mn-0.35Si-0.80Cr-1.79Ni-0.33Mo (wt%) steel with different amounts of retained austenite shows that the increase in retained austenite in the microstructure increase the hydrogen embrittlement [70]. Hydrogen trapping on retained austenite is still not well understood, it should not be forgotten that by applying different plastic strains, retained austenite tends to transform into martensite which alters the hydrogen trapping behaviour [64]. Another important characteristic of

retained austenite is that its shape can range from blocky (Figure 2.15) to thin laths, as is the case of superbainite (Figure 2.16). Retained austenite is undoubtedly important both because of its low diffusivity and high solubility, but its interface character should not be neglected. This topic will be further investigated in this thesis.

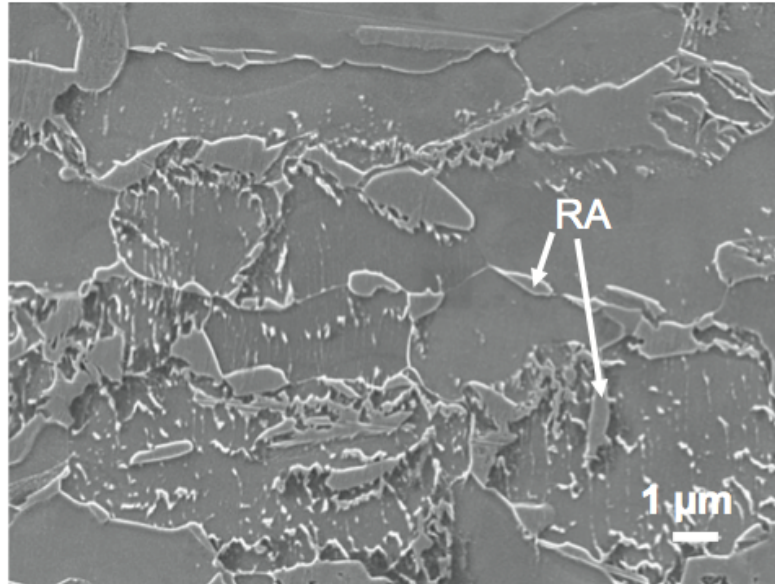


Figure 2.15: Scanning electron micrograph of retained austenite in a bulk form in 0.17C-1.6Mn-0.4Si-2Al (wt%) steel. 2% nital etching [15].

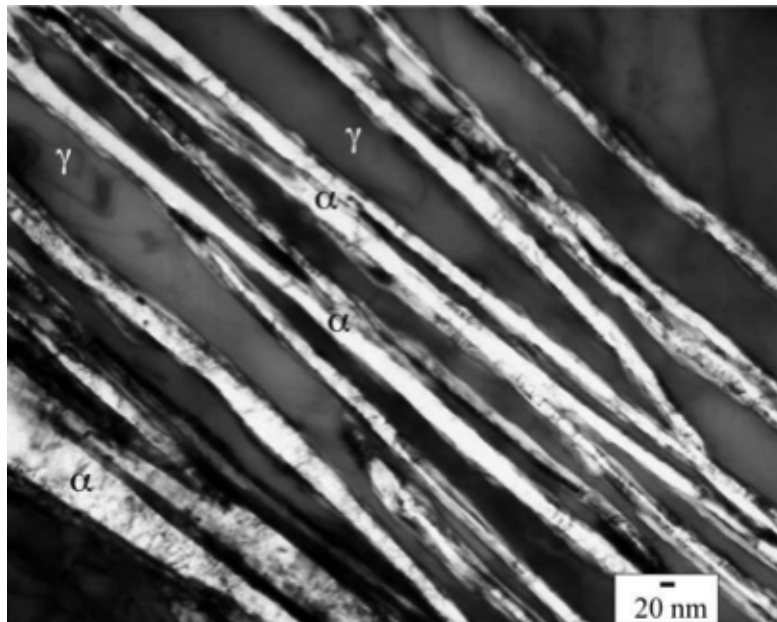


Figure 2.16: Transmission electron micrograph of retained austenite in lath form in Fe-0.98C-1.46Si-1.89Mn-0.26Mo-1.26Cr-0.09V superbainite (wt%) [71].

2.3.3 Trapping on dislocations and other defects

Dislocations are common crystal defects amenable to hydrogen trapping that are present in all microstructures. Their activation energy is relatively low and strongly depend on carbon content (Table 2.3). It was claimed by Hagi and Hayashi that trapping on dislocations was lessened probably by carbon segregation towards dislocations [72]. It was shown by Enomoto and Hirakami that carbon has a great influence on peak height and broadening for dislocation traps during thermal desorption analysis [62]. Hydrogen might diffuse from dislocation traps fast since it is not strongly trapped there. The activation energy for hydrogen trapping on the strain around dislocations in pure iron is just 26.8 kJ/mol [51], but it can rise even to 45 kJ/mol in 0.82C-0.17Si-0.48Mn-0.02Cr (wt%) [62]. The thermal desorption peak from dislocation vanishes much faster than in retained austenite. This gives a strong indication that dislocations are very weak hydrogen traps and allow hydrogen to diffuse out from their vicinity completely in one week from charging (Figure 2.14). Dislocations have also been related to HELP [31, 37, 38].

Microvoids are stronger hydrogen traps than dislocations, their activation energy is ~ 35.2 kJ/mol in pure iron [51]. Hydrogen was reported to enhance void nucleation and growth [73]; as the size of microvoids increases they tend to trap hydrogen more strongly, and accumulate hydrogen gas pressure causing internal stresses which can lead to cracks nucleation [9]. Hydrogen pressure in cavities strongly was reported to depend on the size the cavity [26].

Many researchers have observed that large incoherent MnS inclusions would form microvoids at the particle/matrix interface, possibly leading to hydrogen trapping [74, 75, 76]. Similarly, void formation was also observed for large carbides. The research by Lee and Goldenberg shows void formation observed between carbides in steel 1090 and 4340 claiming that void formation is characteristic for these steels after hydrogen charging (Figure 2.17) [77, 78]. Microvoid formation is related to Hydrogen Enhanced Strain Induced Vacancy mechanism.

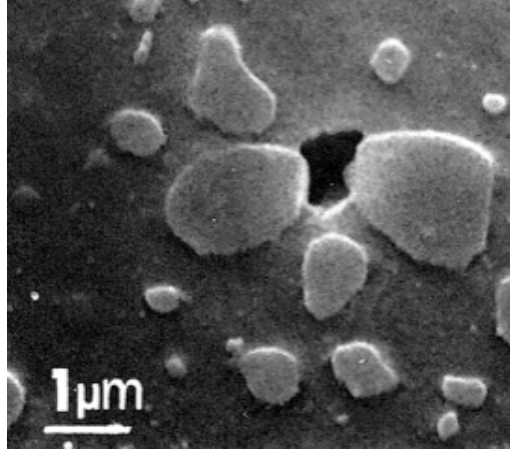


Figure 2.17: A formation of void between two carbides in 1090 steel [77].

Hydrogen trapping on grain boundaries was reported in many studies [79, 80, 81] showing to be weak. Hydrogen trap activation energy for grain boundaries in pure iron was estimated to be 17.2 kJ/mol [51]. However, just low angle grain boundaries with misorientation angles in the range of 2-5 °C are able to trap hydrogen efficiently with trapping strength comparable to dislocations. Conversely, grain boundaries with high angle misorientation are claimed to be ineffective for hydrogen trapping, displaying therefore a negligible effect on hydrogen embrittlement [82].

2.4 Factors influencing life of bearing steels

Bearing steels are used in numerous industries including the automotive, marine and aerospace sectors. These steels might be exposed to very severe working conditions such as high static and dynamic loads, high temperatures, severe friction and exposure to highly corrosive environments. All these conditions make bearings prone to accelerate both wear and damage due to lubricant-steel and metal to metal interactions. Working conditions have a dramatic effect on the in-service mechanical properties of bearing steels throughout their life. The properties of typical hydrogen embrittlement resistant steels are different, however, since they are usually employed in automobile bodies, and their strength is significantly lower than that of bearing steels.

2.4.1 Chemical composition and cleanliness

Bearing steel chemical composition is based on the Fe-C-Cr system; Some of the common compositions are listed in Table 2.4. For comparison, some hydrogen embrittlement resistant steel chemical compositions are listed in Table 2.5. The most visible differences between Tables 2.4 and 2.5 are the carbon and manganese contents. Therefore, the influence of these two elements will be discussed first.

Table 2.4: Chemical composition of common bearing steels (wt%).

Grade	C	Mn	Si	Cr	Ni	Mo	Cu	S	P	Others	Reference
100Cr6	0.98	0.38	0.16	1.39	0.07	0.02	0.12	0.06	0.12	-	[83]
AISI 1070	0.71	0.76	0.20	0.09	0.08	0.02	0.07	0.012	0.006	-	[84]
ShKh4	0.98	0.18	0.17	0.38	-	-	-	-	-	-	[85]
ShKh15	1.05	0.28	0.28	1.50	0.11	-	0.06	0.015	0.013	-	[86]
SJU2	1.03	0.37	0.23	1.35	0.51	-	0.15	0.023	0.018	-	[87]
100CrMo7-3	0.97	0.66	0.27	1.79	0.11	0.26	0.15	0.007	0.009	0.0005	[88]
52CB	0.85	0.35	0.85	0.90	-	0.60	-	-	-	-	[89]

Table 2.5: Chemical composition of reported high strength hydrogen embrittlement resistant steels (wt%).

Author	C	Mn	Al	Ti	Mo	V	Nb	Ni	Reference
Yamasaki	0.10	2.00	0.03	-	1.59	0.56	-	-	[6]
Yamasaki	0.10	2.00	0.03	-	0.40	0.56	-	-	[6]
Yamasaki	0.10	2.00	0.03	-	0.40	0.30	-	-	[6]
Wei	0.05	-	-	-	-	-	0.41	2.00	[59]
Wei	0.05	-	0.20	-	-	-	-	2.00	[59]
Wei	0.05	-	-	-	-	0.24	-	2.00	[59]
Takahashi	0.03	0.20	3.00	0.01	-	-	-	-	[11]

Generally, carbon content in bearing steels varies from 0.10 (wt%) in high-temperature bearings steels to approximately 1.05 (wt%) in through-hardening bearing steels. The high content of carbon in the latter should ensure greater hardness and wear resistance. It is well known that an increase in carbon content raises the amount of carbides and retained austenite, and decreases the martensite start temperature. Fine carbide precipitates in both martensitic and bainitic bearing steel microstructures also contribute to the strength of the material. Aimed at increasing hardenability of bearing steels, also other elements are added, for example: Mn, Cr, Mo and Ni, the last being rather costly. Carbide

forming elements like Mn, Cr and Co, control the cementite particle size via reducing the dissolution rate of the spheroidized cementite. Manganese content in bearing steels is in the range from 0.2 to 1.2 wt% [90].

As opposed to bearing steels, carbon content in hydrogen embrittlement resistant steels is very low in order to retain both formability and weldability, providing better mechanical properties and greater resistance to atmospheric corrosion than conventional carbon steels. In terms of manganese, hydrogen embrittlement resistant steels contain around 2 (wt%) in order to improve hardenability and grain refinement, since manganese lowers the austenite to ferrite transformation temperature. Takahashi's steel is exception, because it contains a lower amount of manganese (0.2 wt%), but higher aluminium content that similarly to manganese moves the transformation curves to longer times on continuous cooling transformation (CCT) diagrams. Additional grain refinement leads to better toughness [91], an important property for automotive steels.

Titanium, vanadium and niobium in hydrogen embrittlement resistant bearing steels can be added for strengthening or hydrogen trapping. In bearing steels these elements are used mainly to prevent austenite growth at higher temperatures and to form carbides for wear resistance [90]. Additionally, molybdenum is claimed to increase the coherency between ferritic matrix and precipitates, increasing hydrogen trapping capacity [6].

Other elements like molybdenum and chromium in bearing steels have a strong impact on heat treatment in terms of hardenability, grain size, consistency of spheroidization [92] and resistance to decarburization [93]. In 100Cr6, chromium is the main substitutional and carbide forming alloying element which has an impact on the lower bainite formation. It was reported that even a small amount of Cr retards the austenite decomposition reaction into bainite when compared with Cr-free steels [94]. The most typical bearing steel, 100Cr6, contains 1.35 to 1.60 wt% Cr; however, chromium content might be much greater, for instance: stainless bearing steels contain 12 to 19 wt% Cr [95], this ensures corrosion resistance at the expense of hardness and strength. Both chromium and molybdenum retard the formation of bainite in bearing steels. Molybdenum delays it very weakly com-

pared to chromium. Additionally, molybdenum and vanadium produce stable carbides and retard recovery at high temperature. Therefore, high-temperature bearing steels usually contain both these elements. In chromium containing bearing steels, the addition of cobalt and aluminium may be beneficial. Since the transformation rate might accelerate the increase in free energy change accompanying the transformation of austenite into ferrite [71]. Moreover, these elements have different effects on the precipitation of cementite in austenite, Al retards cementite precipitation since it is not solvable in cementite [96], similar to Si [97], while Co is a carbide former. Nickel does not form carbides in steel, but instead decreases the ductile-brittle transition temperature for case-hardening bearing steels it is typically added in the range of 0.4 to 4.3 wt%.

The continuous improvement of steelmaking processes such as controlling the reoxydation phenomena allows the steelmakers to produce grades with very low oxygen (less than 0.002 wt%) and sulphur (max. 0.015 wt%). Impurity levels in commercial steels are listed in Table 2.6.

Table 2.6: Reported dissolved impurity levels in commercial steels. After [4].

Solute	P	C	S	N	H	O	Ti
Concentration / ppmw	10	5	5	10	<1	3	10

2.4.2 Mechanical properties

Numerous properties must be displayed both by bearing as well as hydrogen embrittlement resistant steels to fulfil in-service requirements. These include strength, fatigue and wear resistance. Additionally, machinability is required to shape bearings, and dimensional stability is paramount for ensuring structural integrity. However, as it can be seen from Table 2.7, bearing steels are not very ductile at room temperature, their elongations are in the range of 2%. Some of the typical mechanical properties displayed by popular bearing steels are listed in Table 2.7.

Table 2.7: Typical mechanical properties of typical bearing steels [95].

Steel	Microstructure	Ultimate tensile	Yield	Elongation	Hardness
		strength / MPa	strength / MPa		
100Cr6	martensite	2300	1700	2	61-64
100Cr6	bainite	-	-	-	58-61
100CrMnSi4-4	martensite	2300	1700	2	61-64
100CrMn6	martensite	2300	1700	2	61-64
100CrMn6	martensite	2300	1700	2	61-64
100CrMo7	bainite	2300	2100	5	58-61
100CrMnMo8	bainite	2300	2100	5	58-64

Steels resistant to hydrogen embrittlement are usually modified high strength low alloy steels. Their applications include automotive, for example. They contain low amount of carbon (0.2 wt%) which limits their strength; this is compensated by grain size refining.

Additional strengthening is achieved by precipitation hardening given by second-phase particles, such carbides and carbonitrides which include Ti(C,N), NbC, VC [98]. Producing carbides such VC, NbC or TiC on ferrite can give a desired hydrogen trapping capacity making the steel hydrogen embrittlement resistant [6], [11], [59]. The ferritic matrix can be further strengthened by solid solution additions. The aim of this thesis is to design a hydrogen embrittlement resistant steel taking as a baseline the existing hydrogen embrittlement resistant steels.

2.4.3 Rolling contact fatigue essentials

Rolling contact fatigue (RCF) causes damage usually below the raceway; this is due to repeated stresses between two components. The damage progress determinates the bearing life. Bearing life is defined as the number of inner ring revolutions that a bearing is able to endure before showing the first sign of fatigue, for example via excessive vibration. According to International Standard ISO 281: 2007 the bearing life is defined by equation 2.6 [99]:

$$L_{10} = 10^6 a_1 a_2 a_3 \left(\frac{c}{p} \right)^n \quad (2.6)$$

where, L_{10} is the number of either revolutions or hours achieved by 90% of bearings subjected to the same load before the first signs of fatigue are recorded, c is often called a basic dynamic load rating and expresses the maximum load carried, which allows one million inner ring revolutions to be reached with a 90% success probability, p is the bearing load applied beneath the actual dynamic loading conditions ($n = 10/3$ for roller bearings and $n = 3$ for ball bearings), a_1 is a reliability factor (a_1 is equal to 1 for 90% reliability, in case of L_{10} and 0.21 for 99% reliability or L_1), a_2 accounts for the material type and a_3 is the adjustment factor depending on the operating conditions.

Rolling contact fatigue happens most often in rolling element bearings and gears. The damage process of rolling contact fatigue involves fatigue crack initiation as well as crack propagation. The failure progress is related to the characteristics of the surface quality, stress distributions and lubrication condition. The main factor that causes rolling contact fatigue failure are surface crack defects.

Cyclic stress fields generated below the raceway surface might contribute to material removal from the surfaces in contact. This can become the origin of crack formation and propagation, leading to rolling contact fatigue [100]. This phenomenon is named spalling fatigue damage, and typically terminates the bearing life.

Cyclic stress may also lead to surface distress, where the accumulation of inhomogeneous micro-plastic deformation results from insufficient lubrication or contamination of tiny solid particles present in the oil or grease. The latter is typified by cracks present beneath the raceway bearing surface which might propagate towards the surface. There are the two types of subsurface generated cracks: white etching bands either perpendicular or parallel to the raceway surface (Figure 2.18), and the so called butterflies (Figure 1.3) which often originate from inclusions, porosity around inclusions, voids or undissolved carbides [101].

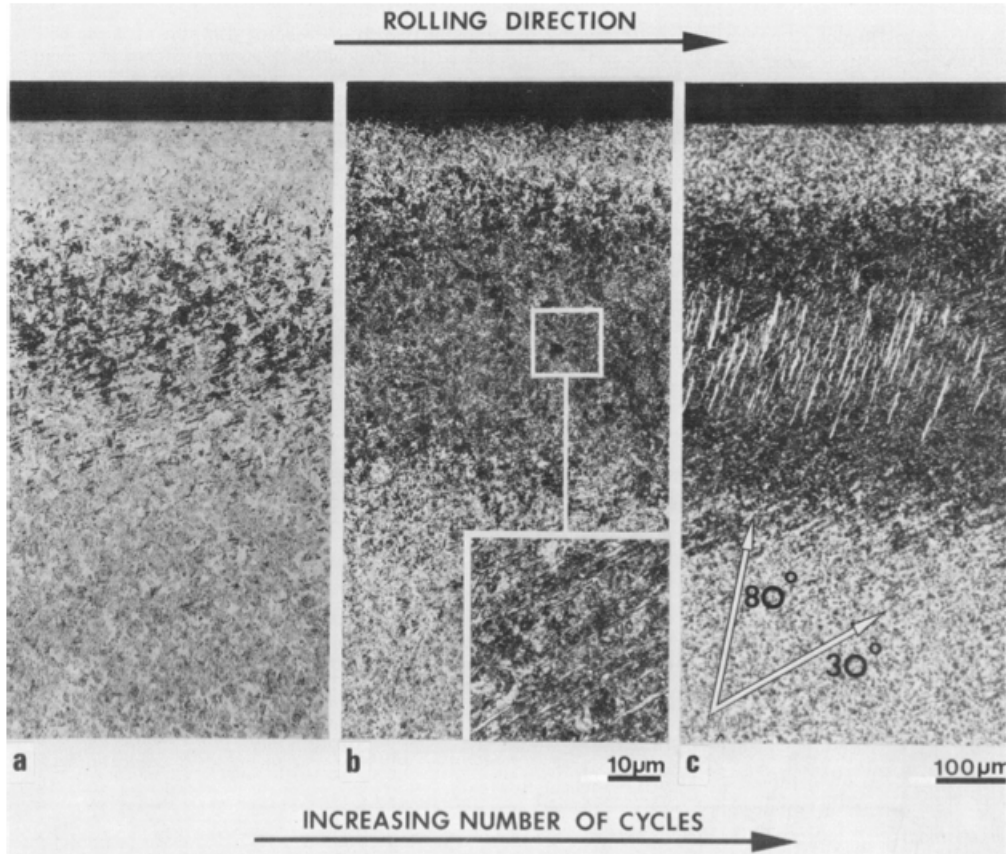


Figure 2.18: The optical microphotographs of a) dark areas formation in early stage, b) fully developed dark-etching regions with magnified 30° bands and c) white-etching regions bands forming at 80° and 30° angle to the tangent of the raceway. After [102].

Subsurface cracks usually develop dark etching regions that appear first, after rolling contact loading approximately 0.3 mm under the surface. These are observed after a several million cycles of rolling contact depending on running temperature and load [4]. The Hertzian normal stress distributions are shown in Figure 2.19. The contact stress is maximum in the centre.

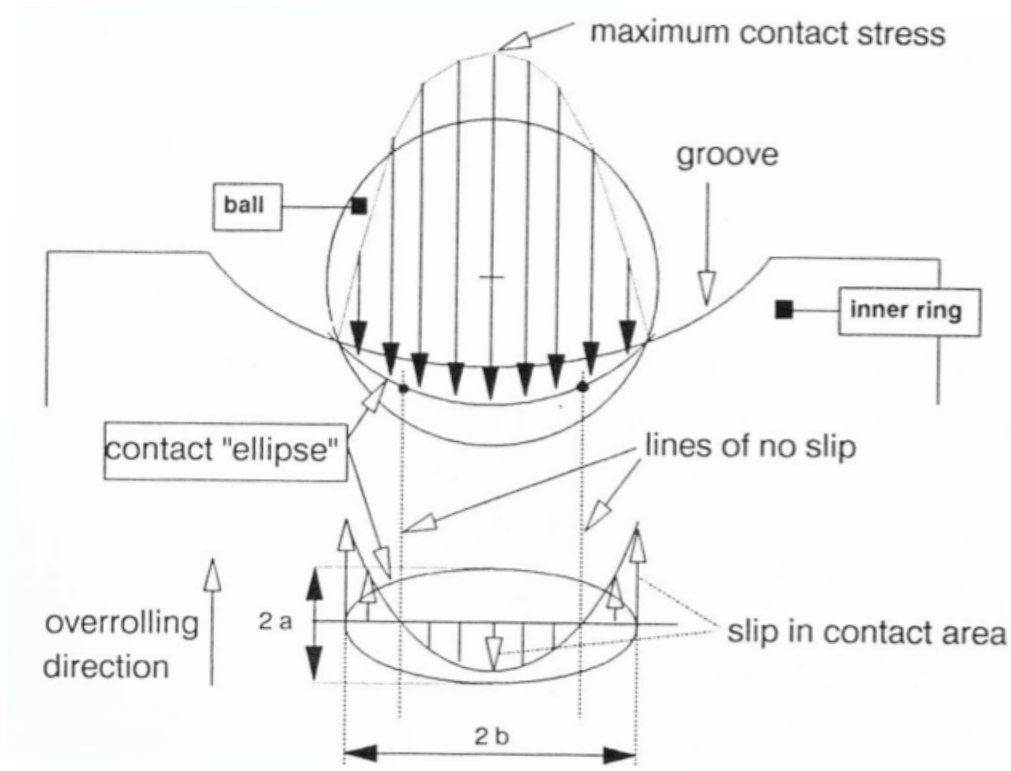


Figure 2.19: Normal stress distribution in bearing inner ring. $2a$ is the width of the contact in tangential direction, $2b$ is the width of the contact in axial direction. After [103].

Rolling contact fatigue can be influenced by inclusion content that are often accompanied with surrounding them porosity. Such discontinuities located close to a hard inclusion can become nuclei for microcracks, which subjected to rolling contact fatigue might rub against each other causing butterfly wings formation and decreasing the bearing fatigue life [104]. Aluminium oxide or silicates might also act as crack nucleation sites, these are highly brittle and produce negative stress fields around them. For example, according to Kerrigan [104], the presence of butterflies is increased by D-type oxysulfide inclusions. As such, D-type inclusions are regarded as being both non-deformable and acting as stress-raisers in the product. For these reason, bearing steels producers perform deoxidation to reduce the oxygen content and inclusions in steel production. Inclusion content is lowered, thereby ensuring steels with consistently high cleanliness and superior fatigue properties [105]. It has been pointed out that the specification in terms of the oxygen and sulphur contents are not sufficient to guarantee good contact fatigue properties [106].

Hence, fatigue endurance is a function of internal defects as mentioned above. It is essential to conceive ways of stopping or postponing crack propagation mechanisms from inclusions, because it is highly probable that they appear even after the refinement of steelmaking processes. Moreover, spalling damage can be also initiated from the surface when a crack size has sufficient size to bridge the distance from the surface to the crack zone under the surface [103]. Some interesting research on surface initiated crack growth and the hydrogen influence on this mechanism was done by Murakami [8]. It is well known and documented that when considering rolling contact fatigue damage, the extremely important and complex role of hydrogen in fatigue crack propagation is considered.

The influence of hydrogen on the fatigue life of bearing elements has been widely studied and investigated. Additionally many attempts at physically explaining this phenomenon have been made; however, no definite explanation has been produced yet. It is known that a metal yields, when subjected to a stress beyond a yield point, and below this critical value the material is elastic on a macroscopic scale. However, even for the stresses well below the yield point, failure due to fatigue may occur after a given number of cycles. After all, the microstructure contains a myriad of crystal defects like dislocations, inclusions, voids, etc. which under a critical shear stress become mobile. The mobility might be counteracted by alloying or a high carbon content. Hydrogen, which is an interstitial in iron, also influences defect mobility. The presence of hydrogen in the bearing steel microstructure is negative, since it decreases fatigue resistance [107]. During high-cycle rolling contact fatigue, low micro-plastic failure mechanisms are active. In the first stages of fatigue, damage accumulation is controlled by small-scale obstacle-controlled dislocation glide. This mechanism generates many crystal defects such as vacancies, dislocations and vacancy-carbon clusters [108], this retards the yielding mechanism and work hardening that occurs afterward. After this stage, often called shakedown, the steady-state occurs, at which the micro-plastic damage rate is much slower than during shakedown. The steady state control is critical for bearing life; during this, the damage rate is controlled by dislocation glide and can be continued when the dislocations, which are previously

trapped by obstacles, become acquitted [109]. The dislocation climb mechanism at usual bearing working conditions (below 100 °C), however, is negligible because the thermal energy at low temperatures is not high enough to permit significant self-diffusion [110]. In addition, the presence of carbon tends to reduce the number of mobile defects and in this way improves the fatigue resistance of the bearing steel. With a rise in atomic hydrogen in carbon-containing steels, the number of mobile point defects is likely to increase. As a matter of fact, the atomic hydrogen encourages the self-diffusion process of iron, so it accelerates the fatigue damage process [111].

There were many studies about hydrogen effects on fatigue properties and rolling contact fatigue. One of them was performed by Murakami *et al.* [8], which describes hydrogen effects on crack propagation behaviour and on the structural fatigue properties (push-pull test) in various steels. The samples were hydrogen charged by using water solution with $\text{H}_2\text{SO}_4 + \text{NH}_4\text{SCN}$. They found that austenitic stainless steel can dissolve more than 100 ppm of hydrogen while tempered low-alloyed steels and ferritic stainless and hardened up to 10 ppm. Apart from this, they also find a remarkable increase of fatigue crack growth in prior hydrogen charged specimens when compared to non-charged ones. The cracks in non-charged samples exhibit zigzag appearance while they were relatively linear in hydrogen-charged samples. Besides, many slip bands were observed in cracks neighbourhood in hydrogen-free material, while only a few slip bands were located in the vicinity of the cracks in the hydrogen charged samples. Hard martensitic stainless steels (0.7 wt% C, 13 wt% Cr) non-charged specimens (0.2 ppm H) fail after 5.5 million cycles (loading with 600 MPa) while the same material but after hydrogen charging (2.4 ppm H) reached only 20 000 cycles to failure (at 350 MPa). These findings show a remarkable influence of hydrogen on martensitic hardened steel. Similarly, the studies about effect of hydrogen conducted by Kino and Otani show a strong link between hydrogen content and flaking mechanism [1]. Their research on Japanese SUJ2 with a chemical composition equivalent to 100Cr6 steel (Table 2.4) clearly demonstrate that hydrogen may diffuse from a lubricant during repeated stress and heat caused by rolling contact conditions and evokes

hydrogen embrittlement flaking by exceeding a hydrogen critical amount of about 1 ppm. It was also pointed out that the flaking mechanism starts from B-type white structures which are parallel to the rolling direction. The influence of hydrogen on rolling contact fatigue crack formation was investigated by Vegter and Slycke [112]. The formation of so-called butterflies is believed to be accelerated by hydrogen content and appeared at a lower load level than the one needed to create damage. The diffusivity in hardened bearing steels is high enough to allow hydrogen to diffuse over millimetres or centimetres during bearing working conditions. This lets hydrogen travel from the raceway surface, for example from the oil to the fatigue-exposed Hertzian subsurface zone. These cracks are believed to develop into larger and more branched cracks, leading to significantly shorter bearing life of components operating in a hydrogen active environment [112].

2.5 Designing H embrittlement resistant bearing steel

Modelling hydrogen embrittlement resistant bearing steels requires knowledge on the thermodynamics and kinetics for a variety of possible phases. This can be drawn from softwares such as MTDATA [113], Thermo-Calc [114] and MatCalc [115]. The principles behind these softwares are described in this section.

2.5.1 Thermodynamic and kinetic modelling reported in the literature

Thermodynamic softwares are able to calculate the phase equilibrium for multicomponent systems in which many phases can co-exist. Programs such as MTDATA and Thermo-Calc are widely used since they are capable to combine experimentally determined data to compute the Gibbs free energy of each phase. MTDATA calculates equilibria by Gibbs energy minimisation procedure. The equilibrium state of the system can be determined by solving, for a given temperature and pressure, the following equation:

$$G^\alpha = \sum_j^N \mu_j x_j \quad (2.7)$$

such that

$$\sum_j^N a_{ij} * n_j = r_i \quad i = 1, 2, \dots, M \leq N \quad n_j \geq 0 \quad (2.8)$$

where is the G^α Gibbs free energy of ferrite which is to be minimised by varying the values of the n_j , $j = 1, 2, \dots, N$; n_j is the moles of species j present in the considered system. Every chemical substance with a different phase designation is considered as a distinct chemical species, N is the number of species in the system, μ_j is the chemical potential of species j , which may be a function of some or all of the species amounts in the same phase; it also depends on temperature and pressure, a_{ij} is the number of units of component i per species j , M is the number of components in the system and r_i is the number of moles of component i in the system. The significance of chemical potential is illustrated in Figure 2.20. The free energies in phase system are shown in Figure 2.21; In this case the average concentration of the alloy is $\bar{x}$, and the concentrations of phase α in equilibrium in γ is $x^{\alpha\gamma}$, and of phase γ in equilibrium with α is $x^{\gamma\alpha}$, and the driving force for the formation of α from γ is $\Delta G^{\gamma-\gamma+\alpha}$.

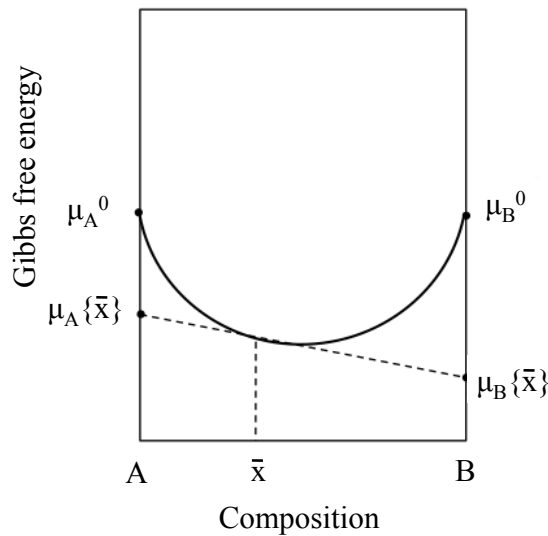


Figure 2.20: The meaning of a chemical potential μ . After [116].

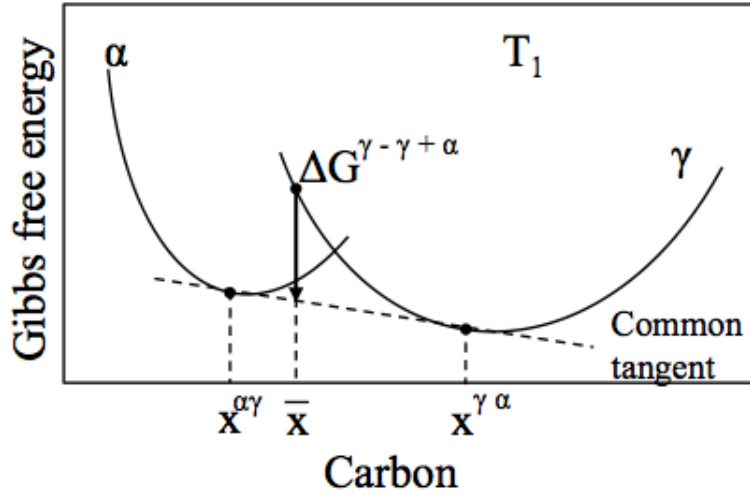


Figure 2.21: The common tangent construction for estimating the equilibrium compositions of two phases at the known temperature T_1 . After [116].

The minimisation of Gibbs free energy in multicomponent and multiphase systems is performed with methods based on Numerical Optimisation Software Library [113, 114]. A lower value of the Gibbs free energy is found at the end of each iteration. More detailed description of the software can be found in Gill, Murray and Wright [117]. Microstructure modelling of steel requires not only the prediction of the equilibrium phases, but also their evolution towards equilibrium. In the case of trapping precipitates, their size distribution plays an important role in achieving desirable hydrogen trapping capabilities. The most effective precipitate size for V_4C_3 or TiC hydrogen trapping is around 10 nm [6, 11].

It is claimed the molybdenum content within M_4C_3 (where $M = V, Mo$) for 10 nm size carbides increases the particle/matrix coherency degree to its optimum, suggesting that via controlling carbide composition, greater hydrogen trapping capacity may be achieved. On this basis it was also stated that the hydrogen trapping capacity does not only depend on the number density of precipitates [6].

As the experimental results show that the optimal precipitate radius for hydrogen trapping approaches that of nucleation [6], the computation of nucleation kinetics may be a good first approximation to optimise the alloy composition and precipitation temperature.

Invoking the classical nucleation theory, the nucleation rate may be expressed as:

$$I = N_0 \frac{kT}{h} \exp \left\{ \frac{-(G^* + Q^*)}{kT} \right\} \quad \text{with } G^* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_V} \quad (2.9)$$

where N_0 is the number of nucleation sites per unit volume of the system, k is the Boltzmann constant, h is the Planck constant, G^* is the activation energy for nucleation, Q^* is the activation energy for the transfer of atoms across the interface (when the nucleus is coherent it approaches the activation energy for diffusion), T is the temperature, σ is the interfacial energy per unit area, ΔG_V is the chemical free energy change per unit volume. The chemical free energy change per unit volume might be calculated by MTDATA or Thermo-Calc software.

Thermodynamic modelling can predict the phases existing in equilibrium at given temperature and pressure. Designing the precipitates coexisting with the desired matrix phase can be challenging. V_4C_3 precipitates were proven to trap hydrogen in their vicinity [6] and therefore have been the focus of the modelling. V_4C_3 atomic arrangement is shown in Figure 2.22.

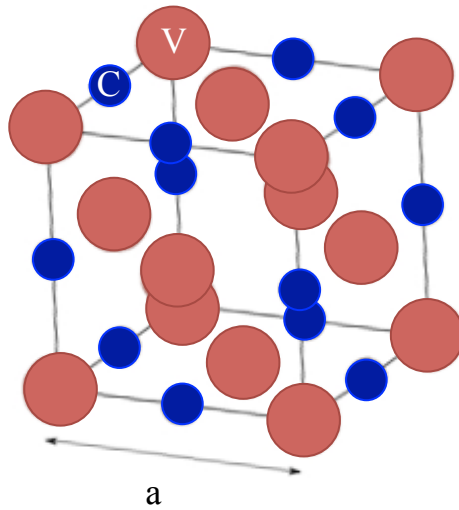


Figure 2.22: Schematic drawing showing V_4C_3 precipitate. Notice one carbon atom missing in the centre of the unit cell.

It was shown [6], that V_4C_3 will grow as thin plates on $\{100\}$ planes, and their size was reported to increase monotonically with tempering time [6]. Precipitation hardening appears for ten hours of tempering, and it was suggested that this time is the most beneficial for coherency strain, which results in a greater trapping capacity [6]. Their results clearly show coherent V_4C_3 precipitates display higher trapping capacity when tempered at 600 °C for 10 hours (Figure 2.23).

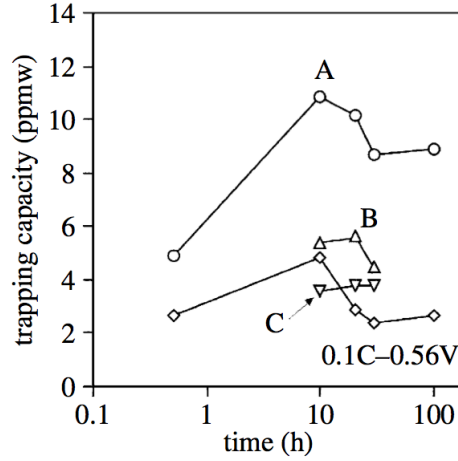


Figure 2.23: Hydrogen trapping capacity as a function of tempering time at 600 °C. Chemical composition of steel A is 0.10C-2.00Mn1.59Mn-0.56V, steel B is 0.10C-2.00Mn-0.40Mo-0.56V and Steel C is 0.10C-2.00Mn-0.40Mo-0.30V in wt %. After Yamasaki [6].

V_4C_3 eligibility is prescribed to both hydrogen trapping ability as well as precipitation strengthening. The presence of hydrogen decreases fatigue properties, whereas hydrogen trapped in the coherency fields of vanadium carbides improves the resistance to hydrogen induced static failure [118].

In Fe-C-Mo-V system the sequence of carbide precipitation is:



V_4C_3 has a Baker-Nutting orientation relationship $\{100\}_{V_4C_3} \parallel \{110\}_\alpha$ with matrix [69]. This orientation relationship between Fe and V atoms on $(100)_\alpha$ which is parallel to $(100)_{V_4C_3}$ is shown in Figure 2.24.

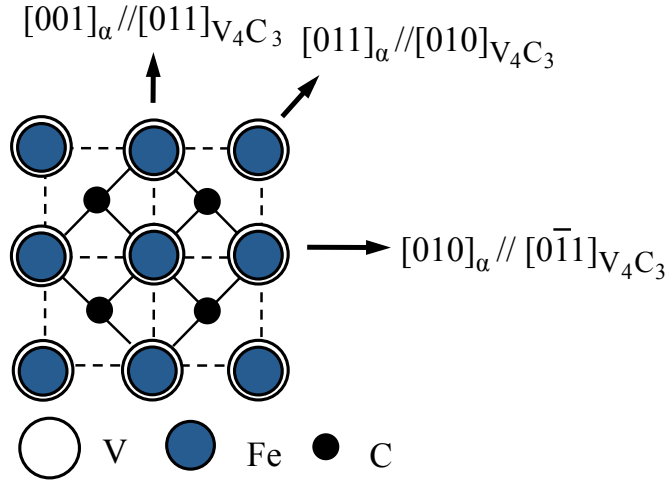


Figure 2.24: Schematic drawing showing orientation relationship between Fe and V atoms on $(100)_\alpha$ which is parallel to $(100)_{V_4C_3}$. Adapted from [119].

V_4C_3 are plate like precipitates with lattice parameter around $4.2 \text{ \AA}$ and their lattice being face centred cubic. V_4C_3 should be formed at tempering in the temperature range from $500 \text{ }^\circ\text{C}$ to $700 \text{ }^\circ\text{C}$ to ensure the nanometre-size of precipitates [6]. Large precipitates would be too coarse to maintain the coherency with the matrix, and therefore there would be a decrease in the trapping strain necessary for immobilising hydrogen in the precipitate vicinity. V_4C_3 are less stable than TiC or NbC, therefore they are easier to dissolve than the latter. V_4C_3 is dissolved more rapidly and at lower temperature than TiC and NbC. V_4C_3 dissolution temperature depends on carbon content. V_4C_3 dissolution temperature is in a range of 1200 to $1350 \text{ }^\circ\text{C}$.

2.5.2 H-charging and analysis reported in the literature

Various methods of hydrogen charging have been conducted, the most common are gaseous hydrogen charging under pressure usually 0.2 MPa at higher temperatures such as $400 \text{ }^\circ\text{C}$ [51], or electrochemical hydrogen charging with using various electrolyte solutions at different temperatures for different durations. The amount of hydrogen introduced to steel strongly depends on the charging process, where the type of electrolyte solution plays a prominent role. Hagihara *et al.* [120] proved that the hydrogen charged after around 24 h

for electrochemical charging, at the same current density and the exact sample geometry, it could vary from ~ 1 ppm (0.1N-NaOH) to ~ 4 ppm (3%NaCl + 0.3 g/L- NH_4SCN) or to even to 8 ppm (3%NaCl + 3 g/L- NH_4SCN). Electrochemical charging is is schematically shown in Figure 2.25.

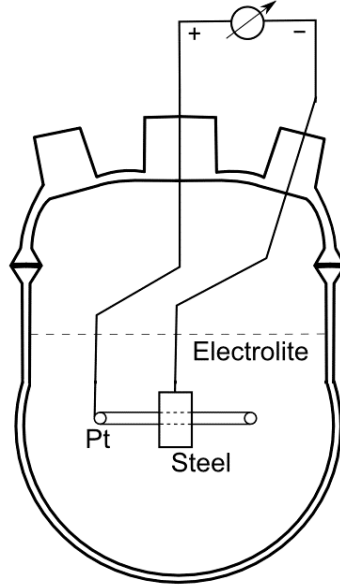
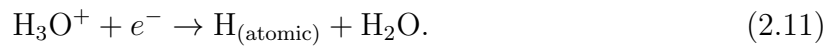


Figure 2.25: Schematic cell for hydrogen charging process. After [112].

The counter electrode is formed by platinum wire. A constant current is applied between the anode and cathode and atomic hydrogen is formed at the steel surface following the reaction



However, if H_3O^+ ions are not present, the hydrogen might form in different forms such as water splitting, the explosive mixture of hydrogen and oxygen. The electrolytical charging conditions such as time, temperature and current density might vary according to the sample size and type of electrolyte.

After hydrogen charging the amount of hydrogen can be analysed by numerous methods; being thermal desorption analysis and melt extraction technique the main hydrogen detection methods. Melt extraction technique commonly employs samples from 0.5 to 1 g weight. The sample is heated up to its melting point temperature for evaporating all dissolved gases from the metal. The gases are taken via a carrier gas (typically nitrogen) through chemical reaction tubes to analysing units, which measure the thermal conductivity of the carrier gas. The hydrogen content from a reference sample of known hydrogen content (usually 6 ppm) and weight (usually 1 g), is melted first, and used for calibration. The weight of the specimen is measured before the analysis by a balance connected to the hydrogen content analyzer and a computer, as shown in Figure 2.26. This calculation is based on the assumption that the carrier gas thermal conductivity is linear with the hydrogen content.



Figure 2.26: Overview of Eltra ONH-2000 hydrogen content analyzer. After [112].

The Thermal Desorption Analysis (TDA) is able to determine the types of hydrogen traps. The hydrogen trap binding energy and the amount of hydrogen trapped by a certain trap is determined. The TDA method is usually conducted on cylindrical dilatometry samples (typically of 8 mm diameter and 7 mm length) heated up at a constant rate, usually in the range of $100\text{ }^{\circ}\text{C h}^{-1}$ to $400\text{ }^{\circ}\text{C}$ [6]. The hydrogen desorption rate can

be measured by using a temperature programmed gas-chromatograph with a carrier gas, usually argon or helium. The choice of carrier gas depends on the detector and a column types used in the gas chromatograph. Thermal desorption analysis equipment is shown in Figure 2.27.



Figure 2.27: Overview of Thermal Desorption Analysis equipment.

The time elapsed between hydrogen charging and desorption analysis might vary according to the purpose of analysis, for example in order to measure hydrogen trapping capacity it should be more than 24 h. Results of thermal desorption analysis are usually plotted as hydrogen evolution rate charts *vs* time, and as the heating rate is changed the time can be easily recalculated. The peaks on the evolution rate charts correspond to different types of traps. The different peak temperatures for different traps at various heating rates are shown in Table 2.3. Steels with a trapping capacity higher than 3 ppmw have a great hydrogen embrittlement resistance [121]. TDA aids in determining whether a newly designed microstructure is hydrogen embrittlement resistant or not.

There were also many attempts of visualising of hydrogen trapped in the microstructure as well; for this purpose hydrogen isotopes such as deuterium and tritium have been used. Tritium isotope is radioactive and therefore make possible the investigations of hydrogen distribution and diffusion within many materials by using autoradiography. Tritium is unstable and decays to helium-3 by emission of a low energy (18 keV) beta

particle which may be detected photographically. Tritium autoradiography displays the tritium distribution in the steel microstructure, which is an aid in understanding the behaviour of hydrogen at a microscopic scale. For example, the autoradiography conducted on Ni based super alloys reveals that the typical hydrogen trapping sites are grain boundaries, inclusions and interface phases [122], as shown in Figure 2.28 for an Inconel 600 super alloy.

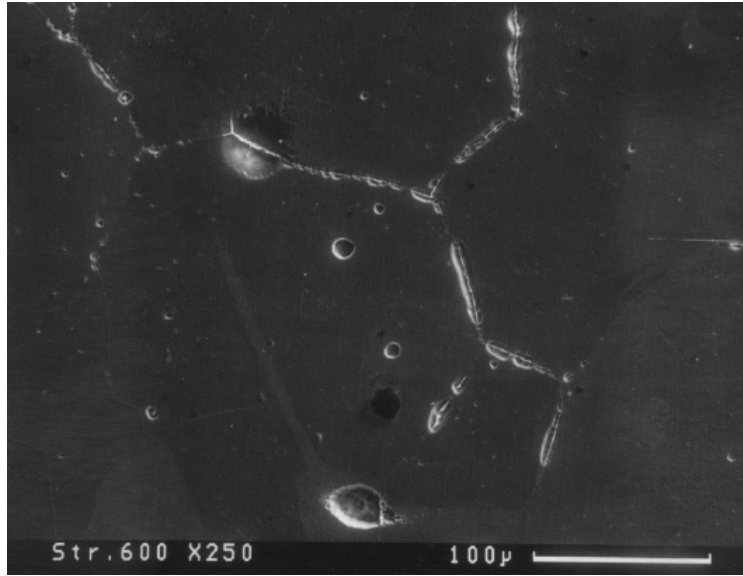
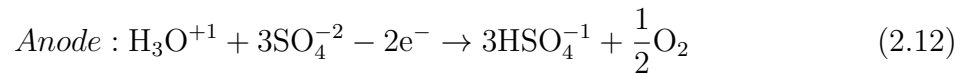


Figure 2.28: Hydrogen trapped on the deformed grain boundaries in Inconel 600 superalloy. After [122].

Charging is usually performed on a tritiated molten salt bath. Figure 2.28 was obtained with the aid of 57 wt% NaHSO₄ and 3 wt% KHSO₄, charging 3 h under a 0.850 V Ag/Ag⁺ potential at 150 °C. The reactions during tritium charging process are as follows:



In order to allow out-gassing of the diffusible tritium after charging, the specimens are kept in a radioactivity-proof glove box for 24 h. Subsequently, the specimens are polished with diamond paste under a fume hood, etched with 3% Br-Methanol solution and vacuum carbon coated to both reduce electron charge effects within the scanning electron

microscope and to protect the surface against chemical interaction with the emulsion. A L4 type ILFORD emulsion usually is used as coating material, and its film is disposed on the sample by a thin wire expandable loop. After coating, the samples are set in a dry ice box for 6 days to expose the emulsion film to β -rays emitted from the remaining tritium in the material. Then, the irradiated silver bromide layer was processed on the specimen into the developer and for 10 min into the fixer. After that, the samples should be washed and dried in a dust-free box overnight. In the end the samples can be observed under scanning electron microscope [122]. The surface emulsion coating layer and the depth of the β -ray source interaction is presented in Figure 2.29.

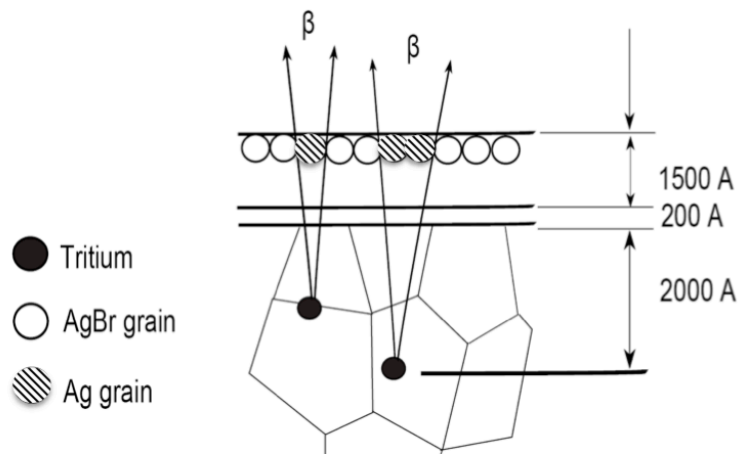


Figure 2.29: Hydrogen trapped on the deformed grain boundaries in Inconel 600 superalloy. After [122].

Deuterium (heavy hydrogen) isotope is used in atom probe tomography (APT) for displaying the hydrogen distribution in steel. APT technique is good for visualising the distribution of heavy hydrogen in the microstructure because of its high spatial resolution, and low specimen temperature that does not increase the diffusivity of the investigated heavy hydrogen in the microstructure. Deuterium is used in order to separate the hydrogen charged into the steel from the hydrogen present in the background. The chemical properties between hydrogen and deuterium are slightly different, for example diffusion coefficient of the former is smaller due to its larger mass. The technique was used by Takahashi and Kawakami and their results are described in [11]. The needle-like steel

sample (Fe-0.03C-0.2Mn-3.0Al-0.1Ti (wt%), was annealed at 580 °C for 4 h and deuterium charged at 250-300 °C for 5 or 10 min in a high vacuum ($\sim 7 \times 10^{-4}$ Pa) charging cell, then rapidly cooled to -100 °C and transported to an analysis chamber with the temperature set below -203.15 °C. Afterwards, APT analysis was done using an energy-compensated three dimensional atom probe (3DAP) with a large-angle reflection. The test conditions are as follows: ultra high vacuum ($\sim 4 \times 10^{-9}$ Pa), -208.15 °C, the total probing voltage was 8-15 kV, a pulse fraction of 25% and a pulse frequency of 20 kHz. The results of it are presented as the maps shown in Figure 2.12. The deuterium (hydrogen) is trapped by tiny and densely distributed TiC precipitates (1.3×10^{17} cm³), with their hydrogen desorption peak estimated at 220 °C by the thermal desorption spectrometry (TDS) performed at a heating rate of 100 °C h⁻¹.

2.6 Summary

There are many possible mechanisms for hydrogen entry into the steel bulk, this is followed by its diffusion in the microstructure at a high pace. Hydrogen can be immobilised and trapped by various defects present in the microstructure, however many of those traps are shallow and will not trap hydrogen strongly, causing hydrogen desorption after a short time. There are many theories reported on hydrogen behaviour and their effect on steel properties. When considering hydrogen embrittlement phenomena, it should be highlighted that delayed brittle fracture in hydrogen-rich steels exposed to static stress starts with small-scale plastic deformations, funnelled by the mobility of crystal defects being increased by hydrogen. The brittle fracture will not appear and proceed without the localised plastic deformations. It is demonstrated that hydrogen is undesirable and damaging when it is in a diffusible state. Therefore there is a tendency in designing steels that are either able to trap mobile hydrogen in the microstructure, or to reduce its diffusion into the steel. Hydrogen trapping can be realised by many trapping strategies; however, due to bearing steel requirements on hardness, the most beneficial trapping sites are

believed to be nano-sized precipitates. After designing the hydrogen embrittlement steel it is crucial to prove its hydrogen trapping capacity. From numerous methods of hydrogen analysis, the most informative and effective seems to be thermal desorption analysis, which provides information about both type of trapping site and hydrogen content trapped.

Chapter 3

Design and modelling of hydrogen-resistant bearing steels

The purpose of the thermodynamic and kinetic modelling performed in this work is to design a hydrogen embrittlement resistant bearing steel, taking as a baseline the common 100Cr6 bearing steel, while considering both bearing steels performance requirements and incorporating up to date hydrogen resistant automotive steels concepts [6, 11]. The hardness of previously designed hydrogen embrittlement resistant steels is insufficient for bearing applications, therefore their microstructure requires alterations in order to produce steels displaying sufficient hardness. The central concept in this alloy design strategy is to conceive a bearing steel possessing V_4C_3 traps. Based on the above considerations, two alloys with the addition of vanadium will be considered in this chapter: 100Cr6+0.5V and 100Cr6+2.75V. The full justification of this choice is provided in the following sections.

3.1 Modelling tools

Thermodynamic modelling was conducted with the aid of MTDATA version 4.81, and Thermo-Calc with TCFE v.6 database. A diagram illustrating the variables for thermodynamic modelling is shown in Figure 3.1, where μ_i^j is a chemical potential of chemical element i in a phase j , α is ferrite, γ is austenite, G^α is the Gibbs free energy of ferrite, G^γ is the Gibbs free energy of austenite, $G^{V_4C_3}$ is the Gibbs free energy of vanadium carbide. The principles of thermodynamic calculations are described in the following subsection.

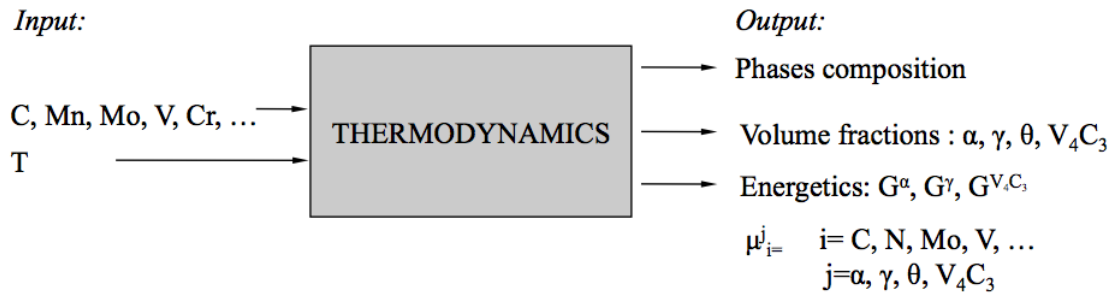


Figure 3.1: Schematic diagram illustrating thermodynamic calculations.

Kinetic modelling was done using MatCalc 5.44 software with the thermodynamic database (mc_fe.tdb) version 1.009 and diffusion database (mc_fe.ddb) version 0.006.

3.1.1 Thermodynamic modelling

Kaufman and Bernstein reviewed and modified the calculation of phase diagrams laying the base for the CALPHAD method [123]. To date, enormous progress in the model description and computational technology advances has been made. Thermo-Calc [114] and MTDATA [113] are the softwares for thermodynamic calculations and phase equilibrium calculations in unary and multicomponent systems. They are based on thermodynamic data assessed with the CALPHAD technique and incorporate Gibbs free energy minimisation algorithms.

It is possible to use Thermo-Calc and MTDATA in user-written computer programs in languages such as Fortran. These can retrieve thermodynamic data and calculate phase

equilibrium following the principles presented in this section. For iterative thermodynamic calculations TQ computing interface was used. TQ interface is a software package for multi-component phase equilibrium calculations, and it allows to write application programs calling Thermo-Calc routines [124].

In performing the calculations, the phases allowed to thermodynamically co-exist are: cementite, ferrite, M_2C , M_4C_3 , M_7C_3 , $M_{23}C_6$ and M_6C . The free energy of phases such as austenite, ferrite, cementite, V_4C_3 and other precipitates that were allowed to co-exist thermodynamically are calculated by using a sub-lattice model. Temperature and pressure are incorporated via the G-HSER format:

$$G^{T,P} - H^{SER} = a + bT + cT \ln T + eT^2 + fT^3 + i/T + \int_0^P v^{P,T} N_A dP \quad (3.1)$$

where $G^{T,P}$ is the molar Gibbs energy at temperature T , and pressure P , H^{SER} is the enthalpy of the element or substance in the reference state at 298.15 K, $v^{P,T}$ is the atomic volume at (T, P) and N_A is Avogadro's number. Parameters such as a , b , c , e , f and i are fitted from thermodynamics databases.

For a given system, the reliability of the calculations depends on the available databases for all considered components and their interactions. For the modelled system, MTDATA calculates the mass fractions and compositions of all the phases at which the Gibbs free energy of the system is minimum. Thermodynamic calculations are not able to predict the time dependence on phase stability, for which kinetic modelling was employed.

3.1.1.1 Influence of chemical elements on V_4C_3 formation and dissolution

For a given Fe-C-Cr-Mn-V-Mo-Si system, the chemical element concentrations were first varied in order to identify the most critical elements influencing V_4C_3 stoichiometry, facilitating its formation at given temperature. The calculation for V_4C_3 formation was performed with MTDATA software and the chemical elements ranges were chosen based on the baseline steel 100Cr6. As V_4C_3 consists mainly of vanadium and carbon, both the elements were given especial attention. By changing just one element at a time for

a given temperature (600 °C), for low 0.1 wt% and higher 1.0 wt% carbon contents, chemical elements such as Mo, Si, V, Cr and Mn were varied step by step. The gathered results are shown in Figure 3.2, the calculation applies to V_4C_3 formation in equilibrium at 600 °C. This was chosen as V_4C_3 lengthens in automotive steels to an appropriate size at such temperature.

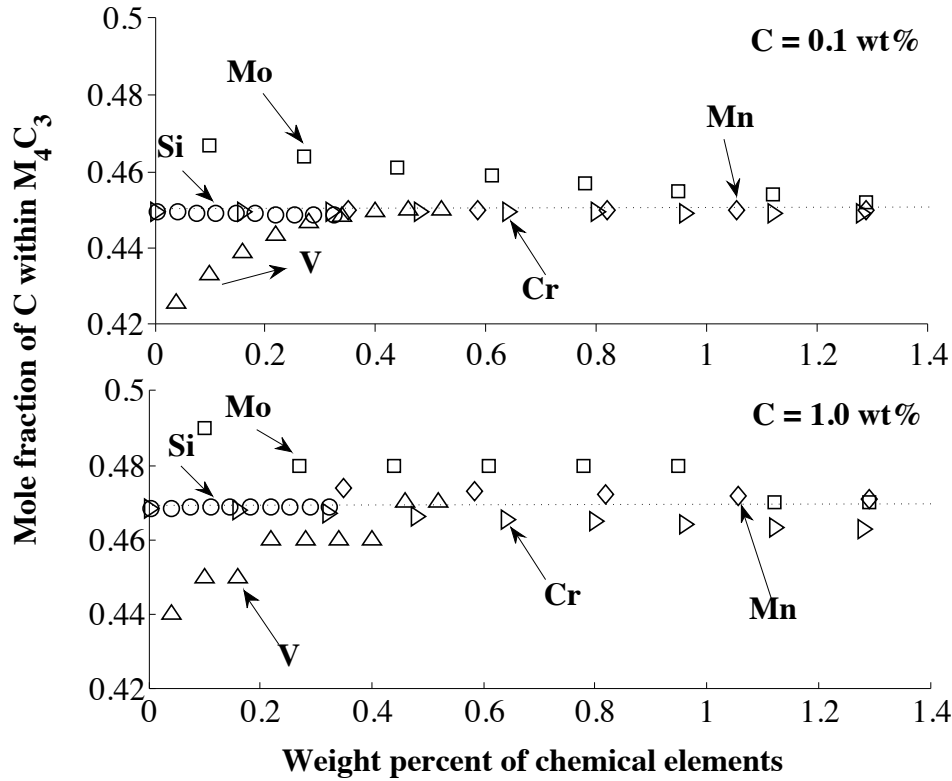


Figure 3.2: Influence of chemical elements on M_4C_3 formation, $M = V, Mo$.

Although the formation of precipitates is crucial, their dissolution is no less important. Figure 3.3 illustrates the influence of vanadium and carbon addition on V_4C_3 dissolution temperature. The calculation was performed with Thermo-Calc employing TCFE v.6 database. The TQ computing interface in a Fortran platform allowed iterative thermodynamic calculations. In Figure 3.3 carbon and vanadium were varied to understand their influence on dissolution temperatures.

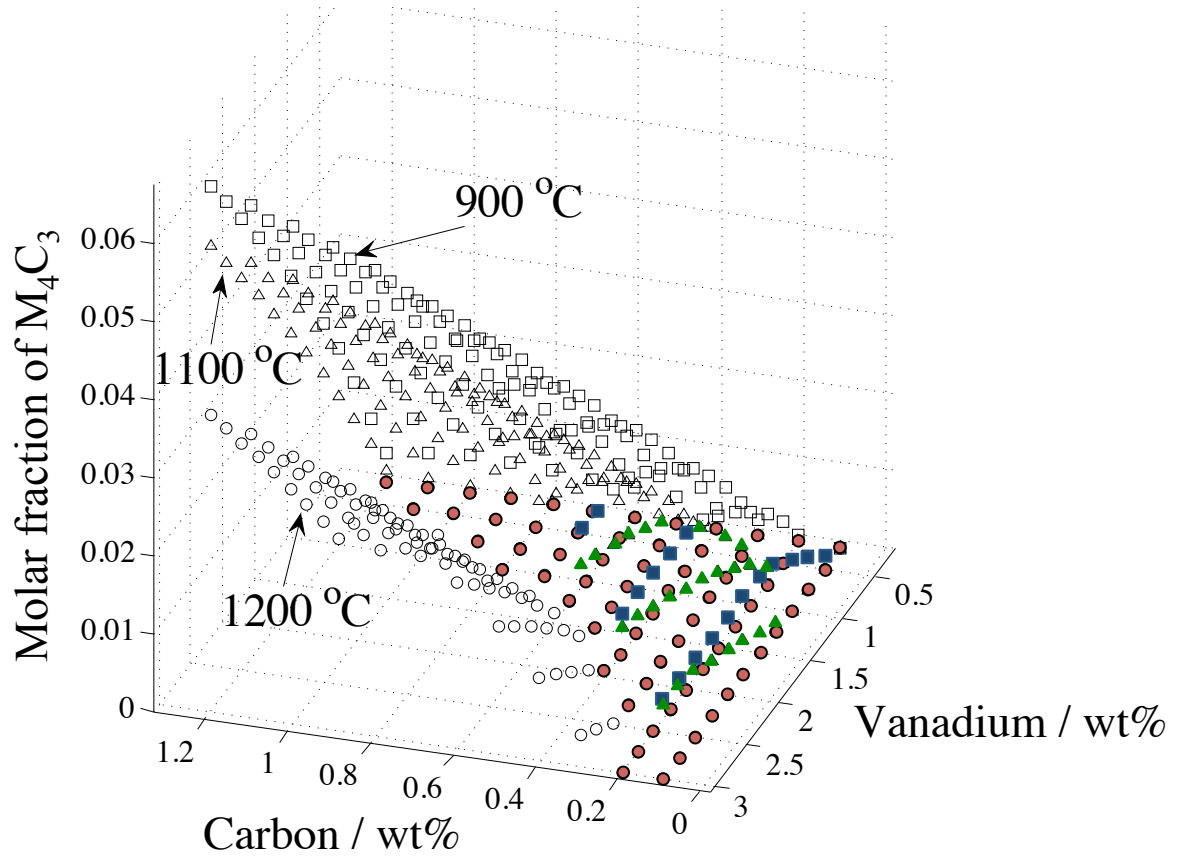


Figure 3.3: Dissolution temperature for M_4C_3 ($M = V, Mo$) for 100Cr6 baseline steel, varying the indicated elements. Filled bullets indicate the molar fraction of M_4C_3 equal to zero, indicating the chemical compositions with the dissolution temperatures: 900, 1100 or 1200 °C sufficient for M_4C_3 dissolution.

Figure 3.2 and Figure 3.3 show that vanadium and carbon have the most significant influence on both M_4C_3 stoichiometry and dissolution, while other elements such as Mo and Cr have much lower impact. It should be noticed additionally that in steels with carbon up to 0.6 wt%, M_4C_3 can be dissolved even at 900 °C.

3.1.1.2 Phase fractions and diagrams for the modelled steels

Phase diagrams give a visual representation of the state of an alloy as a function of temperature, pressure and concentrations of the constituent components. The calculations were done by using Thermo-Calc software with all the possible phases allowed to thermodynamically co-exist, except for diamond and graphite. The calculation was done for two considered steels: 100Cr6+0.5V and 100Cr6+2.75V, consisting of 100Cr6 base composition (Table 2.4) with 0.5 wt% and 2.75 wt% vanadium. Phase diagram sections plotted for lower and higher vanadium contents (0.5 wt% and 2.75 wt%, respectively) are shown in Figure 3.4 and 3.5, respectively.

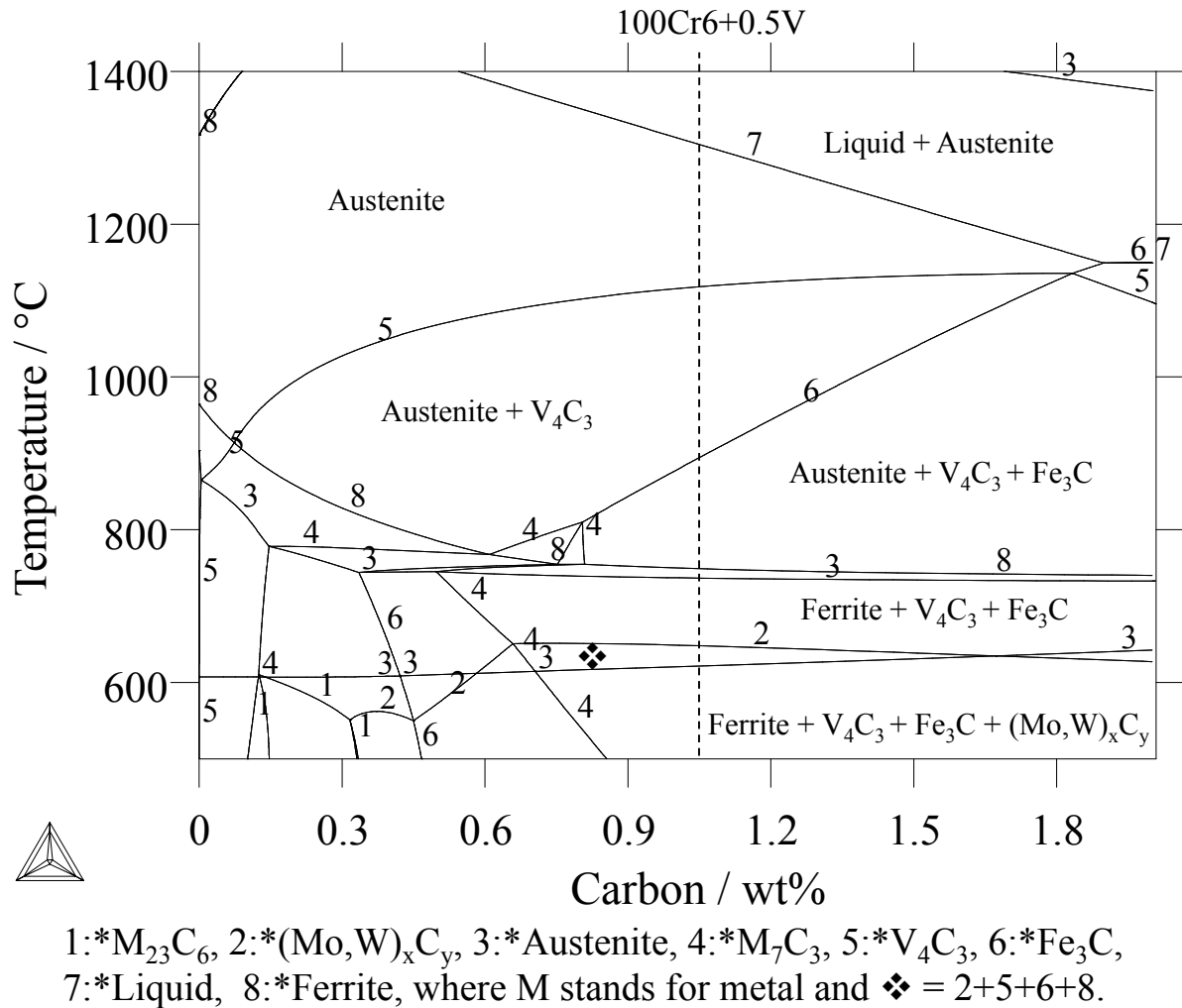
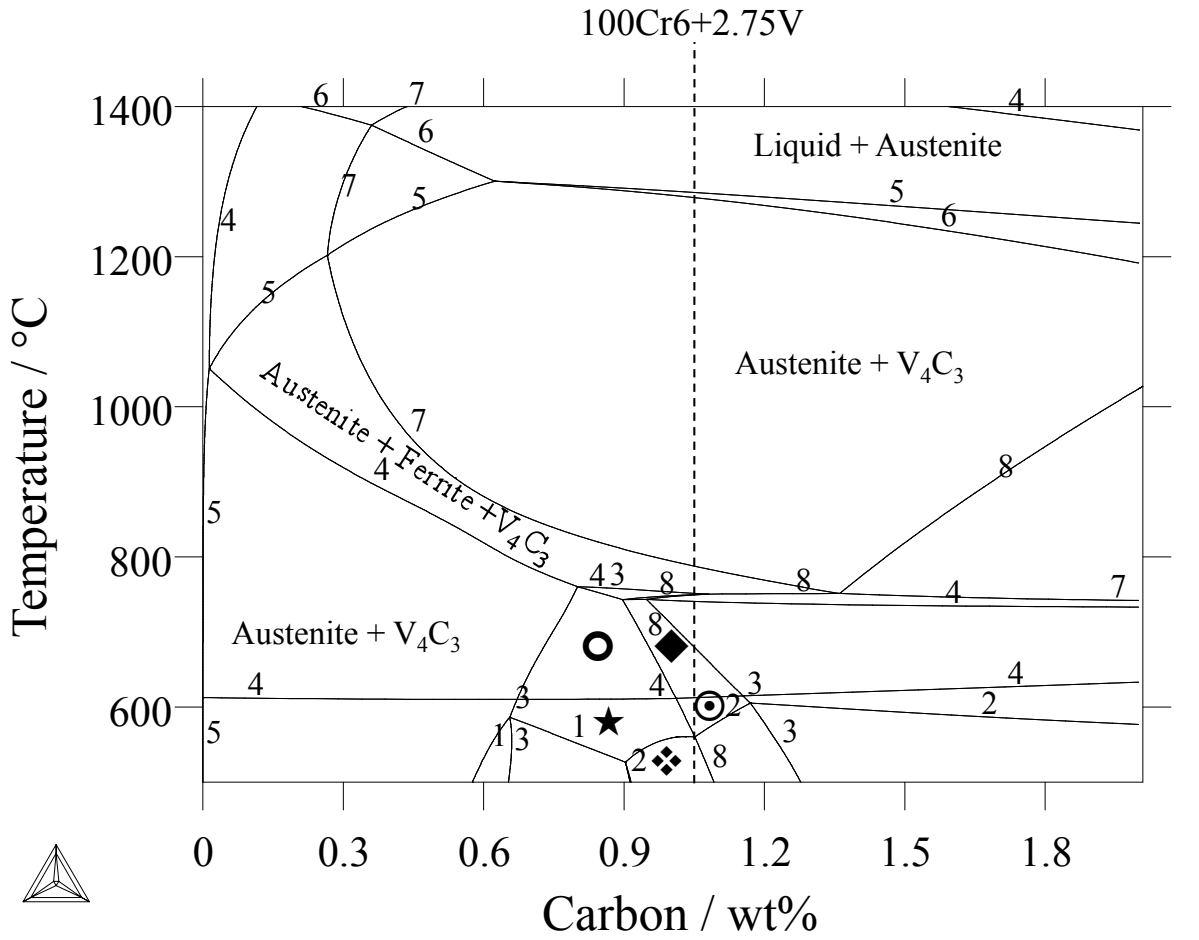


Figure 3.4: The major phases in 100Cr6+0.5V.



$\bigcirc = 3+5+7$, $\blacklozenge = 3+5+7$, $\star = 3+5+7$, $\odot = 2+3+5+7$, $\blacklozenge = 5+7+8$.
 1: M_{23}C_6 , 2: $(\text{Mo}, \text{W})_x\text{C}_y$, 3: M_7C_3 , 4: Austenite, 5: V_4C_3 , 6: Liquid, 7: Ferrite, 8: Fe_3C , where M stands for metal.

Figure 3.5: The major phases in 100Cr6+2.75V.

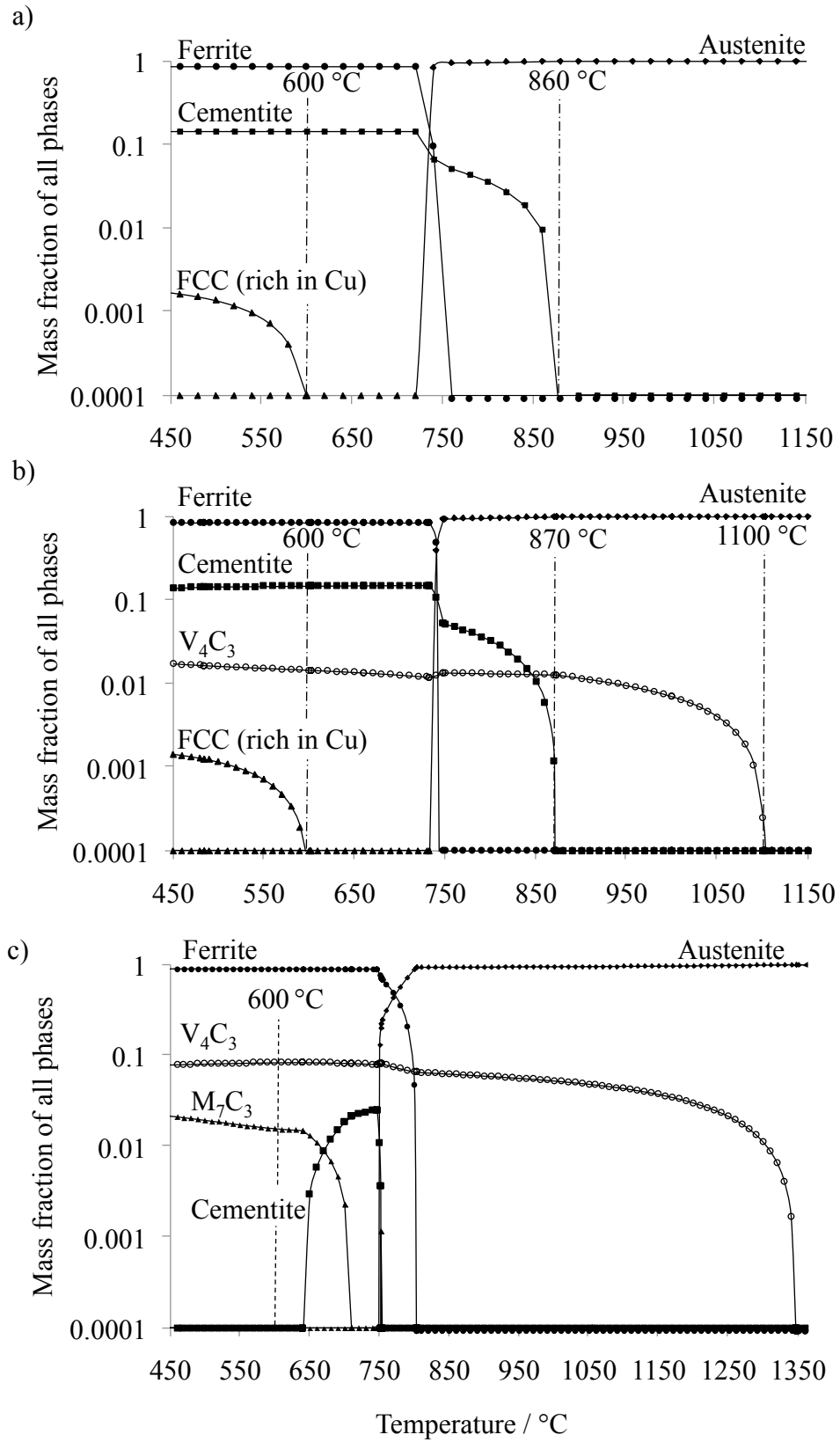


Figure 3.7: Phase fractions in a) 100Cr6, b) 100Cr6+0.5V and c) 100Cr6+2.75V.

3.1.2 Algorithm for designing hydrogen embrittlement resistant steels

Thermo-Calc was employed with TCFE v.6 database. TQ computing interface was run in a Fortran platform for iterative thermodynamic calculations. An algorithm was followed for the simultaneous variation of chemical elements in the ranges specified in Figure 3.8, which were chosen to correspond with bearing steel compositional specifications [84, 85, 87]. Vanadium content was fixed, since it has been already demonstrated that 0.5 wt% is necessary for V_4C_3 formation in Fe-C-Cr-V. The algorithm was an aid for finding an alloy with no cementite in equilibrium at the V_4C_3 formation temperature (600°C). The results of this computatorial approach are shown in Figure 3.9 and 3.10, where the chemical element amounts are plotted with respect to cementite and V_4C_3 content, respectively.

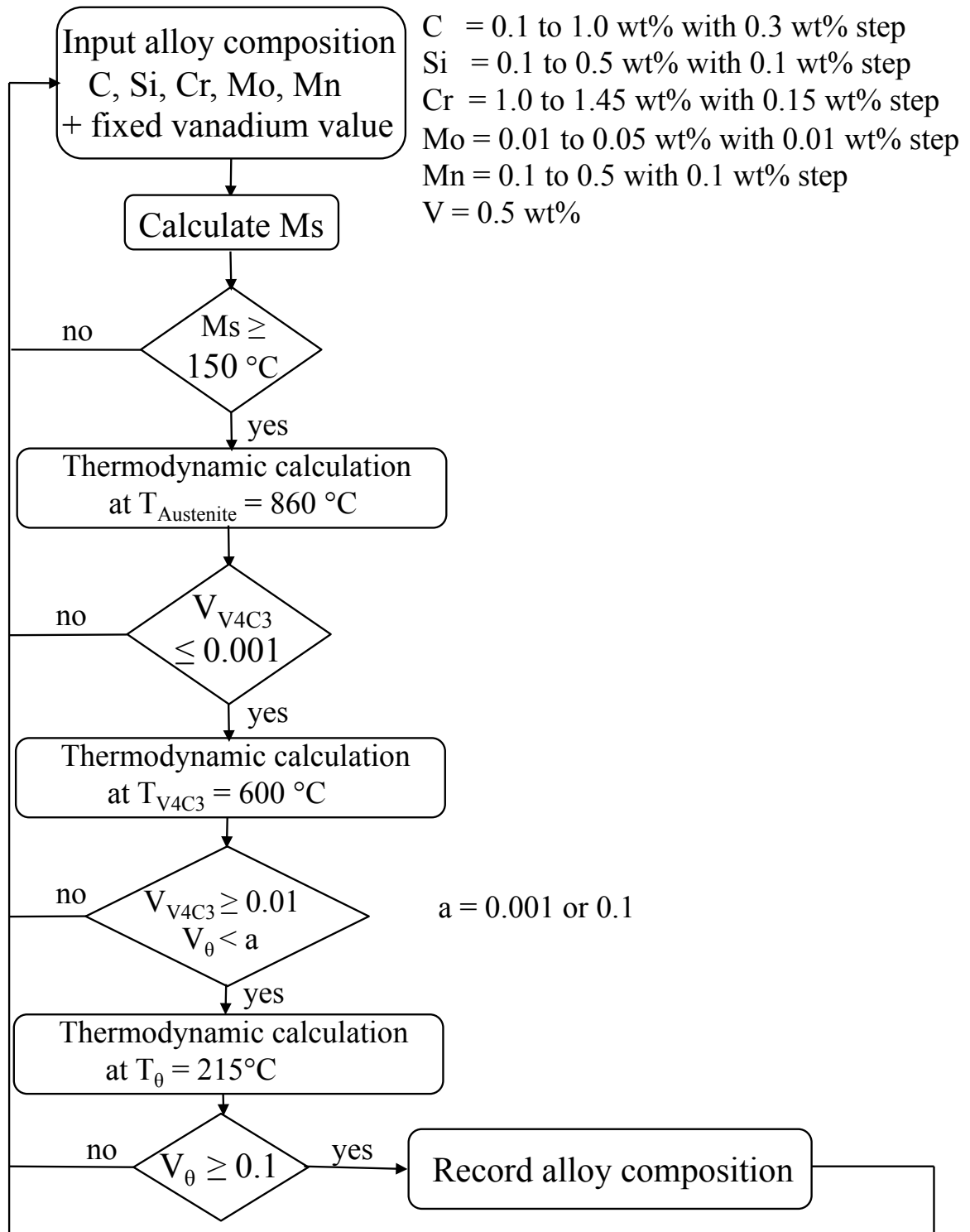


Figure 3.8: Algorithm for investigating the influence of chemical elements on cementite and V_4C_3 presence at 600 °C and 860 °C, respectively. Where M_S is martensite start temperature, V_θ is volume fraction of cementite and $V_{V_4C_3}$ is volume fraction of V_4C_3 .

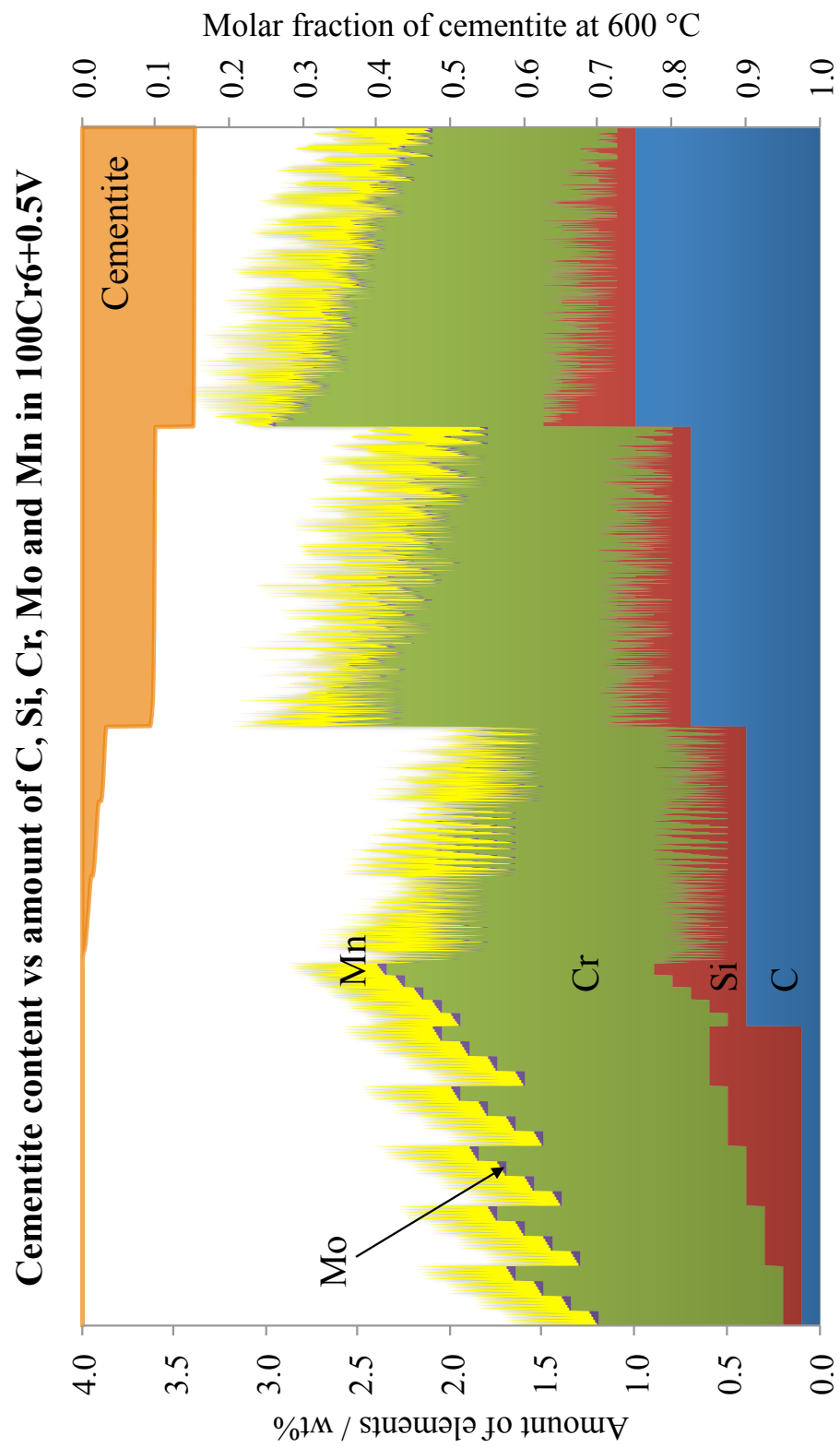


Figure 3.9: Maps of variations in chemical element concentrations influencing the cementite formation at 600 °C.

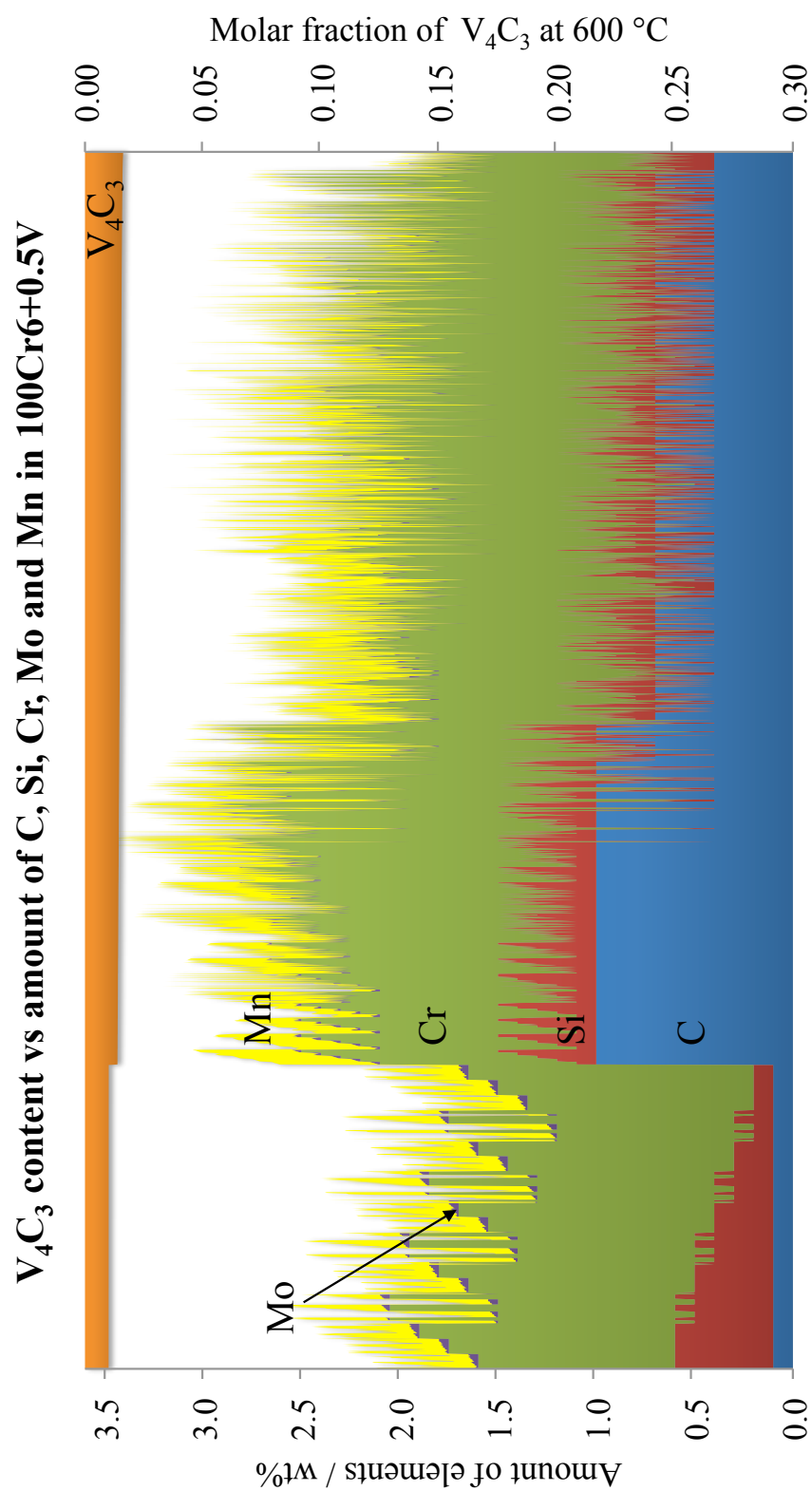


Figure 3.10: Maps of variations in chemical element concentrations influencing the V₄C₃ formation at 860 °C.

3.1.3 Kinetic modelling

MatCalc is composed by three modules: equilibrium thermodynamics, precipitation kinetics and microstructure evolution. Equilibrium provides thermodynamic input to the other modules, and can be used for precipitation kinetics and microstructure simulation. The typical stages in precipitation can be categorised into three [125]:

- Nucleation: Precipitate formation takes place as a result of a strain, interfacial and volume energy competition.
- Growth: Solute is incorporated into the precipitate from the solution; the pace is mainly dictated by diffusion.
- Coarsening: Dissolution of small precipitates and growth of larger ones as a result of an overall decrease in interfacial energy per unit volume.

3.1.3.1 Precipitation nucleation

The kinetics of precipitate nucleation in MatCalc is calculated from the classical nucleation theory extended to multi-component systems. The nucleation rate J is given by:

$$J = N_0 Z \beta^* \exp\left(\frac{-G^*}{kT}\right) \exp\left(\frac{-\tau}{t}\right) \quad (3.2)$$

$$\tau = \frac{1}{2\beta^* Z^2} \quad (3.3)$$

Where τ is the incubation time, given by equation 3.3 and G^* is the critical energy for nucleus formation, given by equation 3.4. N_0 is the total number of potential nucleation sites, Z is the Zeldovich factor that considers nuclei which can be destabilised by thermal excitations as compared with the inactivated state. β^* is the atomic attachment rate taking into account long-range diffusive transport of atoms, that is needed for nucleus formation if the chemical composition of the matrix is different from the chemical com-

position of the precipitate. T is the temperature, k is the Boltzmann constant and t is time.

$$G^* = \frac{16\pi}{3} \frac{\sigma_E^3}{(\Delta G_{vol} - \Delta G_s)^2}, \quad (3.4)$$

where σ_E is an effective interfacial energy, ΔG_{vol} is the volume free energy change, and ΔG_s is the misfit strain energy per unit volume. The misfit strain energy change is given by equation 3.5.

$$\Delta G_s = \frac{E}{1 - \nu} \varepsilon^2 \quad (3.5)$$

where E is Young's modulus, ν is the Poisson constant of the matrix and ε is the linear misfit strain approximated by

$$\varepsilon = \frac{1}{3} \frac{V_{mol}^P - V_{mol}^M}{V_{mol}^M}, \quad (3.6)$$

where V_{mol}^P and V_{mol}^M are the molar volumes of the precipitate and the matrix, respectively. Nucleation rate depends on N_0 , the number of possible nucleation sites. In MatCalc, the number of nucleation sites varies depending on their type, they include: the bulk, dislocations, grain boundaries, subgrain boundaries, grain boundary edges, grain boundary corners and other precipitates. The nucleation sites employed for V_4C_3 and cementite growth specified in the kinetic calculations are grain boundaries and dislocations acting simultaneously [125].

3.1.3.2 Precipitate growth

Precipitate growth generally follows nucleation, although some overlap between both processes may occur for low temperatures in dilute solutions. MatCalc incorporates the concept of Svoboda-Fischer-Fratzl-Kozeschnik (SFFK) model [125], which is outlined here. The model is based on the thermodynamic extremum principle suggested by Svoboda and Turek [126]

In a closed system, under constant temperature and pressure, independent state parameters q_i are considered. The total Gibbs free energy of the system G may be expressed in terms of q_i , and then the rate of the total Gibbs free energy dissipation Q is given as a function of q_i and $\dot{q}_i$. The three dissipation processes are:

- a) Interfacial migration, which depends on the interfacial mobility.
- b) Diffusion in the precipitate, which is controlled by the diffusivity in the precipitate.
- c) Diffusion in the matrix, which is influenced by the diffusivity in the matrix.

During precipitate growth, soft impingement occurs altering the matrix diffusion process. The flux in the matrix is represented by the radial flux within a sphere; on the centre of the coordinate system lies the precipitate particle. The sphere radius is defined as the mean particle distance; therefore, the radius depends on the number density of particles. While the particle grows, the solute amount in the sphere changes and soft impingement is taken into account indirectly. If Q is the positive definite quadratic form of $\dot{q}_i$, then

$$\frac{\partial G}{\partial q_i} = -\frac{1}{2} \frac{\partial Q}{\partial \dot{q}_i}. \quad (3.7)$$

The precipitate radius (r_k) and the concentration of component i in the precipitate (C_i^k) are considered to be the independent state parameters to give a set of linear equations

$$\frac{\partial G}{\partial r_k} = -\frac{1}{2} \frac{\partial Q}{\partial \dot{r}_k} \quad (3.8)$$

$$\frac{\partial G}{\partial C_i^k} = -\frac{1}{2} \frac{\partial Q}{\partial \dot{C}_i^k} \quad (3.9)$$

Solving above equations, the growth rate of the precipitate ($\dot{r}_k$) and the evolution rate of its composition, $\dot{C}_i^k$, can be calculated.

3.1.3.3 Precipitate coarsening

Precipitation coarsening is incorporated in MatCalc via the influence on pressure of the equilibrium between two phases α (matrix) and β (precipitate). From the interfacial energy of the curved interface between a precipitate and matrix pressure P originates. This pressure, however, mainly affects β stability. α composition is changed at the α/β interface. The curvature induced pressure is the key mechanism driving Ostwald ripening or grain/precipitate coarsening. This mechanism is illustrated in Figure 3.11 with a Gibbs free energy diagram.

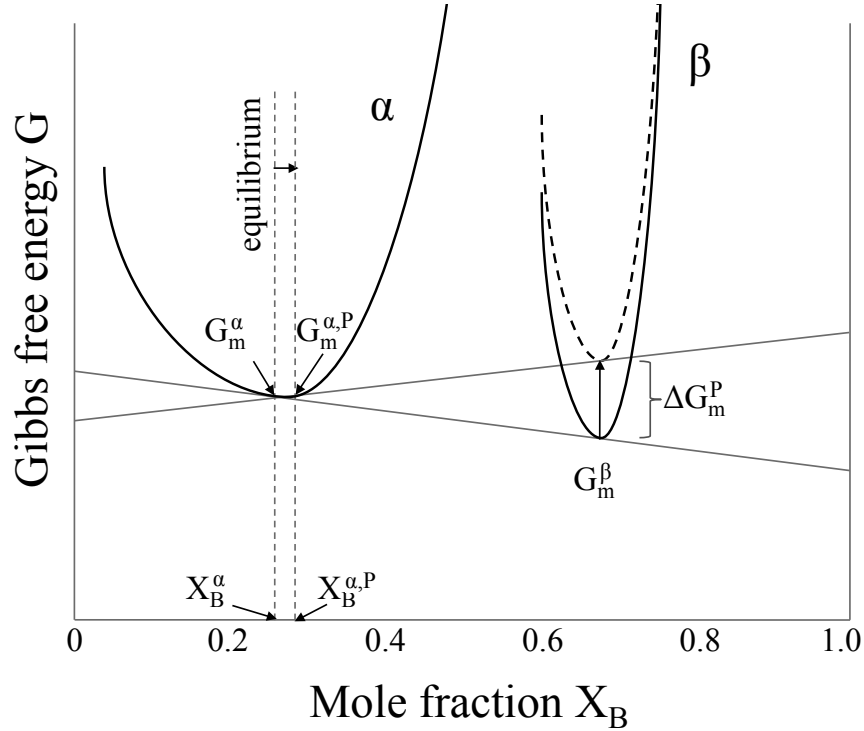


Figure 3.11: Influence of curvature induced pressure on a precipitate β and α matrix. The solid curve represents the unstressed Gibbs energy of β , the dashed line is the Gibbs energy including the effect of pressure P . After [125].

Figure 3.11 shows the Gibbs free energy tie-line construction for the matrix and the precipitate with and without the effect of curvature induced pressure. G_m^α is the Gibbs free energy of α in the precipitate state, $G_m^{\alpha,P}$ is the Gibbs free energy of α in the precipitate state with additional pressure and G_m^β is the Gibbs free energy of β in the precipitate state. An excess Gibbs energy (ΔG_m^P) shifts the Gibbs energy curve of the precipitate β to higher values. The mole fraction of B in α (X_B^α) increase to higher mol fraction of B in α under pressure ($X_B^{\alpha,P}$). This increase of internal pressure P in β , simultaneously, the equilibrium concentration of B in the solution phase α is shifted to the right, therefore is shifted to higher mole fraction X_B .

The higher the extra pressure P is the equilibrium concentration of B around a small particle is higher than the equilibrium concentration of B around a large particle. If a small and a large precipitate are located next to each other, a composition gradient will exist between the two, which will cause a net flux of B atoms from the smaller to the larger particle. This effect is generally known as precipitate coarsening or Ostwald ripening [125].

Considering the influence of pressure on the thermodynamic properties of a precipitate β with the assumption that the Gibbs free energy of the precipitate phase increases by $P^\beta V_m^\beta$, V_m^β being the molar volume of β , and P^β the extra pressure acting on the β precipitate.

The extra pressure P inside a precipitate due to the curvature of the interface is

$$P = \frac{2\xi}{\rho} \quad (3.10)$$

where ρ is a precipitate radius and ξ is the interfacial energy.

The Gibbs free energy of the precipitate phase β is then given by

$$G_m^\beta = H_m^\beta - TS_m^\beta + \Delta G_m^P, \quad (3.11)$$

where H_m^β is the enthalpy of β , S_m^β is the entropy of β , ΔG_m^P is the excess Gibbs free energy and T is temperature.

The excess Gibbs free energy ΔG_m^P caused by interfacial curvature is

$$\Delta G_m^P = P^\beta V_m^\beta = \frac{2\xi V_m^\beta}{\rho} \quad (3.12)$$

The equilibrium concentration of component B in the surrounding matrix changes and pressure in the precipitate increases. In Figure 3.11, the slope of the tangent to the Gibbs energy curves of the stressed and unstressed β phases is:

$$\frac{\partial G_m^\alpha}{\partial X_B} = \frac{G_m^\beta - G_m^\alpha}{X_B^\beta - X_B^\alpha} \quad \text{and} \quad \frac{\partial G_m^{\alpha,P}}{\partial X_B} = \frac{G_m^{\beta,P} - G_m^{\alpha,P}}{X_B^{\beta,P} - X_B^{\alpha,P}} \quad (3.13)$$

where superscript P corresponds to variables under the influence of pressure.

$$\frac{\partial^2 G_m^\alpha}{\partial X_B^2} = \frac{\frac{\partial G_m^{\alpha,P}}{\partial X_B} - \frac{\partial G_m^\alpha}{\partial X_B}}{X_B^{\alpha,P} - X_B^\alpha} \quad (3.14)$$

Substituting equations 3.13 into 3.14 and assuming that the distance $X_B^\beta - X_B^\alpha$ is large enough compared to the shift in compositions in the individual phases, we find

$$X_B^{\alpha,P} - X_B^\alpha = \left[(X_B^\beta - X_B^\alpha) \cdot \frac{\partial^2 G_m^\alpha}{\partial X_B^2} \right] \cdot P V_m^\beta. \quad (3.15)$$

Equation 3.15 gives an approximate value for the equilibrium composition of B in the proximity of the precipitate, if the precipitate and matrix composition are different from each other. Nevertheless, the equation contains the second derivative of the Gibbs energy, and this unknown is not readily available. If we assume that the solution is close to ideal, which it does in the dilute solution limit of low X_B , we can replace the derivative by

$$\frac{\partial^2 G_m^\alpha}{\partial X_B^2} \approx \frac{RT}{X_A} + \frac{RT}{X_B} = \frac{RT}{X_A X_B} \approx \frac{RT}{X_B} \quad (3.16)$$

Substituting equation 3.12 and 3.16 into 3.15 the composition shift due to the pressure can be obtained

$$X_B^{\alpha,P} - X_B^\alpha = \frac{X_B^\alpha}{X_B^\beta - X_B^\alpha} \cdot \frac{2\gamma V_m^\beta}{RT} \cdot \frac{1}{\rho} \quad (3.17)$$

or

$$X_B^{\alpha,P} = X_B^\alpha \cdot \exp \left(1 + \frac{2\gamma V_m^\beta}{(X_B^\beta - X_B^\alpha) \cdot RT} \cdot \frac{1}{\rho} \right). \quad (3.18)$$

Equation 3.18 is the linearized form of the Gibbs-Thomson equation used in MatCalc for calculating precipitate coarsening [125].

3.1.3.4 Precipitation dissolution

Dissolution in MatCalc is modelled by creating an artificial heat treatment through which particles are grown to a desired size [125], and then their dissolution can be simulated by applying an isothermal holding at high temperature predicted via thermodynamic modelling. The holding temperature is the temperature at which the phase starts to become unstable and its Gibbs free energy increases.

Accordingly to Howard and Gerald [127], the total time for dissolution of a precipitate in austenite γ is approximated by:

$$t_M = \frac{R_0^2}{|g| D_P} \quad (3.19)$$

where D_P is a diffusion coefficient of a precipitate in austenite, g is a constant, R_0 is a radius of the precipitate and t is time.

$$k = \frac{2(X_B^\gamma - X_\gamma)}{X_B - X_B^\gamma} \quad (3.20)$$

where X_B^γ is a concentration in the matrix at the precipitate-matrix interface, X_γ is a matrix composition at a point remote from the precipitate and X_B is the composition of the precipitate.

3.1.3.5 Results of kinetic modelling

MatCalc software with mc_fe.tdb thermodynamic database, and with mc_sample_fe.ddb database for the precipitation of cementite and V_4C_3 , was employed for modelling the microstructure development in hydrogen embrittlement resistant steels. The phases thermodynamically allowed to co-exist were the same as for MTDATA and Thermo-Calc. The results of kinetic modelling are shown in Figure 3.12.

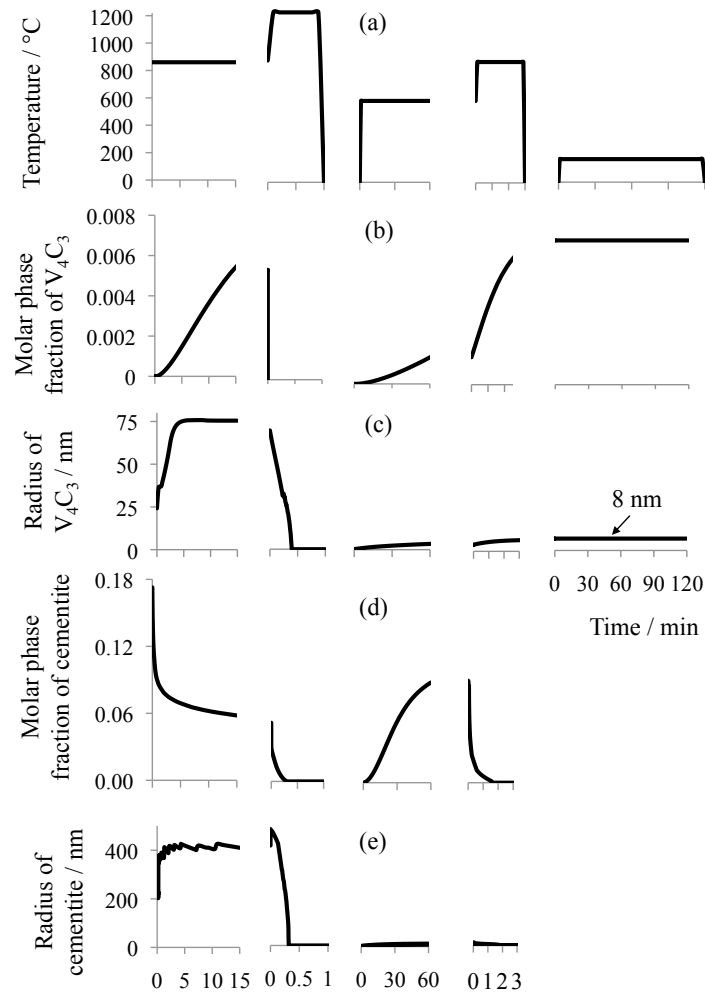


Figure 3.12: Kinetic calculation results for the heat treatment of 100Cr6+0.5V. Note that the time scales vary for subsequent stages, but the units is min in all cases.

Assuming a diffusion coefficient of V in austenite as

$$D_V = 0.25 \exp \left(\frac{-Q_V^\gamma}{RT} \right) 10^{-4}, \quad (3.21)$$

and a diffusion coefficient of C in austenite as

$$D_C = 1.5 \exp \left(\frac{-Q_C^\gamma}{RT} \right) 10^{-5}, \quad (3.22)$$

where R is the gas constant, Q_V^γ is the activation energy for diffusion of vanadium in austenite and equals 264 kJ, Q_C^γ is the activation energy for diffusion of carbon in austenite and equals 142 kJ and T is temperature.

When using Equation 3.20 and employing the equilibrium values taken from MTDATA. For V_4C_3 at 1200 °C: $X_B^\gamma = 0.0044$, $X_\gamma = 0.00528$ and $X_B = 0.43$, expressed in mole fraction. For cementite at 860 °C: $X_B^\gamma = 0.0039$, $X_\gamma = 0.0385$ and $X_B = 0.25$, expressed in mole fraction. Employing these values in equations 3.21 and 3.22, the dissolution times in austenite for 50 nm V_4C_3 and 800 nm cementite become:

- $t_M = 51.77$ s for V_4C_3 ,
- $t_M = 31.68$ s for cementite.

The dissolution depends on a mean radius of a precipitate and its phase fraction. This relationship can be corroborated by MatCalc calculations on V_4C_3 as illustrated in Figure 3.13.

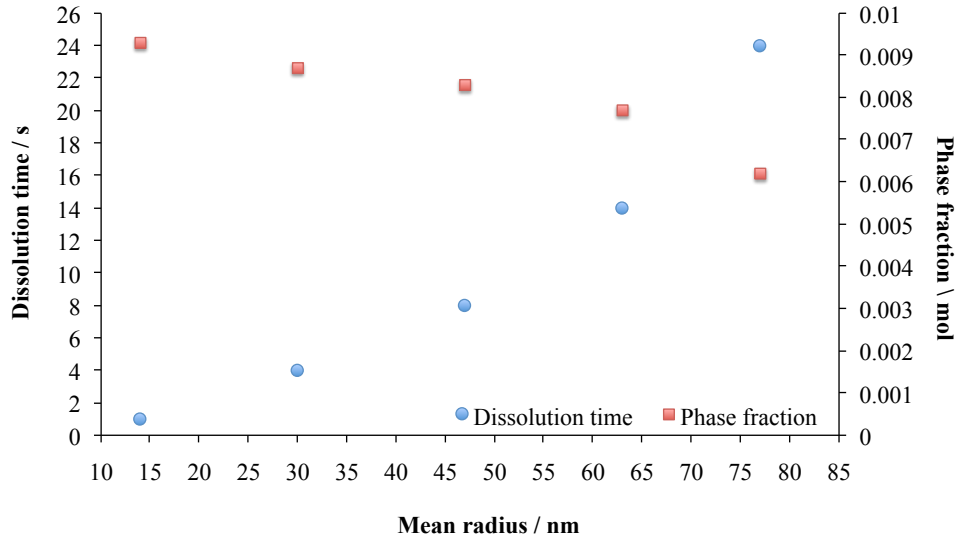


Figure 3.13: The relationship between a mean radius of V_4C_3 precipitate, its dissolution time and phase fraction at 1200 °C.

3.2 Chemical compositions and proposed heat treatments

The grades introduced in Section 3.1.1.2 were subjected to the heat treatment schedules shown in Figure 3.14. The compositions employed in the calculations are shown in Table 3.1, which follows the cast concentrations to be discussed in a later chapter.

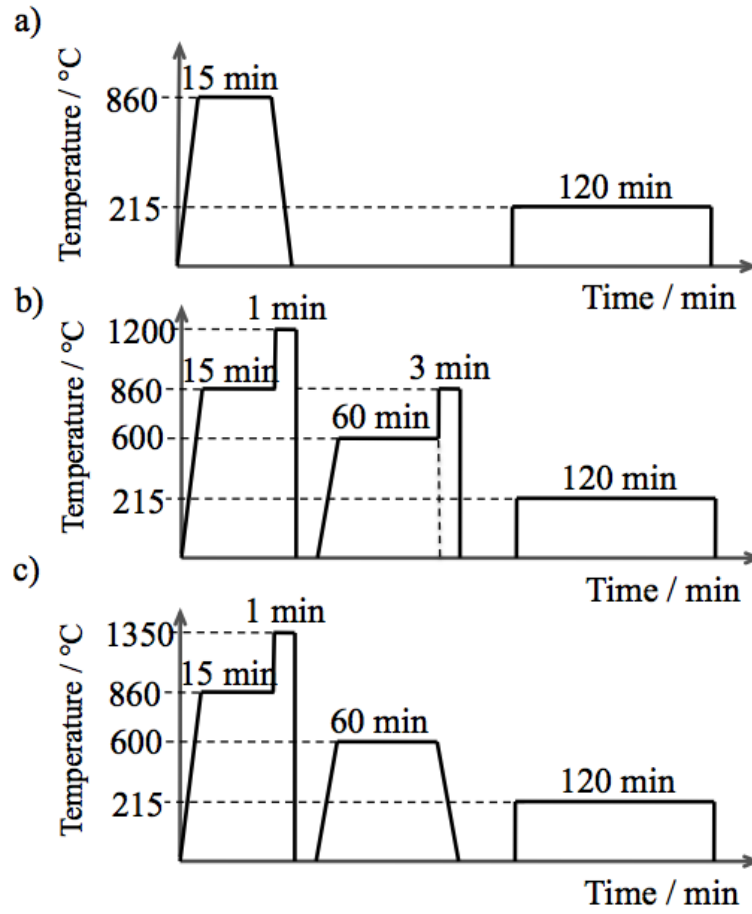


Figure 3.14: Heat treatment schedules of a) 100Cr6, b) 100Cr6+0.5V and c) 100Cr6+2.75V.

Table 3.1: Chemical composition of the modelled steels (wt%).

Grade	C	Si	Mn	Mo	Cr	Ni	Al	Cu	P	S	V	O
												ppm
100Cr6	0.974	0.282	0.276	0.06	1.38	0.18	0.042	0.210	0.010	0.017	0.00	11.2
100Cr6+0.5V	0.994	0.272	0.282	0.09	1.42	0.01	0.003	0.247	0.004	0.003	0.549	14.1
100Cr6+2.75V	0.981	0.270	0.280	0.06	1.37	0.25	0.040	0.213	0.007	0.009	2.75	14.6

3.3 Hardenability and hardness of the proposed steels

Steel hardenability is essential for selecting an appropriate combination of alloy steel composition and heat treatment to decrease thermal stresses and distortions in steel. Hardenability describes the capacity of the steel to harden in depth under a given set of conditions. A steel of a high hardenability might transform to a high martensite fraction to depths of several millimetres under relatively slow cooling. Hardenability is mainly affected by austenite grain size, carbon content and alloying elements [128]. Carbon content and grain size influence on hardenability is shown in Figure 3.15.

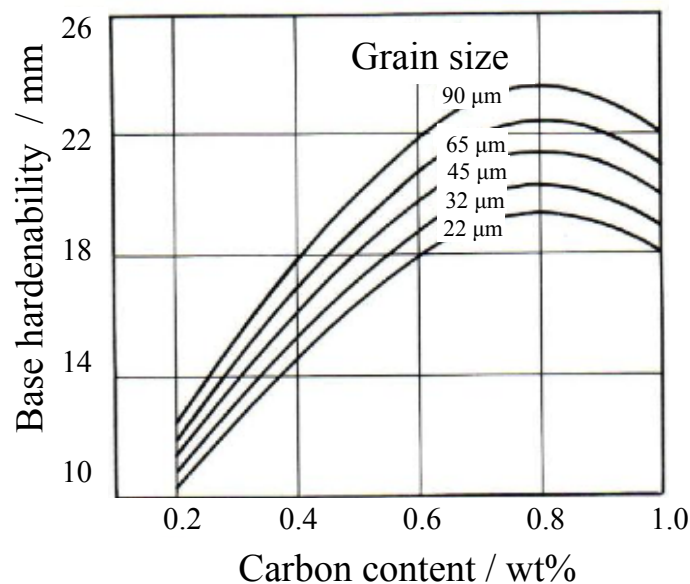


Figure 3.15: Influence of grain size and carbon content on hardenability. After Thelning [128].

For the proposed steels, the concentration of carbon in austenite is shown in Figure 3.16 and Figure 3.17, which were calculated from Thermo-Calc. The amount of carbon in austenite at the austenitisation temperature can be used to predict bearing hardness [129].

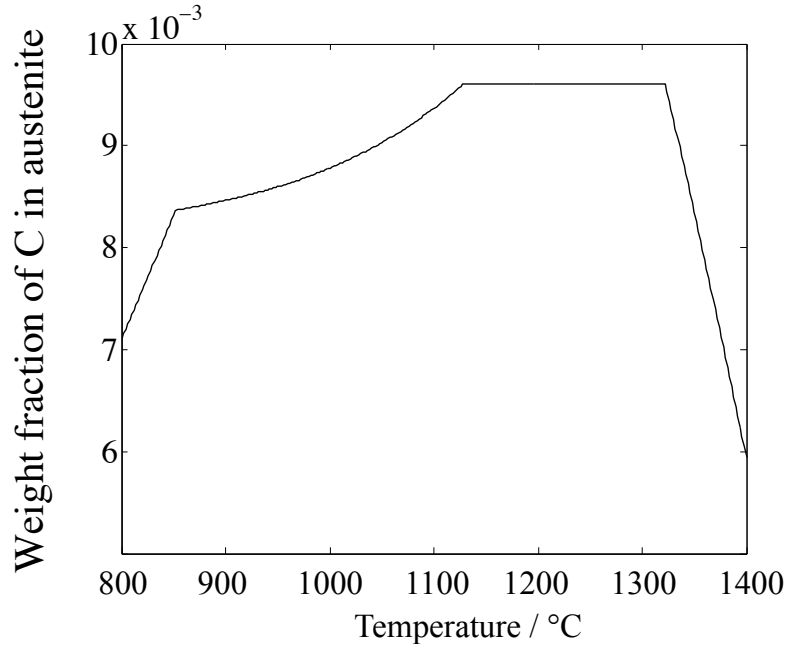


Figure 3.16: Carbon content in austenite for 100Cr6+0.5V.

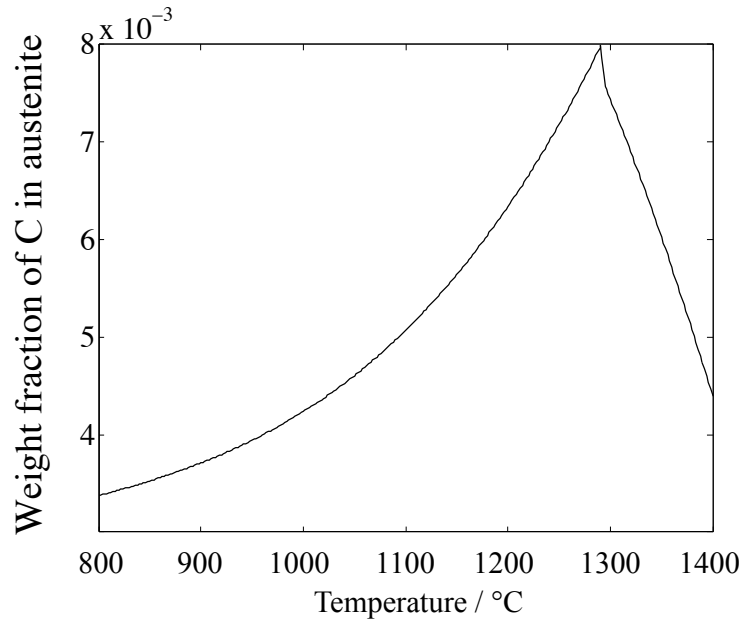


Figure 3.17: Carbon content in austenite for 100Cr6+2.75V.

For the proposed steels (Table 3.1) and 100Cr6, Time-Transformation-Temperature (TTT) diagrams are obtained from MUCG83 program [130] and are shown in Figure 3.18. The TTT diagram helps to predict when the transformation starts and ends for an isothermal heat treatment of a previously austenitised steel. MUCG83 incorporates thermodynamic and kinetic theory and data needed to calculate a TTT diagram.

The diffusional transformation products are ferrite and pearlite, whereas displacive reactions refer to Widmanstätten ferrite, bainite and martensite [131]. Figure 3.18 also shows the M_S temperatures calculated from Ishida's equation [132]:

$$M_S = 545 - 330C + 2Al + 7Co - 14Cr - 13Cu - 23Mn - 5Mo - 13Ni - 7Si + 3Ti + 4V \quad (3.23)$$

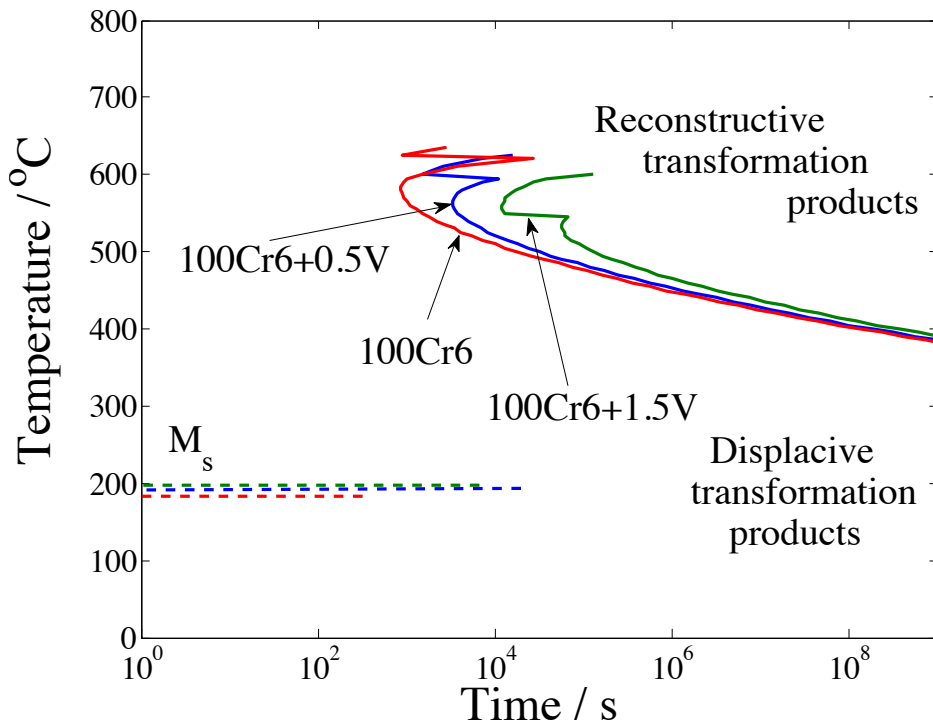


Figure 3.18: TTT diagrams for baseline and proposed steels with their M_S temperatures calculated from equation 3.23.

The results of M_S calculated via equation 3.23 are as follows: 184 °C for 100Cr6, 187 °C for 100Cr6+0.5V, 195 °C for 100Cr6+2.75V. Martensite content can be estimated by applying the Koistinen–Marburger equation:

$$1 - V_{\alpha'} = \exp[-0.011(M_S - T_Q)] \quad (3.24)$$

where $T_Q = 20$ °C represents the temperature below M_S . The martensite fraction depends on the undercooling below the M_S temperature. The fractions of martensite at room temperature are calculated to be $V_{\alpha'} = 0.84$ for 100Cr6, $V_{\alpha'} = 0.84$ for 100Cr6+0.5V and $V_{\alpha'} = 0.85$ for 100Cr6+2.75V, leading to retained austenite contents of $V_\gamma = 0.163$ for 100Cr6, $V_\gamma = 0.159$ for 100Cr6+0.5V and $V_\gamma = 0.145$ for 100Cr6+2.75V.

3.4 Discussion

The discussion and results of this chapter are presented in the order shown in Figure 3.19.

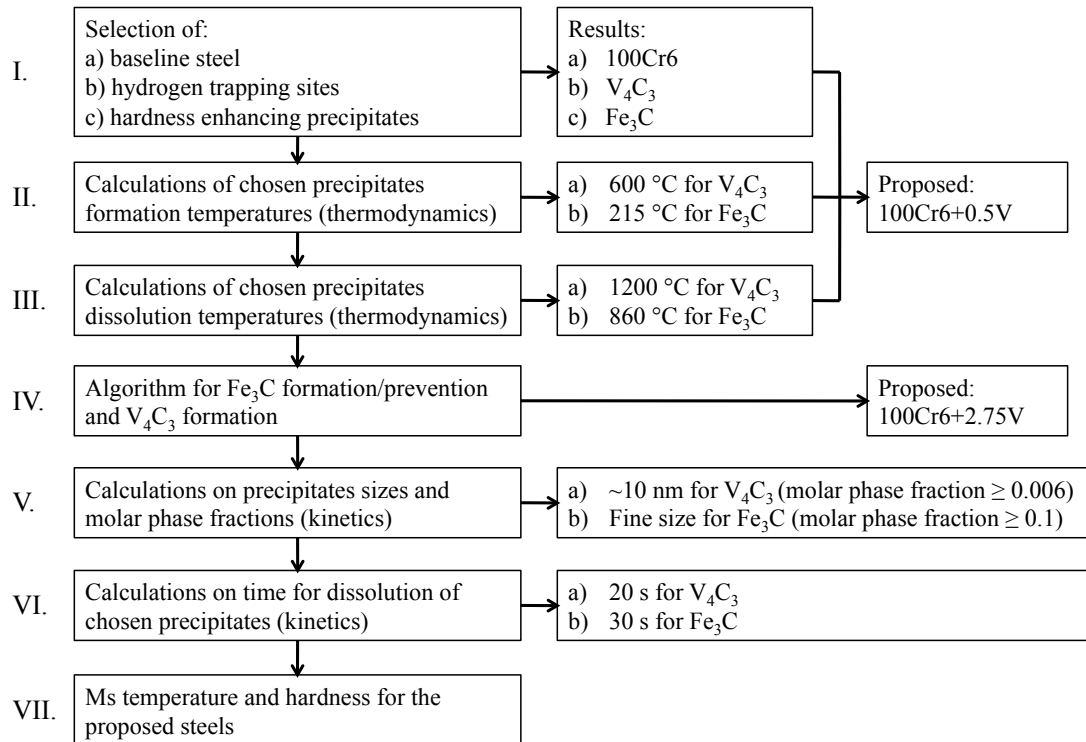


Figure 3.19: Discussion and results order presented in this section.

I.

The design of a hydrogen resistant bearing steel has combined thermodynamic and kinetic modelling of V_4C_3 and cementite, the former to act as hydrogen trap, and the latter to supply hardness and wear resistance. A typical bearing steel (100Cr6) has been chosen as baseline. The chemical composition of 100Cr6 was varied in order to produce V_4C_3 and Fe_3C . V_4C_3 was chosen as the trapping precipitate species based on a literature review and on observation of hydrogen trapping activity in automotive steels. V_4C_3 characteristics were discussed in Section 2.5.1. Fe_3C is widely known as a hardening precipitate which is present in bearing steels.

II.

By using MTDATA and Thermo-Calc thermodynamic softwares both the formation and dissolution temperatures of the precipitates were calculated. V_4C_3 formation was considered at 600 °C, since this temperature is sufficient for growing V_4C_3 to the desired size in a relatively short time. At 600 °C, V_4C_3 was found to be formed in its most effective scale for hydrogen trapping capacity (~ 10 nm) [6, 11]. Figure 3.2 shows the influence of composition on V_4C_3 stoichiometry. Molybdenum and vanadium show their influence on both lower (0.1 wt% C) and higher (1.0 wt% C) carbon content steels. Mo has rather moderate influence on V_4C_3 formation and is not required for the carbide formation itself, but it has been reported to have an influence on V_4C_3 coherency, influencing the strain that traps hydrogen in vicinity of the precipitates [6]; therefore its addition may be beneficial. For 1.0 wt% C steel, chromium starts to play a role in influencing carbide stability, but this influence is rather insignificant. Fe_3C formation temperature was estimated to be similar to its formation temperature in standard bearing steels (215 °C), which is beneficial from a processing point of view, as it requires minimum changes in tempering schedules.

III.

The dissolution temperatures for both the discussed precipitates were calculated with Thermo-Calc. For industry it is important to dissolve undesired phases at the lowest temperature possible. Coarse V_4C_3 and coarse cementite are undesired, and it is essential to produce these carbides in a fine scale. The dissolution of V_4C_3 carbides formed on casting and hot rolling has to be performed to turn them into nano-sized particles. The dissolution temperature results are illustrated in Figure 3.3. V_4C_3 is not stable and is predicted to easily dissolve at 900 °C for lower carbon content (~ 0.5 wt%) and with vanadium up to ~ 1.25 wt%. However, for the baseline steel, a content 1.0 wt% C is present, the dissolution temperature is increased to 1200 °C. For lower carbon contents it is easier to dissolve the V_4C_3 , but it would also result in lower hardness, which is undesired for bearing steels. Undoubtedly, the addition of vanadium is necessary for producing V_4C_3 in the baseline steel, therefore if the carbon limit is fixed to ~ 1.0 wt% and vanadium is increased to 0.5 wt% or 2.75 wt%, as it can be seen in Figure 3.4 and Figure 3.5, dissolution around 1200 °C is required. Moreover, on examining those figures it can be concluded that at 600 °C V_4C_3 will form along with cementite. Cementite at this temperature is predicted to grow to a large size, which softens the matrix. Therefore, the cementite is regarded as undesired when formed at 600 °C, and it needs to be dissolved and further reprecipitated at a lower temperature (~ 200 °C). The dissolution of coarse cementite was estimated from Figure 3.7. This can be performed by adding a temperature spike after V_4C_3 formation.

IV.

The formation of cementite occurs along with V_4C_3 formation at $\sim 600^\circ\text{C}$, which is not beneficial for the steel properties. Such coarse cementite can either be dissolved as discussed above or avoided by altering the chemical composition. The formation of V_4C_3 without the simultaneous formation of cementite was modelled by using the algorithm shown in Figure 3.8. This algorithm employs Thermo-Calc incorporated with Fortran program and allows the variation of many chemical elements at the same time and at various temperatures. The results are plotted in Figures 3.9 and 3.10. Figure 3.9 shows that for lower carbon contents (0.6 wt%) the amount of cementite at 600°C is slight. Therefore for the fixed vanadium amount (0.5 wt%) any of the chemical element composition variants could be chosen. A similar tendency is shown for V_4C_3 at 860°C , which molar fraction is also mainly influenced by carbon content (Figure 3.10). As mainly C influence on cementite, it was found that this can be avoided at 600°C by increasing vanadium content to 2.75 wt%. This alteration will also result in a simpler heat treatment schedule, but a higher V_4C_3 dissolution temperature (Figure 3.3) reaching $\sim 1300^\circ\text{C}$. It should be highlighted that full V_4C_3 dissolution is not necessary, as V_4C_3 can be beneficial for averting the austenite grain growth resulting in higher hardness [128].

V, VI.

Kinetic modelling estimates the time and phase fraction for precipitate growth and dissolution. As it can be seen from Figure 3.13, the precipitate fraction and dissolution time depend on the particle mean radius. It takes more time for a bigger V_4C_3 particle to dissolve; but in 100Cr6+0.5V there is a larger fraction of small particles present. The kinetic calculation results for 100Cr6+0.5V are shown in Figure 3.12. Cementite and V_4C_3 particles were respectively grown to 200 nm and 25 nm, to reproduce the expected initial microstructures. Those sizes were assumed based on TEM investigations after spheroidization treatment. The dissolution temperatures for V_4C_3 and cementite were assumed to be 1200°C for V_4C_3 and 860°C for cementite dissolution. Figure 3.12a shows the heat treatment of 100Cr6+0.5V and Figures 3.12b-e show V_4C_3 and cementite

evolution. In Figure 3.12e, cementite is shown to double its size during austenitisation, weakening the matrix by depleting it from carbon. However, the first temperature spike dissolves all precipitates in less than 30 s (Figure 3.12). During the next stage of heat treatment V_4C_3 and cementite grow and their molar phase fraction increase to 0.002 for V_4C_3 and 0.1 for cementite. V_4C_3 is a desired phase at this temperature ($\sim 600^\circ\text{C}$), but cementite needs to be dissolved as it is beneficial just if it is formed finely at a low temperature. The second spike ($\sim 860^\circ\text{C}$) dissolves cementite and allows further growth of V_4C_3 to ~ 10 nm. The last stage of heat treatment does not influence V_4C_3 , but is added in order to form fine cementite, which is not included in this calculations, since it is formed in paraequilibrium; MatCalc calculations assumed an equilibrium state for performing the described calculations. The dissolution times were also confirmed by using Equation 3.21, giving $t_M = 51.77$ s for V_4C_3 dissolution and $t_M = 31.68$ s for cementite dissolution. Taking that into consideration, the dissolution temperature spike times are assumed to be 1 min for V_4C_3 dissolution at $\sim 1200^\circ\text{C}$, which should not strongly alter the austenite grain size, and 3 min at $\sim 860^\circ\text{C}$ for cementite dissolution and further V_4C_3 growth. The chemical compositions of the two proposed steels with their respective heat treatments are shown in Table 3.1 and Figure 3.14. As thermodynamic calculations show, no cementite formation along with V_4C_3 at 600°C appears in 100Cr6+2.75V, thus the second temperature spike is unnecessary for cementite dissolution in this grade, simplifying the heat treatment (Figure 3.14c). It should be noticed that the presented heat treatments are just a first-try approach to verify the modelling concepts, and they can be further optimised.

VII.

It is known that, if the carbon fraction in the austenite at austenitisation temperature is in range of 0.5 to 0.6 then it will provide a hardness higher than 58 HRC (690 HV) [129]. The hardness of the proposed steels has been considered in Figure 3.16 and Figure 3.17 via the carbon content. In the case of 100Cr6+0.5V (Figure 3.14b), two austenitisation temperatures are considered 1200 °C and 860 °C, and for both temperatures the weight fraction of carbon is higher than 0.6. At 1200 °C almost all the carbon is in austenite leading to the desired hardness after quenching. This fact could also cause internal stresses and cracking during quenching, which is the reason why the first temperature spike is just one minute. This short spike (Figure 3.14b), should dissolve a great amount of V_4C_3 , but still needs to be shorter to avoid austenite grain size growth. Hardness can be manipulated by changing austenitisation or the spikes temperature. Figure 3.17 shows that all carbon will be in austenite at 1300 °C, but this temperature is regarded to be high for an industrial heat treatment; however, it can be seen that even a spike to 1200 °C, will lead to 0.6 weight fraction of carbon in austenite and therefore a potential hardness greater than 58 HRC. This hardness might be considered as relatively low for martensitic bearing steels, but additionally the hardness is believed to increase due to the fine V_4C_3 . Moreover, V_4C_3 stays at the austenite grain boundaries restricting their growth and increasing hardness, as predicted by the Hall-Petch equation [133].

It should be mentioned that vanadium addition to the baseline steel brings many benefits, such as improving bearing steel hardneability. It can be noticed from Figure 3.18 that, vanadium moves TTT curves to the longer times, therefore making the heat treatment of large bearings more favourable because cooling rates can be lowered. Vanadium also increases M_s temperature, what can also be seen on the discussed figure. M_s temperature increases from 184 °C to 187 °C with 0.5 wt% V addition, and to 195 °C with 2.75 wt% V addition (Equation 3.23). The increased M_s results in higher martensite content, $V_{\alpha'}$ increases from 0.837 (baseline) to 0.842 (100Cr6+0.5V) and 0.855 (100Cr6+2.75V), therefore decreasing retained austenite from 0.163 (baseline) to 0.159

and 0.145 for 100Cr6+0.5 and 100Cr6+2.75V, respectively. This may bring benefits for dimensional stability [4].

3.5 Summary

Carbides are highly important in bearing steels as they provide the essential hardness and wear resistance necessary for good rolling contact fatigue. In the production of commercial bearing grades with alloying elements, large MC carbides are formed due to the slow cooling rate and cause porosity in hot rolling. The presence of porosity and voids around these large precipitates decreases rolling contact fatigue performance. Moreover, it is demonstrated that rolling contact fatigue life is decreased significantly with increasing hydrogen content. However, this damaging influence is expected to be stopped when trapping hydrogen on fine V_4C_3 precipitates. The precipitation of these carbides can be predicted by using thermodynamic modelling, which prescribes the presence of the phases in equilibrium at a certain temperature. With the use of kinetic modelling the size and phase fraction of V_4C_3 precipitates can be modelled at certain stages of heat treatment. It is essential to produce small carbides in the steel microstructure, hence the controlled dissolution of carbides should be also considered. In this chapter employing thermokinetic modelling, the compositions and heat treatments of a low and a high vanadium bearing steels are presented. The new grades are expected to be resistant to hydrogen embrittlement.

Chapter 4

Experimental techniques and hydrogen analysis

4.1 Observations and experimental methods used for H-detection

This chapter describes the response of the different steel microstructures to hydrogen charging, since it has been reported that different phases can store a certain amount of hydrogen, and crystallographic defects or phase interfaces can act like hydrogen traps [6, 51, 50]. The amount of hydrogen absorbed by steels is quantified with melt extraction technique (MET). The type of traps present in the steel along with their trapping capacity has been determined via thermal desorption analysis (TDA). The techniques were applied to 100Cr6+0.5V since a decrease in mechanical properties is expected due to hydrogen, which might be present in bearing steels [2, 8, 21, 23]. As 100Cr6+0.5V consists of martensite, cementite, V_4C_3 and retained austenite, different steels with various amounts of these phases are included in the analysis. The 100Cr6+0.5V was tested by using MET and TDA simultaneously with the baseline steel (100Cr6 without V_4C_3 traps), SB300 and SB200 with different retained austenite content and pure iron (99.8 % Fe). The chemical compositions of tested steels were determined using a glow discharge atomic

emission spectrometer, LECO GDS850A, are listed in Table 4.1, while they heat treatment schedules are shown in Table 4.2. The martensitic heat treatment schedules of 100Cr6 and 100Cr6+0.5V were introduced in Section 3.2 in Figure 3.14a and 3.14b, respectively.

Table 4.1: Chemical composition of the characterised steels (wt%).

Grade	C	Si	Mn	Mo	Cr	Ni	Al	Cu	V	Co	P	S	O ppm
100Cr6	0.974	0.282	0.276	0.06	1.38	0.18	0.042	0.21	-	-	0.010	0.017	11.2
100Cr6+0.5V	0.994	0.272	0.282	0.09	1.42	0.01	0.003	0.25	0.549	-	0.004	0.003	14.1
SB200 and SB300	0.820	1.560	2.030	0.25	0.98	-	1.010	-	-	1.52	0.002	0.001	5.00

Table 4.2: Heat treatment schedules of analysed steel samples.

Grade	microstructure	austenitisation	tempering	isothermal holding
100Cr6	bainite	860 °C for 0.25 h	-	235°C for 2 h
SB200	superbainite	920 °C for 0.50 h	-	200°C for 72 h
SB300	superbainite	920 °C for 0.50 h	-	300°C for 6 h

4.1.1 Melt extraction technique

Melt extraction technique was introduced briefly in Section 2.5.2, and an overall picture of the equipment can be seen in Figure 2.26. A broader explanation of the method is presented in this section. The measuring procedure is explained with the aid of Figure 4.1; $\langle i \rangle$ will be employed to designate item in the equipment, $i = 1, 2, \dots, 20$ in Figure 4.1. During melt extraction, a small piece of steel is weighed and placed in the sample drop $\langle 7 \rangle$ and further into the graphite crucible $\langle 8 \rangle$, where it is melted by the high temperature caused by the electric current flowing through the crucible. Hydrogen and oxygen separate from the sample and are taken by the carrier gas (nitrogen) to the cleaning tube $\langle 12 \rangle$ and then to the catalyst furnace $\langle 16 \rangle$. CO converts to CO_2 and the CO_2 is detected in the IR-cell. This detection is based on infrared radiation of gases, since gases absorb specific characteristic spectral wavelengths of infrared radiation (IR). An absorption spectrum is analysed based on the number, configuration and type of atoms in the gas molecules. After the IR-cell, the measured gas is sucked through the chemical tubes $\langle 18, 19 \rangle$ where is cleaned, and flows further to the thermal conductivity cell.

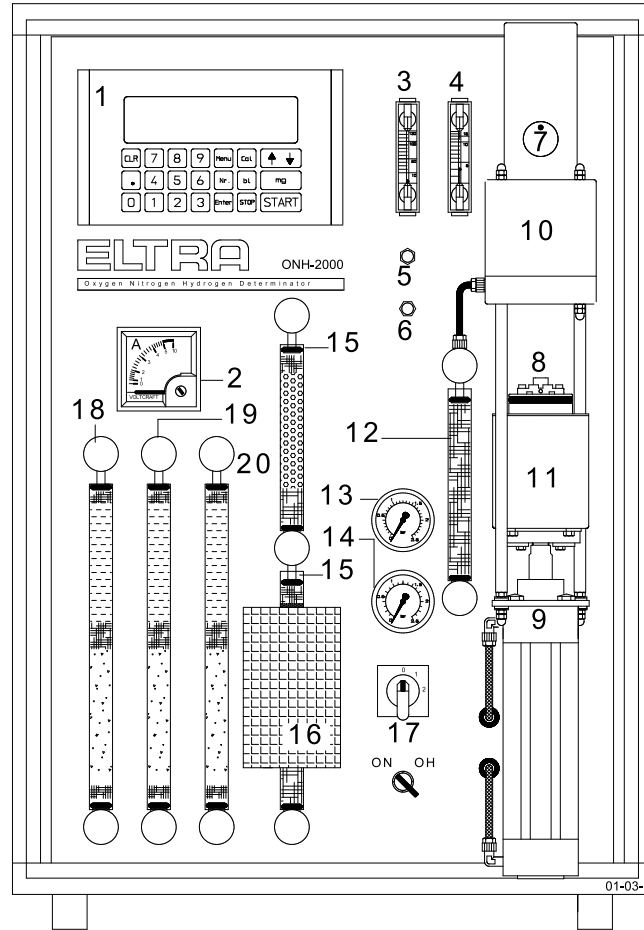


Figure 4.1: Schematic drawing of the melt extraction technique machine front panel: $\langle 1 \rangle$ electronics unit, $\langle 2 \rangle$ current meter, $\langle 3 \rangle$ general flow, $\langle 4 \rangle$ carrier gas flow, $\langle 5 \rangle$ purge flow regulator, $\langle 6 \rangle$ carrier gas flow regulator, $\langle 7 \rangle$ sample drop, $\langle 8 \rangle$ crucible, $\langle 9 \rangle$ is pneumatic lift, $\langle 10 \rangle$ is upper furnace, $\langle 11 \rangle$ lower furnace part, $\langle 12 \rangle$ dust trap, $\langle 13 \rangle$ carrier gas pressure gauge, $\langle 14 \rangle$ compressed air gauge, $\langle 15 \rangle$ Copper Oxide catalyst, $\langle 16 \rangle$ catalysis furnace, $\langle 17 \rangle$ main switch, $\langle 18 \rangle$ gas pre-cleaning, $\langle 19 \rangle$ H_2O - trap and $\langle 20 \rangle$ IR-cell purge [134].

The changes in hydrogen content in the gas cloud going through the cell are detected by measuring thermal conductivity with respect to a reference; in order to get better resolution, the reference is usually the pure carrier gas. The signals from the thermal conductivity cell are converted into the electronic units and displayed as results on the computer screen. The measurement is always performed in two steps. The first measurement is for the determination of the thermal conductivity of the carrier gas, that includes the hydrogen coming out from a reference sample; that mixture contains a known amount of hydrogen (5 ppm). The hydrogen in the reference sample is chemically bonded, thereby not able to be released at room temperature even after a very long time; this step is called calibration. Calibration is necessary and immediately after it the sample to be measured can be analysed, and its unknown quantity of hydrogen can be estimated in the thermal conductivity cell. The calculation of the hydrogen content in the sample considering its weight is done by the software, and is made on the basis that the thermal conductivity of the carrier gas and its linear variation with hydrogen content. The overall gas flow diagram is shown in Figure 4.2.

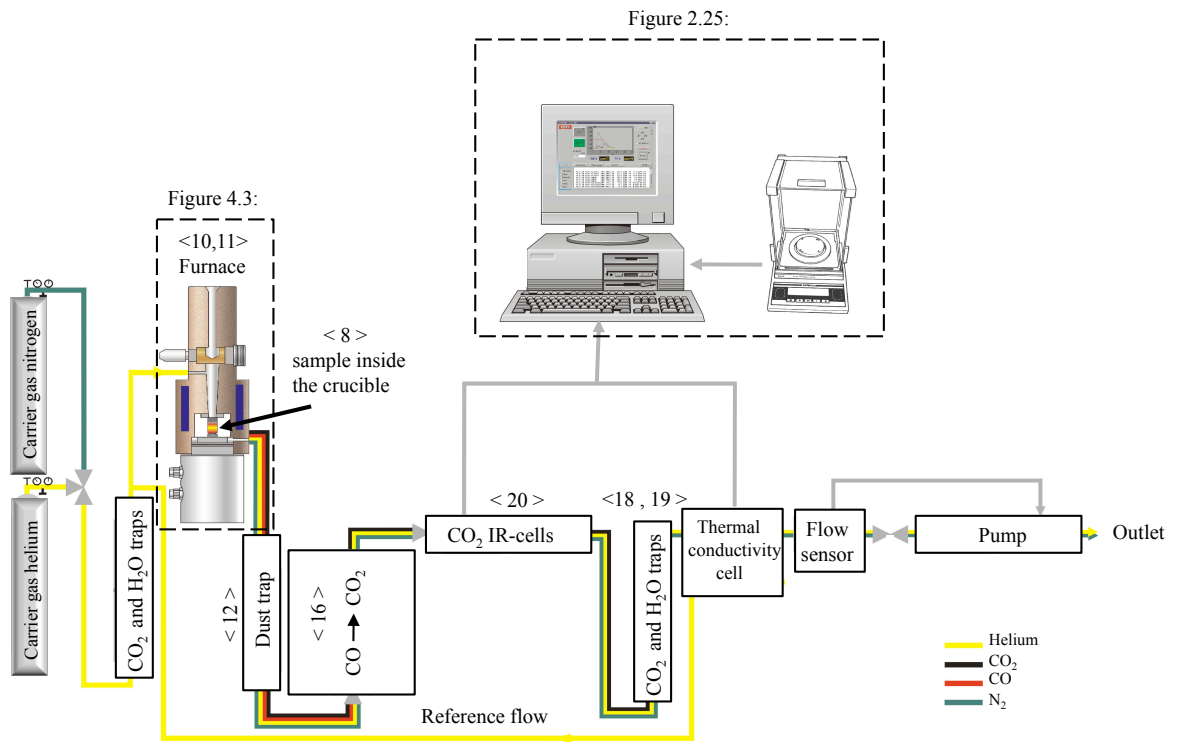


Figure 4.2: Gas flow diagram through the Melt Extraction equipment [134]; where $\langle 8 \rangle$, $\langle 10,11 \rangle$, $\langle 12 \rangle$, $\langle 16 \rangle$, $\langle 18,19 \rangle$ and $\langle 20 \rangle$ were already described in Figure 4.1. Figure 2.26 was employed from the overview of MET equipment introduced in Section 2.5.2.

4.1.2 Thermal desorption analysis

Thermal Desorption Analysis (TDA) was introduced in Section 2.5.2. This section describes the equipment built for the completion of this work at SKF Engineering and Research Centre, the Netherlands (Section 4.1.2.1) the principles on which the technique is based are also explained.

Thermal desorption analysis can be explained through the escape reaction of hydrogen from a trapping, given that sufficient energy is supplied for such ejection (Choo and Lee [51]):

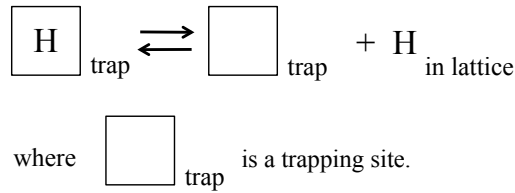


Figure 4.3 shows the energy levels of interstitial sites (B) and trapping sites (A) where hydrogen can reside. The hydrogen escape (desorption) rate from a trapping site is:

$$\frac{dx}{dt} = A(1 - x)e^{-\frac{E_a}{RT}} \quad (4.1)$$

where E_a is the trapping activation energy, $x = \frac{K_0 - K}{K_0}$, K_0 is an amount of hydrogen in trapping site at $t = 0$, K is an amount of hydrogen in trapping site at $t \neq 0$, T is an absolute time, R is the gas constant and A is a constant.

To reach a maximum desorption rate with a stable heating rate, the below equation should be applied:

$$\frac{d}{dt} \left(\frac{dx}{dt} \right) = \frac{dx}{dt} \left(\frac{\phi E_a}{RT^2} - Ae^{-\frac{E_a}{RT}} \right) = 0, \quad (4.2)$$

where $T = T_0 + \phi t$, T_0 is the initial temperature and ϕ is the heating rate.

$$\frac{E_a \phi}{RT_c^2} = Ae^{-\frac{E_a}{RT_c}}, \quad (4.3)$$

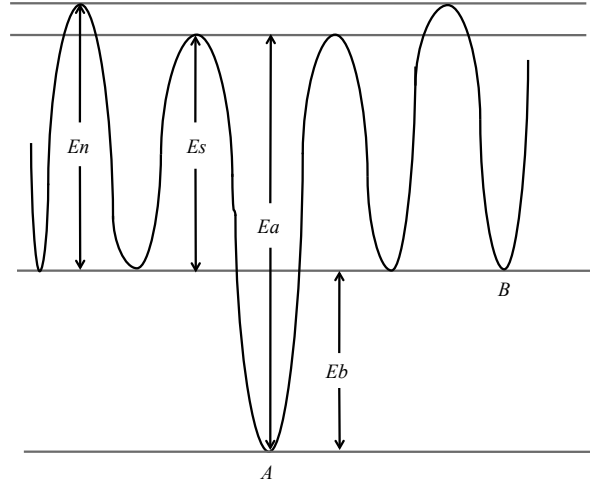


Figure 4.3: Trapping site model, where E_n is diffusion activation energy for hydrogen in a normal lattice site, E_s is the saddle point energy around the trapping site, E_b is the interaction energy between trapping site and hydrogen, E_a is trapping activation energy equal to $(E_s + E_b)$ [51].

where T_c is the temperature at which the maximum hydrogen escape occurs (the peak in a TDA plot, as will be shown in Section 4.4).

Taking the logarithm on both sides of Equation 4.3, and differentiating with respect to $\frac{1}{T_c}$, E_a can be easily calculated, for known (e.g. TDA results) ϕ and T_c , from the plot of $\ln\left(\frac{\phi}{T_c^2}\right)$ vs $\frac{1}{T_c}$, since:

$$\frac{\partial \ln\left(\frac{\phi}{T_c^2}\right)}{\partial\left(\frac{1}{T_c}\right)} = -\frac{E_a}{R}. \quad (4.4)$$

The mathematical details can be found in [51].

The trapping activation energy is related to the maximum desorption temperature peak T_c . Numerous TDA investigations have been performed and a number of T_c temperatures have been reported for a variety of traps. The examples of known hydrogen trapping activation energies and therefore various peak temperatures have been gathered and introduced in Table 2.3 (Section 2.3).

4.1.2.1 Gas chromatography with pulsed discharged detector

There are two main parts that combine the Thermal Desorption Analysis equipment employed in this investigation: the pyroprobe unit (PU) and the gas chromatography unit (GC). The equipment can be seen in Figure 4.4; where (HSTD) is a bottle with a calibration gas of known hydrogen content (10.2 μmol of hydrogen in 1 mol of helium) used before the analysis for calibration.

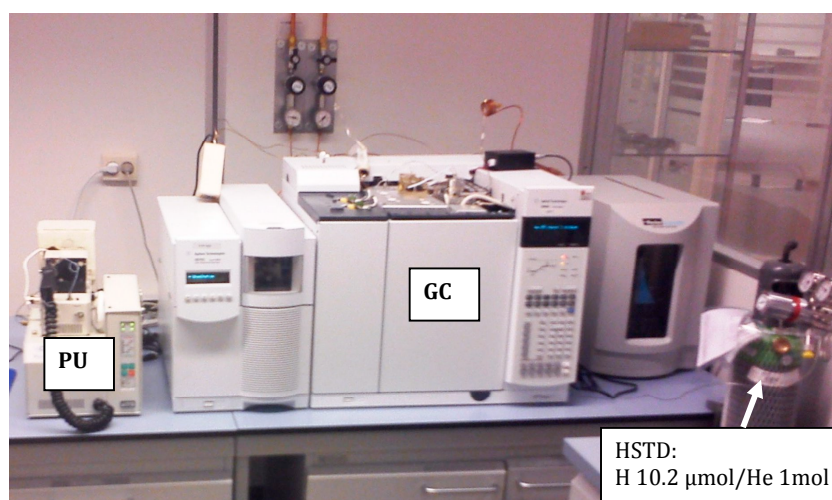


Figure 4.4: Thermal Desorption Analysis equipment

The pyroprobe unit, which holds the sample, is a small induction oven that heats the sample from 30 to ~ 700 $^{\circ}\text{C}$ at stable heating rate 2.6 $^{\circ}\text{C s}^{-1}$. As the temperature of the sample increases, the gases separate from the sample and are taken by the carrier gas (helium) to the GC unit where the content analysis of the gases is conducted. The GC unit contains many parts that combined together are used for hydrogen, oxygen and nitrogen detection; its main parts are the valve (V), the Pulse Discharge Detector (PDD) and the column (C). The top view on the GC unit is shown in Figure 4.5 and its front part with the column in Figure 4.6.

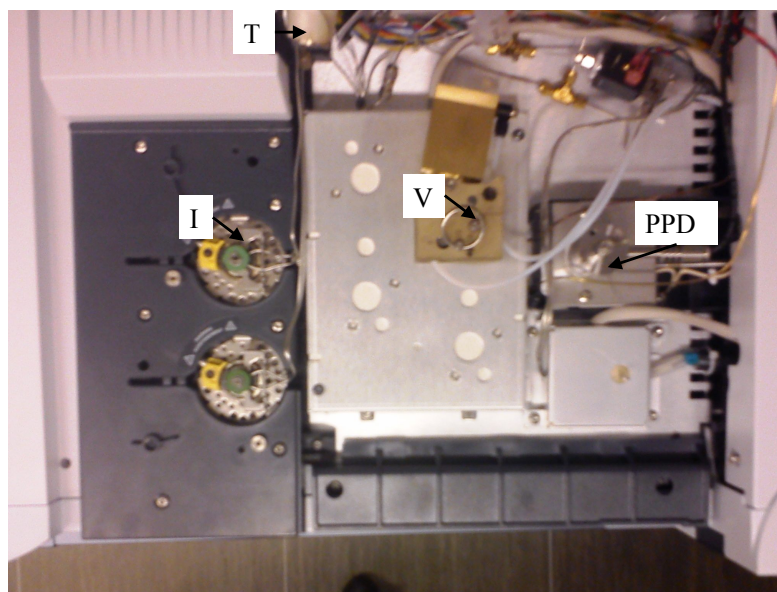
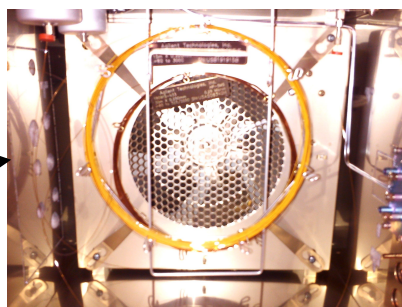
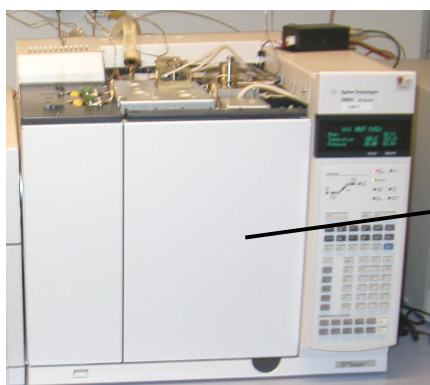


Figure 4.5: The top of the gas chromatography unit, where V is the valve system, PDD is the Pulse Discharge Detector, I is the back inlet and T is the transfer line.



Column from the inside of the GC oven

Figure 4.6: The front of the gas chromatography unit with the column located inside.

The gas flow through the system is shown in Figure 4.7.

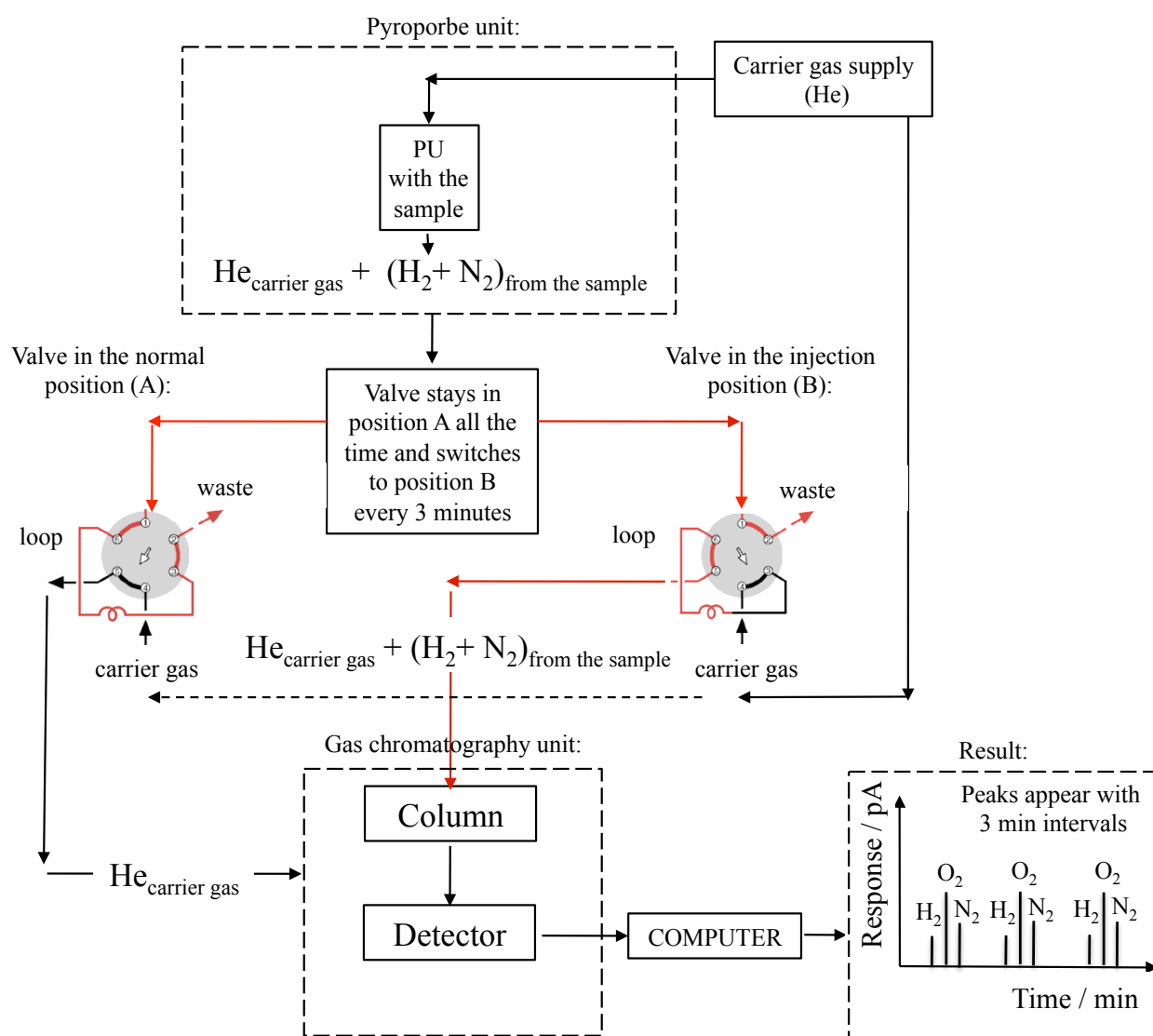


Figure 4.7: The overall gas flow through the system.

The gases separate from the sample (carrier gas + gases released from the steel sample in PU) continuously, with stable temperature increase ($2.6\text{ }^{\circ}\text{C min}^{-1}$); the test may last for ~ 5 hours. PU is connected to the GC unit through the interface (transfer) line, which one is connected to the valve box. As the test lasts for a long time, and the amount of hydrogen is released in a small quantity, the valve box needs to be installed to the system. Its purpose is to gather a certain amount of the gases in the loop and then inject them to the column.

The installed valve box allows a 0.5 ml gas sample from the loop to be injected into the column to be analysed by the detector for 3 minutes. The valve box is always in its normal position A, in which the the gases separated from the sample in the PU with carrier gas are disposed, but the carrier gas from the other side of the valve flows continuously through to the detector (this a standby position). Every 3 minutes the valve switches to the position B for only 0.5 minute, to inject the content from the loop to the column to be analysed (this is an injection position). This procedure is repeated throughout.

In the column, the separation of the gases occurs. The column is a thin tube of a $25\text{ }\mu\text{m}$ diameter with its inside walls coated by a stationary phase, which may consist of particles of a capillary, fibrous material that reacts with the floating gases inside the column. (The exact nature of this material was not disclosed by the supplier.) The separation of the gases is due to the interaction of the compound (hydrogen, oxygen and nitrogen) evaporated from the sample and carried by the helium carrier gas to the column, with the stationary phase inside it. The stronger the interaction between the compound and the stationary phase is, the longer the compound remains attached to the stationary phase, and the more time it resides in the column. The column used for hydrogen, oxygen and nitrogen gases separation in the system was Agilent 19091P-MS7 of $15\text{ m} \times 320\text{ }\mu\text{m} \times 25\text{ }\mu\text{m}$. This is a capillary column where the inner surface is coated with a layer of solid porous material. From the column the gases flow towards the pulse discharge detector (PDD), shown in Figure 4.8.

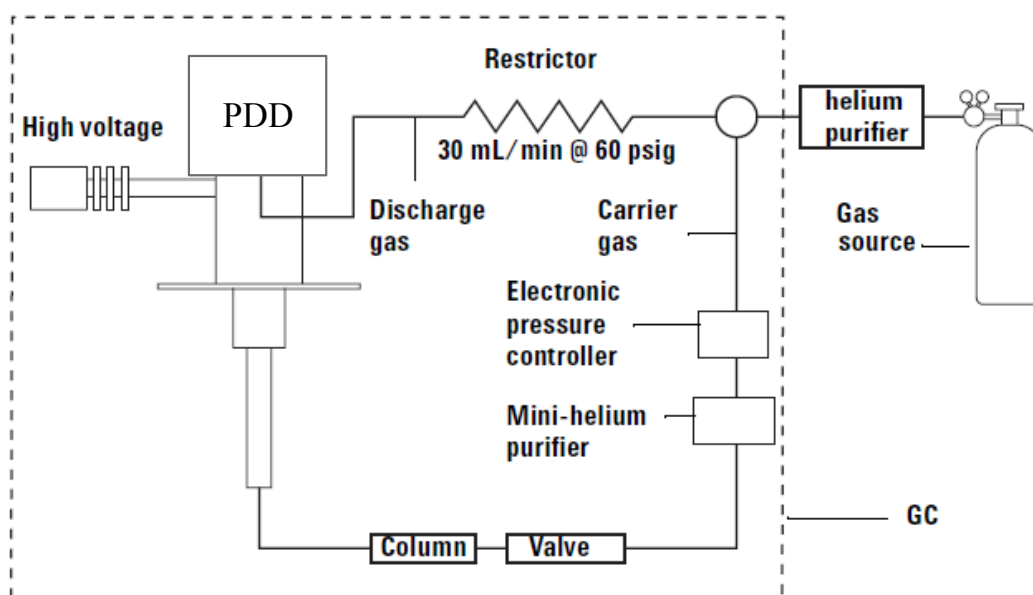


Figure 4.8: The functional diagram of the Pulse Discharge Detector located on the top of the GC unit.

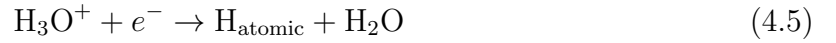
The principal mode of ionization of the gases by PDD is photo ionization by radiation produced from the transition of diatomic helium He_2 to the dissociated 2He . A photon energy from the He_2 continuum is in the range of 13.5 to 17.7 eV. The gases entering the PDD from the column are ionized by photons from the helium discharge region. The resulting electrons are focused towards the collector electrode by two bias electrodes. The collected electrons are converted to a signal that is displayed as a plot of response versus time, showing numerous sets of three peaks that are repeated every 3 minutes. After the test, the area under the hydrogen peaks is integrated giving the amount of hydrogen desorbed from the sample, and its variation with temperature. This allows the determination of a peak in desorption temperature, from which the trap nature can be determined. As the sample is heated up at a stable heating rate, the conversion from time to temperature is applied. The amount of hydrogen can be estimated from the previous calibration, which involves an additional TDA run with a standard gas of a known hydrogen content.

A more detailed description of this equipment can be downloaded from http://www.msm.cam.ac.uk/skf/hh/tda_manual.pdf.

4.2 Hydrogen charging experiment

Hydrogen charging is outlined in Section 2.5.2, and more extensively discussed here as it precedes both melt extraction and thermal desorption, and may be influenced by many factors. These factors have a huge impact on the hydrogen absorbed by the steel sample and in the later stages of mechanical testing [2].

The principle behind electrochemical hydrogen charging is the transfer of an electron at the the steel sample surface to an H_3O^+ -ion according to the following reaction:



After adsorption and dissociation, the dissolved hydrogen can react with iron following further reactions [135]:

Volmer reaction of the anodic dissolution of Fe:



Tafel reaction of the recombination of adsorbed hydrogen:



and the absorption of H_{ad} :

$$\text{H}_{\text{ad}} = \text{H}_{\text{dissolved}}. \quad (4.8)$$

As hydrogen is dissolved in the steel its concentration follows Sieverts law [136]:

$$c_{\text{H}} = K_{\text{S}} \cdot \sqrt{p_{\text{H}_2}} \quad (4.9)$$

where, c_{H} is the concentration of dissolved hydrogen atoms [mol cm^{-3}], K_{S} is Sievers constant and p_{H_2} is the hydrogen pressure in the environment [bar].

Hydrogen solubility in iron at room temperature is 3×10^{-6} at%, but it increases with the temperature and can reach 1.6×10^{-2} at% at 900°C [135]. Therefore the amount of hydrogen charged into the sample can be manipulated by increasing the temperature of the electrolyte or current density [137].

The charging conditions were varied according to the sample dimensions and amount of hydrogen required for the considered tests. The heat treated samples used for the hydrogen charging were machined to meet the test requirements. For investigating if the required amount of hydrogen was achieved, numerous charging trials on dummy samples were conducted, and the charged hydrogen content was measured by melt extraction technique for different electrochemical charging conditions. Hydrogen was introduced to the specimens with cathodic electrolysis using an electrolyte solution of 1 dm^3 distilled H_2O , 4g NaOH and 4 g Thio-urea. The samples were put into the charging cells and surrounded by platinum wires (counter electrode), the polarity of the samples was negative. Subsequently, the cell was connected to the current source specified in Table 4.3, since it depends on the sample dimensions. The charging process took 24 h and the electrolyte was stirred and kept at a constant temperature of 80°C during the whole process. After charging, the samples were gently polished and ultrasonically cleaned with petroleum ether and acetone, respectively. Hydrogen within the samples was measured by means of thermal desorption, melt extraction and mechanical testing (Table 4.3). Samples for Charpy test and rolling contact fatigue test just after charging were stored in the freezer at -80°C to prevent the hydrogen to escape in between the end of charging process and the tests execution; a more detailed description on this process is described in the sections devoted to the respective tests 5.4 and 5.6.

Table 4.3: Hydrogen charging conditions used in these studies. The column labelled ‘Section’ indicates where details on the sample dimensions can be found.

Test	Sample geometry	Sample dimensions mm	Current mA	Charging temperature °C	Charging time h	Section
MET	cylinder	$10 \times \varnothing 3$	8	80	24	4.3.1
MET	cylinder	$6 \times \varnothing 4$	8	80	24	4.3.2 & 4.3.3
TDA	cylinder	$6 \times \varnothing 4$	8	80	24	4.4
Charpy	rectangular prism	55×10	56	80	24	5.4
Hydro-Hardness	cylinder	$20 \times \varnothing 8$	25	80	24	5.5
RCF	cylinder	$110 \times \varnothing 9.53$	187	80	24	5.6

4.3 H-content measurements results

H-content measurements were done by using MET. The experimental conditions were first determined for pure iron (Section 4.3.1) and the samples were measured in two conditions: immediately after hydrogen charging and 24 h after it. The lag between charging and MET or TDA is called exposure or degassing time. Exposure time is the period during which a sample with absorbed hydrogen (for example from electrochemical H-charging) is exposed to air at room temperature; during this time the hydrogen from the sample may diffuse out into the atmosphere as a function of time [138]. The test conditions and the obtained results are described in Sections 4.3.2 and 4.3.3.

4.3.1 Experiment on hydrogen desorption time from pure iron

Rods of 5 mm diameter and 50 mm length from high purity iron (99.8 wt% Fe) were swaged to 3 mm and then cut into 10 mm cylinders. The swaging was chosen due to the initial sample geometry being irregular, making it difficult to machine. The samples for optical microscopy were further cut to 2 mm cylinders and mounted in conductive bakelite, ground using 1200 grit SiC paper and polished with 6 μm and 1 μm diamond paste. The samples were etched in 1.5% nital (1.5% Nitric acid and 98.5% Methanol). Zeiss Axioplan2 optical microscope was employed. The microstructure obtained just after swaging is shown in Figure 4.9a and 4.9c. This highly deformed microstructure was later heat treated in order to reduce the number of dislocations and increase the grain size.

During this heat treatment the samples were placed in a furnace at 900 °C for 5 min. The microstructure after this process is shown in Figure 4.9b and 4.9d.

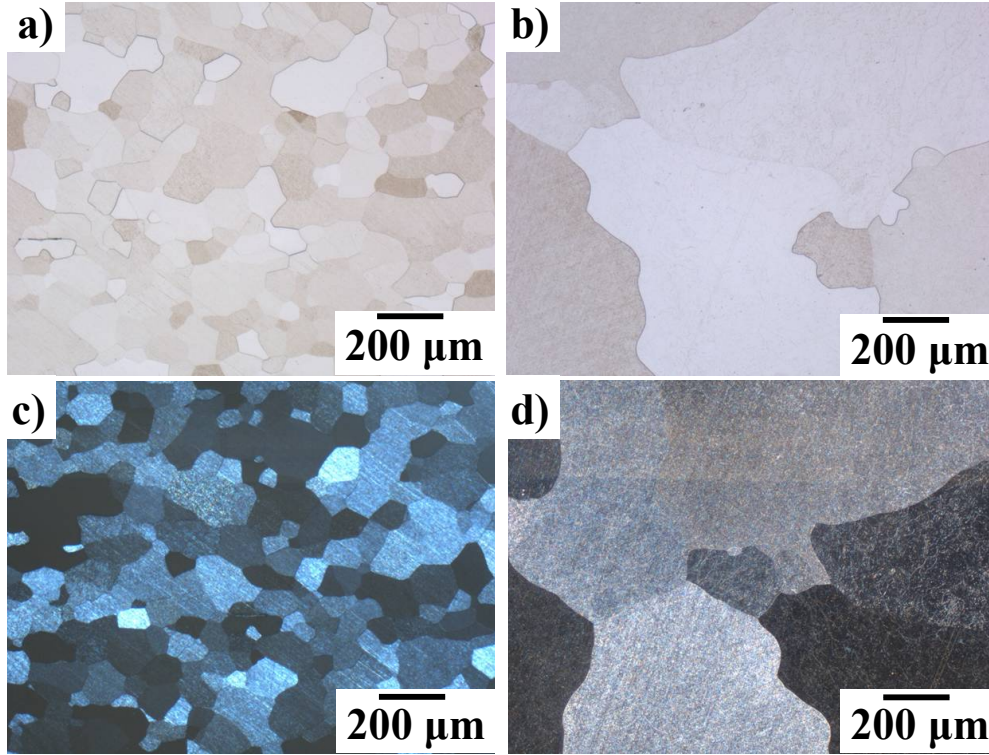


Figure 4.9: The microstructure of pure iron. Bright field image (a) after swaging and annealing. Differential interference contrast (c) after swaging and (d) annealing. The samples were etched in 1.5 % Nital.

The rods were then hydrogen charged by using electrochemical charging with the conditions described in Table 4.3. After H-charging the samples were cleaned ultrasonically with petroleum ether and acetone, and analysed in an ELTRA ONH-2000 melt extraction machine. The samples were analysed immediately after, 2 h after and 8 h after charging. The obtained results are shown in Figure 4.10.

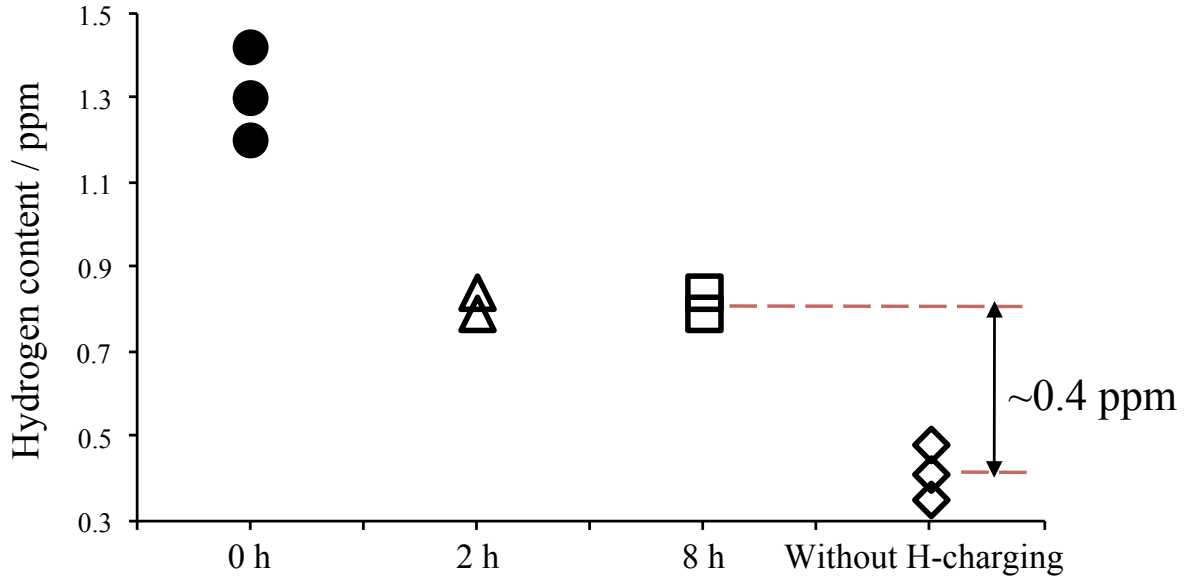


Figure 4.10: The melt extraction results showing hydrogen content in pure iron samples. The analysis were conducted at different times between finishing the H-charging process and starting the melt extraction analysis. 0 h, 2 h and 8 h mean that the samples were tested just after, 2 h and 8 h after H-charging, respectively.

4.3.2 Hydrogen absorption experiment

The hydrogen absorption experiment was performed on 100Cr6, 100Cr6+0.5V and superbainite transformed at 200 and 300 °C. Their chemical compositions and treatments are described in Section 4.1. All the samples were cut into 4 mm diameter and 6 mm length rods. Hydrogen was introduced into the specimens as described in Section 4.2. The charging conditions are listed in Table 4.3. The total hydrogen content was measured by means of the melt extraction technique (MET). The samples were tested in two conditions: just after hydrogen charging and 24 hours hydrogen charging (Figure 4.11); where α' means that the final sample microstructure was martensite, α'_B means that the final sample microstructure was bainite, SB200 is the sample with superbainite microstructure transformed at 200 °C, SB300 is the sample with superbainite microstructure transformed at 300 °C. Pure iron results from the previous section (Section 4.3.1) were added for comparison.

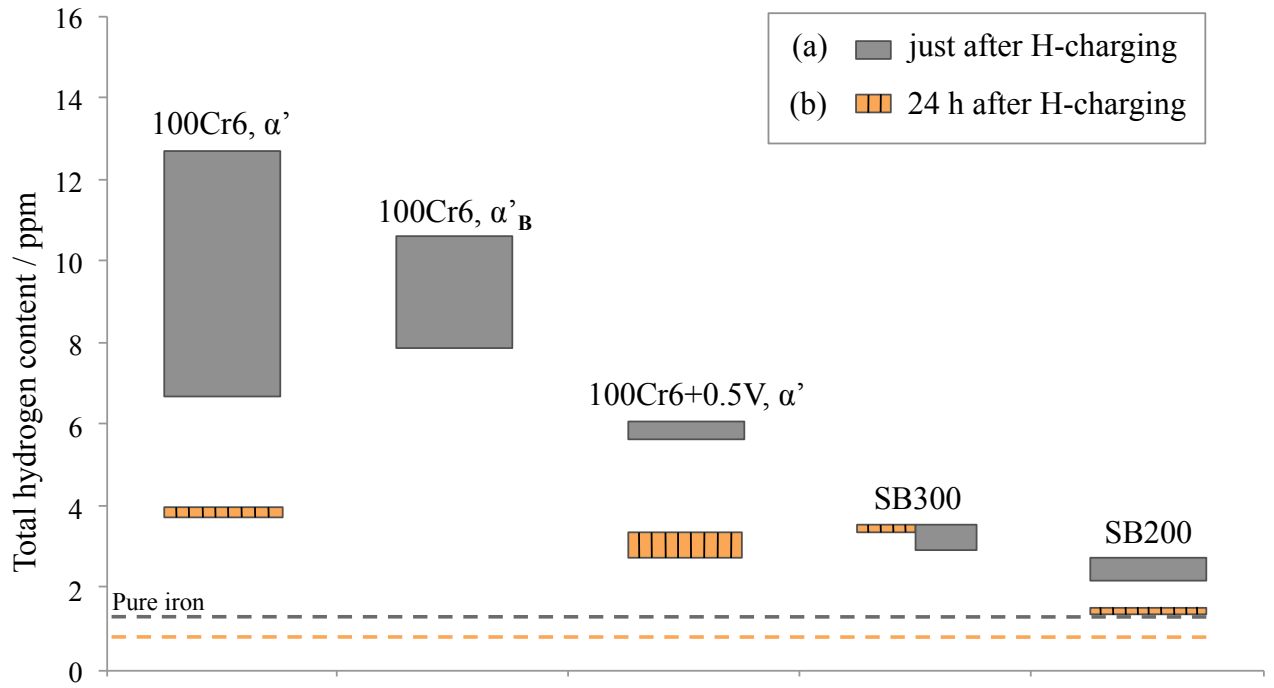


Figure 4.11: Melt extraction results. The test was performed (a) immediately and (b) 24 h after H-charging

4.3.3 Retained austenite influence on hydrogen content in superbainite

As superbainite microstructures (SB200 and SB300) results showed much lower hydrogen absorption (Figure 4.11), their microstructure was further examined and this analysis presented here. SB200 and SB300 samples were respectively subjected to additional annealing at 500 °C for 1 h (SB300^A) and for 2 h (SB200^A) in order to reduce the retained austenite content. The samples were then hydrogen charged and analysed by MET. The results are shown in Figure 4.12, where the samples with higher retained austenite content (SB300 and SB200) show more hydrogen absorbed in their microstructure. SB200⁰ and SB300⁰ were not subjected to hydrogen charging. This suggests that a trapping site in the superbainite microstructure is retained austenite/matrix interface rather than retained austenite interior, as it is suggested in the literature [70, 62, 15]. In the case of bulky retained austenite present for example in 0.17C-1.6Mn-0.4Si-2Al (wt%), or other reviewed

in Section 2.3.2 steels, the hydrogen can be lodged in the retained austenite due to lower hydrogen diffusion coefficient in austenite rather than in its surrounding ferritic matrix, but in the case of lath retained austenite in superbainite, the results show that the steels with a lower amount of retained austenite absorbed a lower amount of total hydrogen content after charging. The explanation of this phenomenon is introduced in Section 4.4, Figure 4.16.

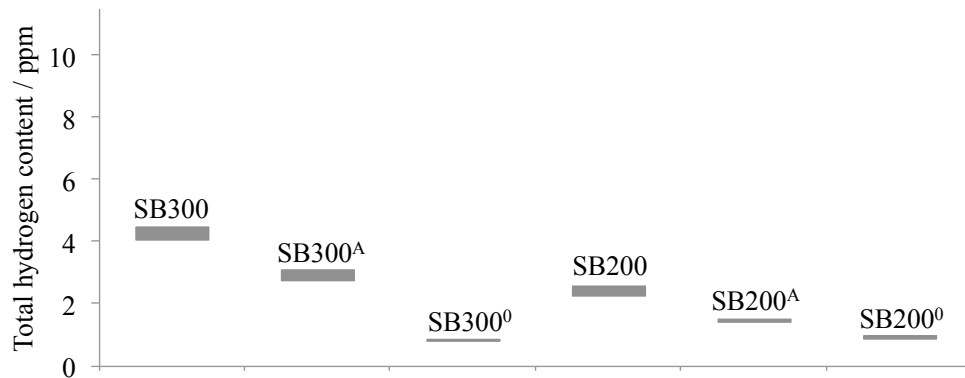


Figure 4.12: Melt extraction results showing hydrogen content in superbainite transformed at 300 °C and 200 °C (Table 4.2).

The amount of retained austenite in the examined samples was measured by X-ray diffraction. 8 mm diameter and 3 mm long samples were ground using 1200 grit SiC paper for smooth surface. Grinding process was followed by etching in concentrated HCl for 20 s for removing deformation caused by grinding. A Bruker AXS D8 Discover X-ray diffractometer was employed. A standard DQUANT software was used to quantify the retained austenite amount. X-ray data were obtained between 35° and 105° 2 θ with a step size of 0.02° and a dwell time of 10 s. A Mo target was used (MoK α 0.7107 Å). The determination of retained austenite in martensite is based on the ratio method for the intensities of four peaks, martensite {200} and {211}, and austenite {220} and {311}. The obtained results for SB300 and SB200 are shown in Figure 4.13 and 4.14, respectively. In both cases the retained austenite decreased from 19 to 16 % for SB300 (Figure 4.13) and from 23 to 14 % for SB200 (Figure 4.14) when additional annealing at 500 °C was introduced for 1 h (SB300) and 2 h (SB200). Longer annealing resulted in lower retained austenite content (Figure 4.14).

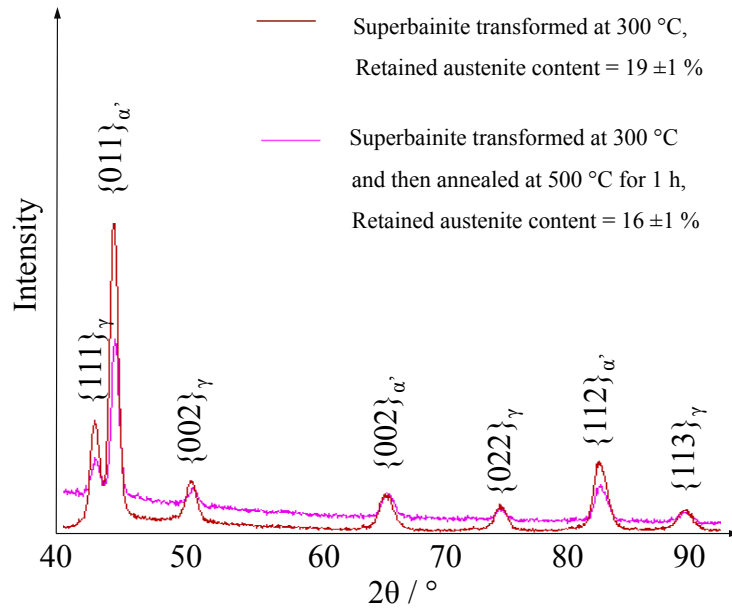


Figure 4.13: X-ray diffraction data for superbainite transformed at 300 °C.

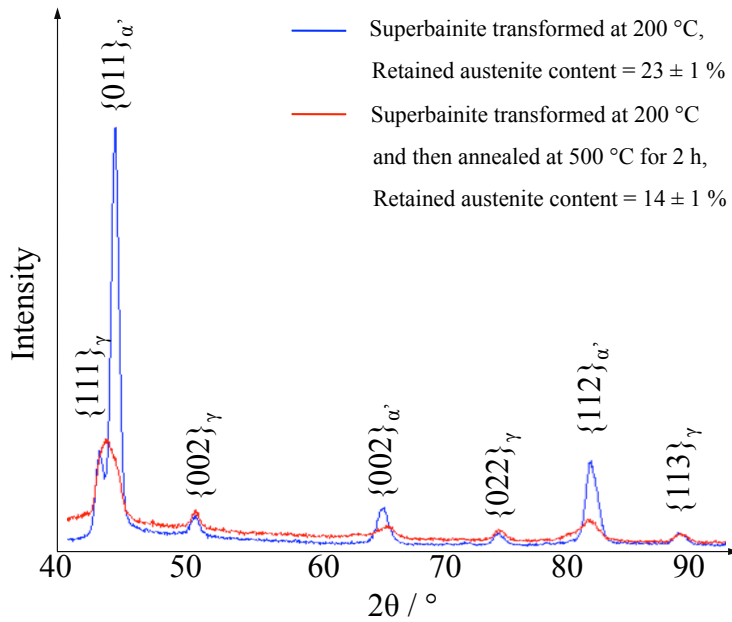


Figure 4.14: X-ray diffraction data for superbainite transformed at 200 °C.

4.4 Thermal desorption analysis results

The samples used for thermal desorption (Section 4.1.2) were 100Cr6, 100Cr6+0.5V, SB200 and SB300. Before the analysis, all the samples were hydrogen charged with the conditions described in Table 4.3. Two situations were considered: TDA just after hydrogen charging, to estimate the total hydrogen content, and 24 h after from charging for estimating the amount of hydrogen trapped by reversible traps. The obtained results are shown in Figure 4.15. The temperature of the maximum thermal desorption peaks (T_{TDA}) helped to determine the type of traps active in the microstructure. When considering the T_{TDA} temperatures in Figure 4.15, the peak at 188 °C corresponds to trapping on dislocations in 100Cr6, but may also correspond to retained austenite/matrix interface in case of SB200 and SB300. When comparing the obtained T_{TDA} in SB300 just after H-charging, 188 °C (Figure 4.15a), with the T_{TDA} obtained in the sample tested 24 h after H-charging, 227 °C (Figure 4.15b), the peak shifts to higher temperature. This suggests that the trapping activation energy of the retained austenite/matrix interface in SB300 is actually higher than the one in SB200; the T_{TDA} for SB200 increased from 188 °C (Figure 4.15a) to 219 °C (Figure 4.15a). This situation can be explained by the presence of diffusible hydrogen content that is included in the sample tested just after H-charging (Figure 4.15a), and is after charging lodges in the weakest traps, the dislocations. The T_{TDA} for 100Cr6+0.5V did not shift, indicating that the hydrogen immediately after entering this microstructure is trapped by the numerous V_4C_3 nanoparticles. Therefore it cannot wander in the microstructure and cause the damage, as it does while it is in a diffusible form. Moreover, the amount of hydrogen in the two analysed conditions did not significantly decrease as well (5.67 to 4.27 ppm), and when comparing it to the 100Cr6 results, where the T_{TDA} also did not change but the amount of hydrogen noticeably dropped by a factor of ten from 1.19 ppm (Figure 4.15a) to 0.12 ppm (Figure 4.15b), it can be concluded that V_4C_3 traps hydrogen rapidly in their vicinity and more effectively than dislocations in 100Cr6 that release almost all hydrogen after 24 h.

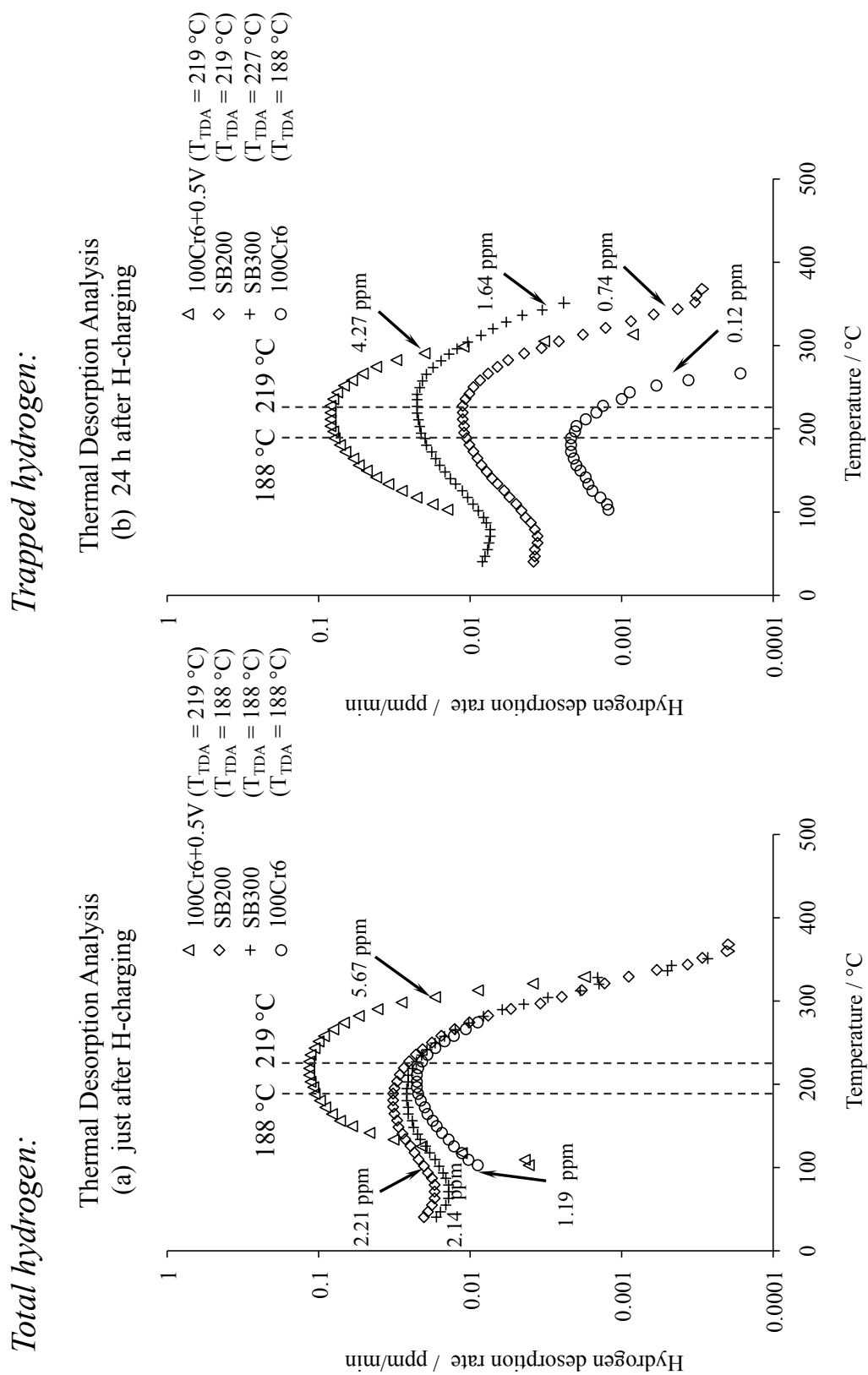


Figure 4.15: Thermal desorption charts (a) just after H-charging, and (b) trapped hydrogen on reversible traps measured 24 h after H-charging.

4.5 Discussion

The results in Figure 4.10 show that almost all hydrogen escapes from the sample within 2 h from hydrogen charging. Hydrogen content measured immediately after charging show some scattering (filled circles in Figure 4.10), this suggests that the total hydrogen content includes diffusible hydrogen, the amount of which rapidly decreases with time, especially during the first few minutes after hydrogen charging. 8 h exposure time seems to be insufficient for all hydrogen to diffuse out from the specimen and approach the initial stage 0.5 ppm. This indicates that ~ 0.4 ppm may be trapped on possible hydrogen traps such as dislocations or grain boundaries [51, 57]. Based on this experiment and a literature review [11, 6, 59], the 24 h exposure time before MET and TDA was estimated for allowing most diffusible hydrogen to escape from the sample and to reveal only the trapped hydrogen.

Figure 4.11 shows the amount of hydrogen absorbed by the analysed microstructures after charging. The results including diffusible hydrogen, measured immediately after charging (Figure 4.11a) show that 100Cr6 (martensitic microstructure) absorbs the most hydrogen, followed by bainitic 100Cr6, martensitic 100Cr6+0.5V and two superbainite samples SB300 and SB200, with the last two showing a surprisingly low amount of absorbed hydrogen. These results confirm that martensite is the most prone to hydrogen embrittlement [8] and indicates that a bainitic 100Cr6+0.5V would possibly have even lower hydrogen absorption than the martensitic 100Cr6+0.5V shown in the Figure 4.11a. It can be noted that 100Cr6 contains higher amount of sulphur compared to the other grades, which might form MnS. These inclusions are usually large and are considered as strong irreversible hydrogen traps (Table 2.3), therefore their presence might increase the total amount of hydrogen content (Figure 4.11a). However, if the hydrogen total amount was influenced by the presence of MnS in 100Cr6, the hydrogen content should not drop so sharply when conducting the same test after 24 h (Figure 4.11b), since such strong trapping sites do not allow hydrogen to escape from their interior at room temperature due to their high activation energy ($E_A = 72.3$ kJ/mol) [63], what further supports the

argument that 100Cr6 microstructure absorbs the most hydrogen. The samples were subjected to the same conditions but after 24 h from charging show a slightly different trend. When comparing the samples immediately after charging and 24 h after it, the average total hydrogen content decreased from ~ 10 to ~ 3.7 ppm (100Cr6), from ~ 6 to ~ 3.2 ppm (100Cr6+0.5V), from ~ 2.5 to ~ 1.5 ppm (SB200) and did not significantly change for SB300 ~ 3.5 ppm. This difference indicates the decrease in the amount of diffusible hydrogen present in the microstructure that may cause hydrogen embrittlement, as described by Kino [1]. It should be pointed out that the amount of this diffusible hydrogen is much lower in 100Cr6+0.5V when compared to the baseline steel, 100Cr6. SB200 and SB300 showed a very low amount of diffusible hydrogen, therefore this phenomenon was further studied.

Experiments on superbainite samples with lowered amount of retained austenite were conducted in order to investigate the slow hydrogen diffusion in superbainite. Retained austenite has been reported to have very low hydrogen diffusion coefficient [70]. Since superbainite contains only retained austenite and ferrite [71], and the diffusivity of hydrogen in austenite is much lower than in ferrite, retained austenite is believed to block the hydrogen diffusion within the bulk, and therefore when comparing hydrogen absorption of superbainite to other steels seen in Figure 4.11, it can be seen that less hydrogen enters this microstructure. This suggests a lower hydrogen intake into the steel. The further results on superbainite with decreased retained austenite content showed that, when hydrogen is already present in the microstructure, both hydrogen content and its interface play a role in the hydrogen trapping (Figure 4.12). The obtained results showed that the superbainite with even lower retained austenite amount SB300^A (SB200^A) tends to absorb even less hydrogen (Figure 4.12). In Figure 4.12, the results suggest that it is rather the retained austenite-ferrite interface a trapping site than retained austenite interior. The hydrogen trapping character of superbainite can be introduced with the aid of Figure 4.16. It can be seen that, when the retained austenite content decreases by the additional annealing of SB300^A and SB200^A, the number of interfaces decrease as well

because the hydrogen has less available sites to be trapped in the microstructure. Therefore the microstructure becomes simpler like pure iron, and the hydrogen total amount in SB300^A and SB200^A is decreased.

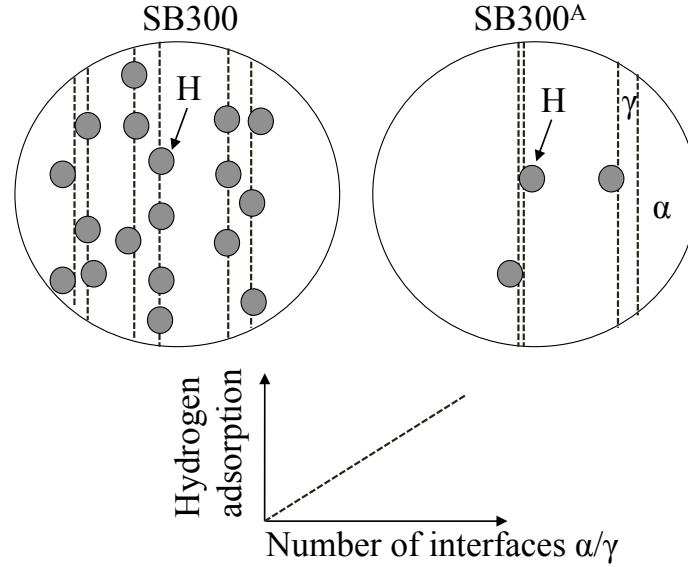


Figure 4.16: Superbainite trapping character.

The results from TDA analysis (Figure 4.15) and a literature review also indicate that it is the retained austenite/ferrite interface what traps hydrogen in superbainite microstructure. As it was reviewed in Section 2.3.2, retained austenite is usually an irreversible type of hydrogen trap that immobilize hydrogen inside itself. The irreversible trap may get saturated with hydrogen until a very high quantity. Hydrogen might be released from this trapping site, but at a higher temperature compared to the reversible traps, so its T_{TDA} appears at higher temperatures such as ~ 600 °C [64, 68] and the activation energy E_A to release it from such a strong trap is higher than 55 kJ/mol. The incoherent precipitates are also in the irreversible trap category. The results presented here showed that T_{TDA} temperatures from SB200 and SB300 appeared at relatively low temperatures (at 219 °C for SB200 and 227 °C for SB300) which classifies them as reversible traps, according to the review presented in Table 2.3. These temperatures are really similar to the temperatures reported for the coherent precipitates such as TiC, V_4C_3 and NbC; all these precipitates have $T_{TDA} \sim 220$ °C (Table 2.3). This shows that the retained austenite-

ferrite interface also needs to be coherent or semi-coherent. Figure 4.17 illustrates the difference in the trapping character between bulky retained austenite (irreversible trap with incoherent or semi-coherent type of interface with matrix) and lath retained austenite (reversible trap with coherent or semi-coherent interface with matrix). Figure 4.17, also shows that the T_{TDA} decreases if the interface coherency increases.

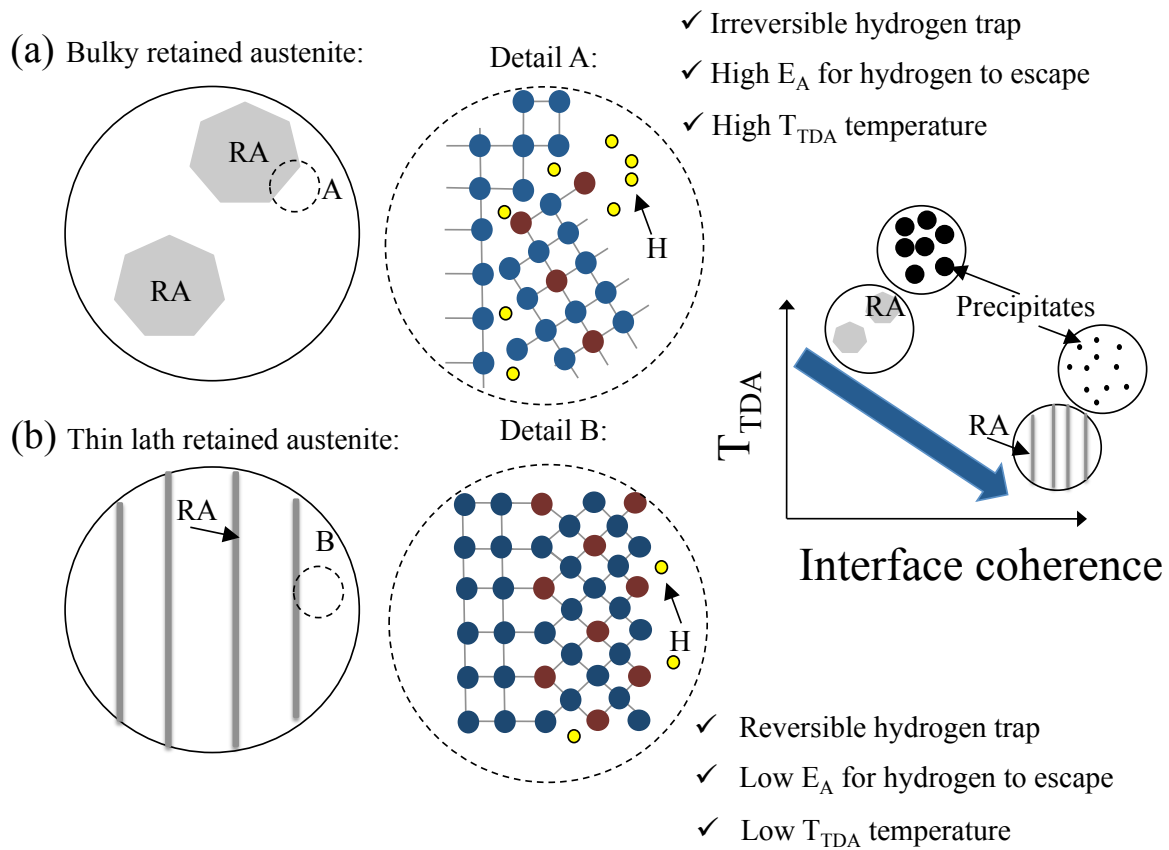


Figure 4.17: Retained austenite/matrix interface character in (a) steel with the bulky retained austenite and (b) superbainite with lath retained austenite, and its influence on thermal desorption results.

The TDA results show the temperature peaks (T_{TDA}) for different steels (Figure 4.15). The total hydrogen predominantly trapped by dislocations in 100Cr6 was ~ 1 ppm, in 100Cr6+0.5V was ~ 5.7 ppm and trapped by retained austenite in SB300 and SB200 was ~ 2 ppm. These results (Figure 4.15a) include the diffusible hydrogen around the considered traps or very weakly trapped by them, however, when allowing 24 h for diffusible

hydrogen to escape (Figure 4.15b) mostly trapped hydrogen is revealed. Figure 4.15b shows that the amount of hydrogen decreased for all the samples with the smallest decrease observed for SB300 (from 2.14 to 1.64 ppm, 23% for SB300) and for 100Cr6+0.5V (from 6.67 to 4.27 ppm yielding $\sim 36\%$ decrease). That suggests that almost all hydrogen was trapped effectively by (V_4C_3) just after entering 100Cr6+0.5V. For other steel grades, the hydrogen content decreased as follows: from 2.21 to 0.74 ppm ($\sim 66.5\%$ reduction for SB200) and from 1.19 to 0.12 ppm ($\sim 90\%$ reduction for 100Cr6). It was also observed that the trapping capacity of (V_4C_3) was over two orders of magnitude hydrogen trapping capacity higher than the baseline steel (100Cr6). The peaks in Figure 4.15 help to investigate the types of traps operating and the amount of hydrogen trapped by them. The type of hydrogen traps was estimated based on a literature review and its comparison to obtained results. Figure 4.18 and 4.19 show the obtained results with data gathered from the literature.

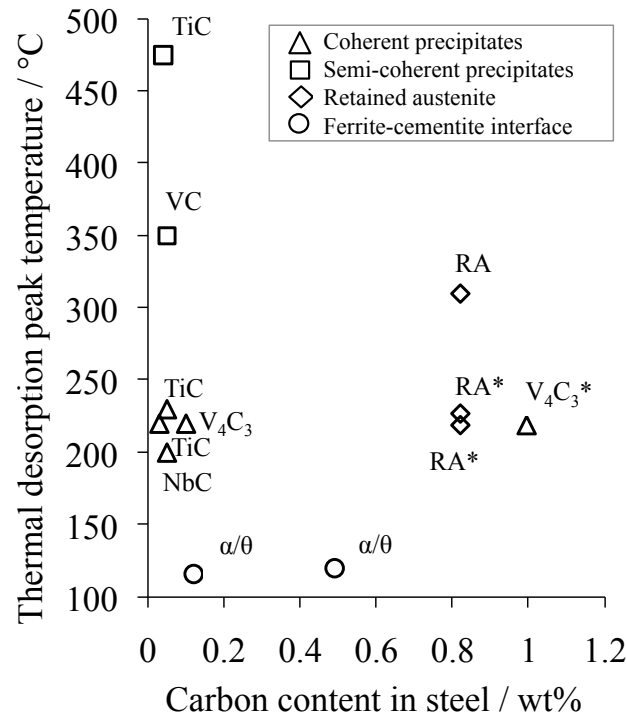


Figure 4.18: Carbon influence on thermal desorption peak temperature in investigated (*) and the reported steels [52, 64, 52, 11, 59, 6].

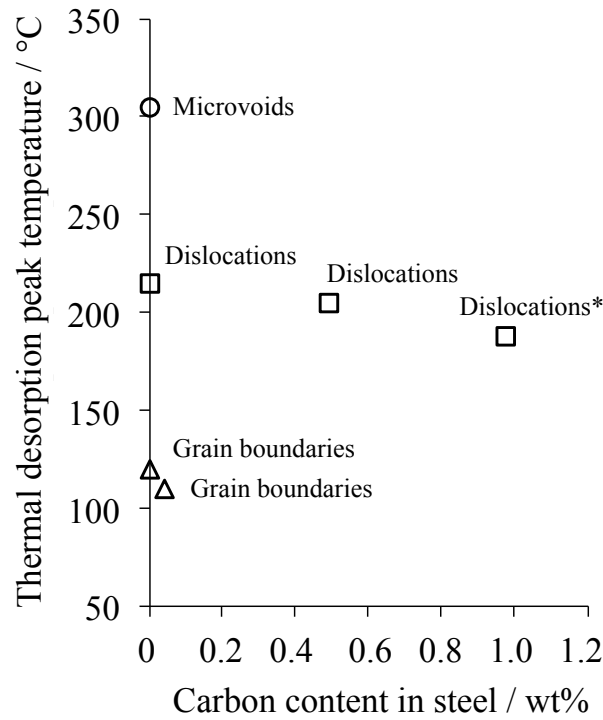


Figure 4.19: Carbon influence on thermal desorption peak temperature in investigated (*) and the reported steels [60, 51].

Figure 4.18 shows that the carbon content present in the tested steels has no influence on hydrogen trapping on the precipitates. V_4C_3 showed the thermal desorption peak at 219 °C (1 wt% C) being very similar to other coherent precipitates in low carbon, less than 0.2 wt% C. However, carbide coherency has noticeable influence on the peak shift for precipitates as well as for retained austenite. Coherency has been pointed out before in the literature review since the size of the precipitates determines if the trap is reversible or irreversible (Table 2.3). Carbon content in the analysed steel has, however, influence on the thermal desorption peak for dislocations and probably grain boundaries as shown in Figure 4.19. Based on these results and the fact that carbide-free microstructure of SB200 and SB300 is combined only of ferrite and retained austenite, the following hydrogen traps were investigated in the analysed steels: dislocations (100Cr6), V_4C_3 (100Cr6+0.5V) and retained austenite/matrix interface (SB300 and SB200). Carbide-free microstructure of SB200 and SB300 combined of ferrite and retained austenite contains

Summarising, the results from MET and TDA techniques are presented in Figure 4.20. It is believed that both the techniques should be combined and their results compared for understanding the hydrogen influence on the microstructure. The results show that all highlighted steels have a relatively low difference between total hydrogen absorbed (just after H-charging) in all the samples investigated by MET, and the hydrogen trapped by reversible traps (24 h after H-charging) investigated by TDA. The steels that are hydrogen embrittlement resistant are represented by the black bullets in Figure 4.20, with SB300 showing the smallest difference between both variables, and therefore showing an interesting hydrogen embrittlement potential that requires further investigations.

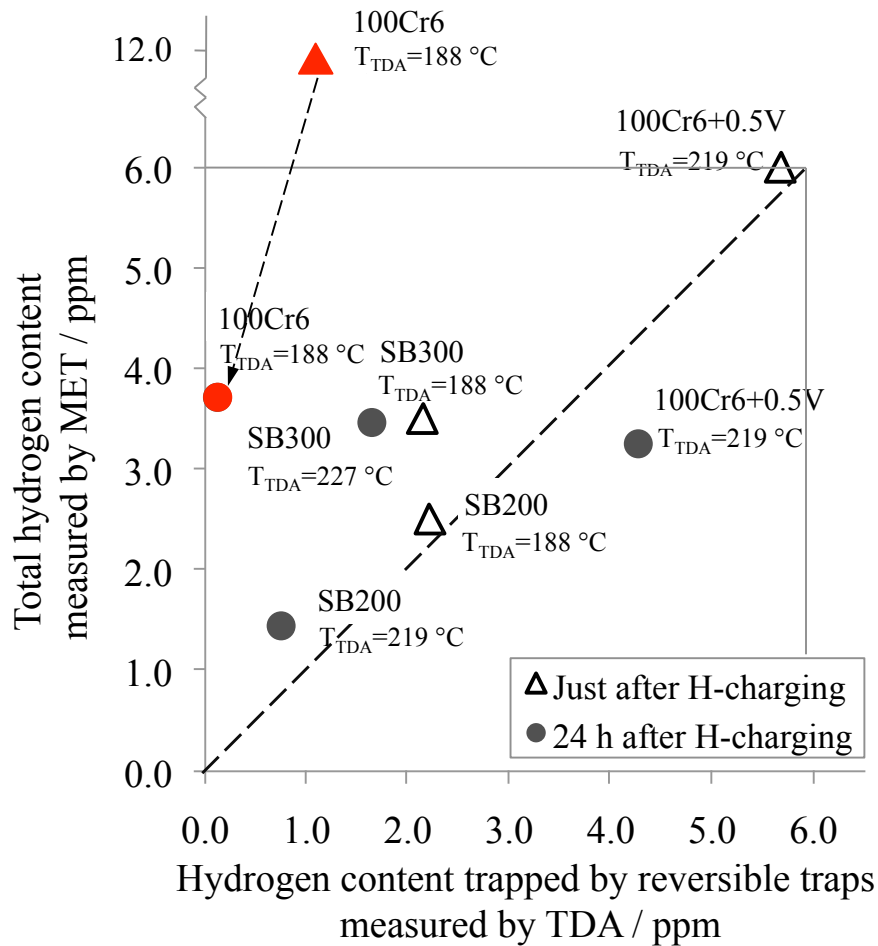


Figure 4.20: Melt extraction and thermal desorption analysis results, where the red and black bullets indicate hydrogen embrittlement susceptible and hydrogen embrittlement resistant steels, respectively.

4.6 Summary

100Cr6+0.5V (martensite) absorbs significantly less hydrogen in its base microstructure compared to 100Cr6 (martensite). Almost all the hydrogen absorbed in 100Cr6+0.5V hydrogen was effectively trapped by V_4C_3 . SB200^A and SB300^A absorb the lowest amount of hydrogen from all tested samples with its amount approaching pure iron. The amount of retained austenite in superbainite has a strong influence on absorbed hydrogen; however lower retained austenite content is more favourable in superbainite due to its coherent interface, which traps hydrogen by the strain induced around this interface, not allowing hydrogen to be stored in the retained austenite leading to its saturation. The type of hydrogen traps was determined for each alloy: 100Cr6 trapping is on dislocations, 100Cr6+0.5V trapping is on V_4C_3 , SB300 and SB200 trapping is on retained austenite/ferrite interface. Possible hydrogen embrittlement resistant steels are 100Cr6+0.5V, SB200 and SB300.

Chapter 5

Alloy characterisation

The designed 100Cr6+0.5V alloy characterisation was performed on a 500 g and an 8 kg casts. Both melts were subjected to various tests and compared to commercial 100Cr6 provided by SKF; additionally many of the hydrogen related properties were also compared to pure iron, SB300 and SB200, since their testing helped in unveiling the nature of the hydrogen embrittlement mechanism evaluation in bearing steels. The 500 g 100Cr6+0.5V cast was produced by Vacuum Induction Melter (VIM) Balzer in the Department of Materials Science and Metallurgy at the University of Cambridge. Its composition after chemical analysis is shown in Table 3.1. This cast was used for tests requiring specimens of a reduced size, such as thermal desorption (TDA) and melt extraction analysis (MET), dilatometry, optical and transmission electron microscopy.

The 8 kg cast was employed for test requiring large samples. The cast was produced at TU Clausthal Institut für Metallurgie. This cast is hereon called 100Cr6+0.5V(G). 100Cr6+0.5V(G) and 100Cr6 chemical compositions used for impact, hydro-hardness (H-H) and rolling contact fatigue (RCF) testing, are shown in Table 5.1.

Table 5.1: Chemical composition of the modelled steels (wt%).

Grade	C	Si	Mn	Mo	Cr	Ni	Al	Cu	P	S	V	O
												ppm
100Cr6	0.97	0.27	0.28	0.06	1.37	0.25	0.040	0.213	0.007	0.009	0.00	8.30
100Cr6+0.5V(G)	0.96	0.29	0.290	0.09	1.35	0.01	0.004	0.221	0.005	0.004	0.54	13.6

5.1 Heat treatment and dilatometry

100Cr6 and 100Cr6+0.5V casts were spheroidized to improve machinability, according to the schedule shown in Figure 5.1. The samples were further cut into rods of 4 mm diameter and 6 mm length for TDA and MET analysis. These small rods were then heat treated in vacuum in a Thermecmaster dilatometer with helium quenching gas at a cooling rate of $25\text{ }^{\circ}\text{C s}^{-1}$.

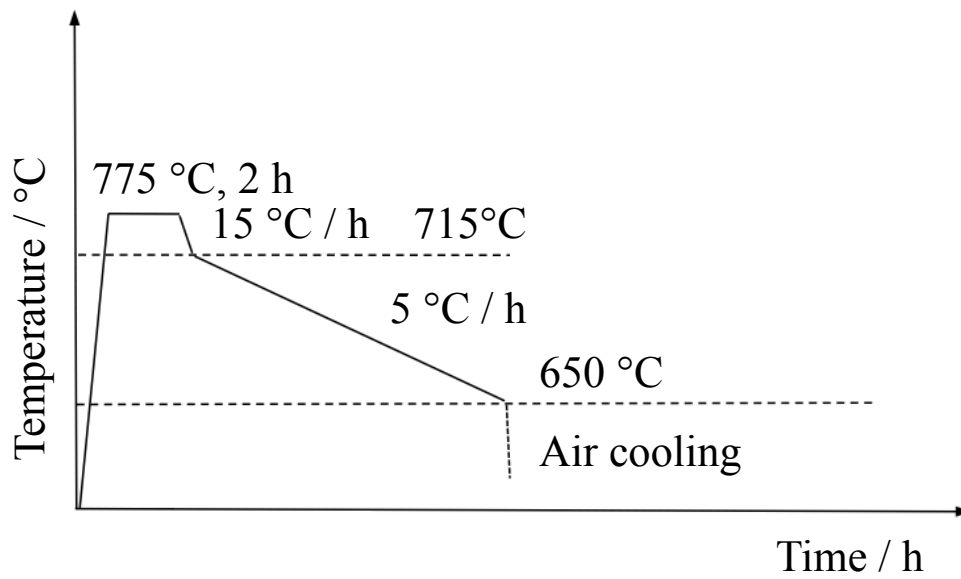


Figure 5.1: Spheroidize annealing applied before machining and hardening of 100Cr6 and 100Cr6+0.5V [139].

Figure 5.2 and Figure 5.3 show the dilatation curves obtained from heat treating 100Cr6 and 100Cr6+0.5V, respectively.

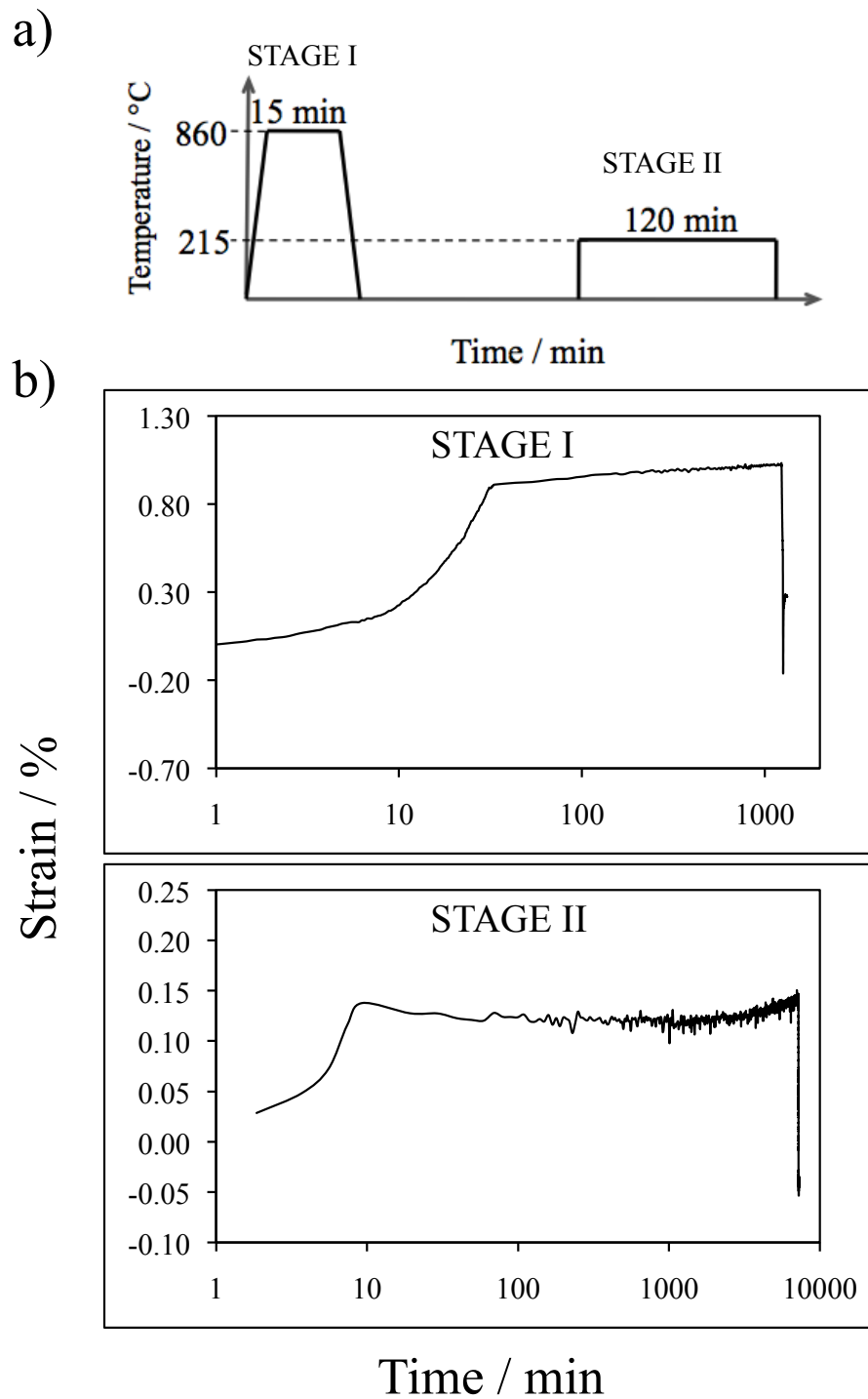


Figure 5.2: Heat treatment of 100Cr6 (a) with obtained dilatation curves (b).

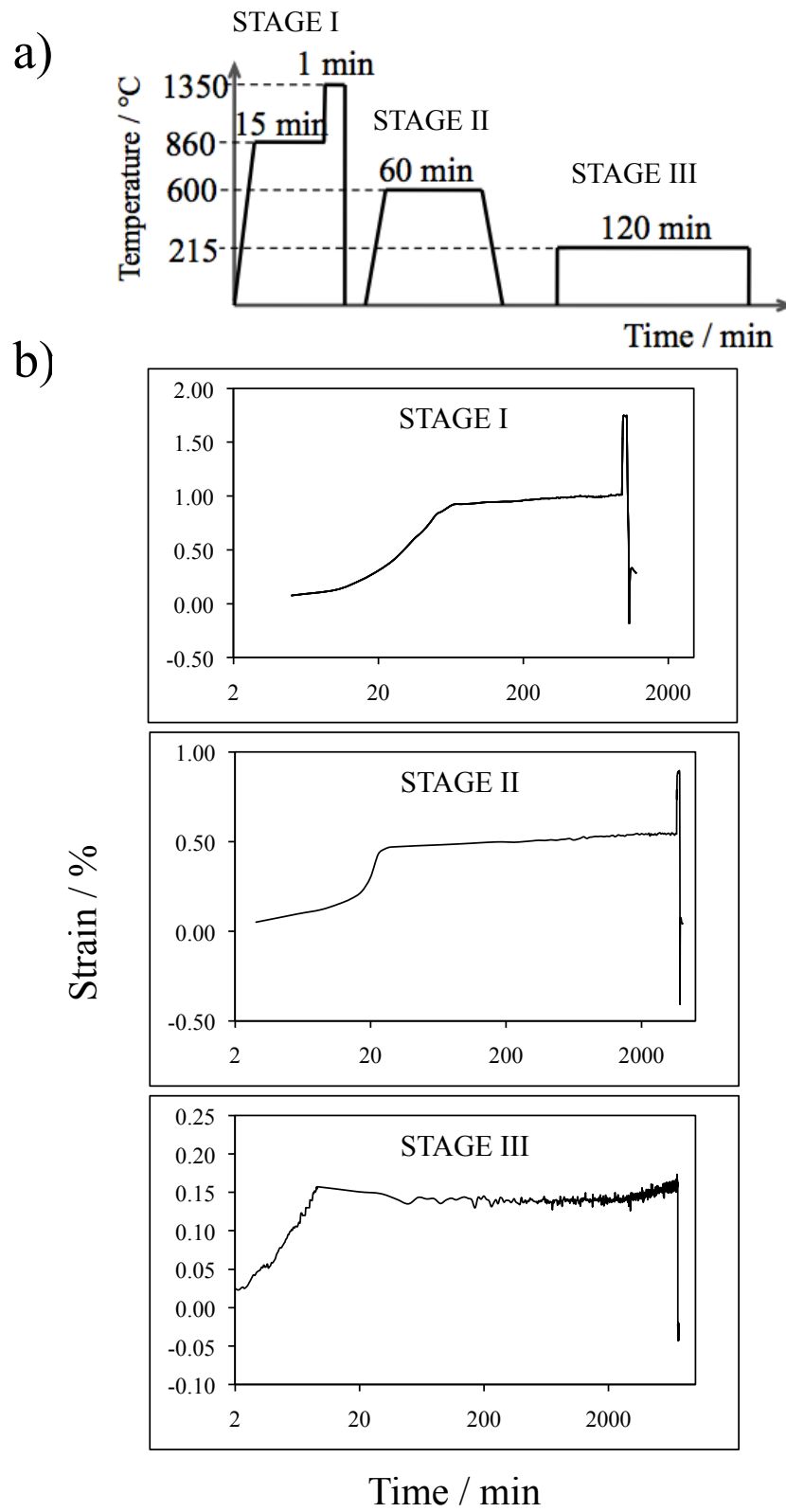


Figure 5.3: Heat treatment of 100Cr6+0.5V (a) with obtained dilatation curves (b).

100Cr6+0.5V(G) was cast and hot-rolled at temperatures ranging from 1200 to 1100 °C into plates, and further spheroidized according to the schedule shown in Figure 5.1. Over-sized samples were cut for Charpy impact, H–H and RCF testing. The samples were then heat treated as shown in Figure 5.4, the process was done in a salt bath instead. The quenching rates were slightly altered to bring the treatment closer to industrial reality. The heat treatment in salt bath was carried out at Summitglow Ltd. in Sheffield, where the conditions were examined several times before reproducing the similar cooling and heating rates as during previous heat treatments done on the dilatometer. After heat treatment the samples were machined to specification.

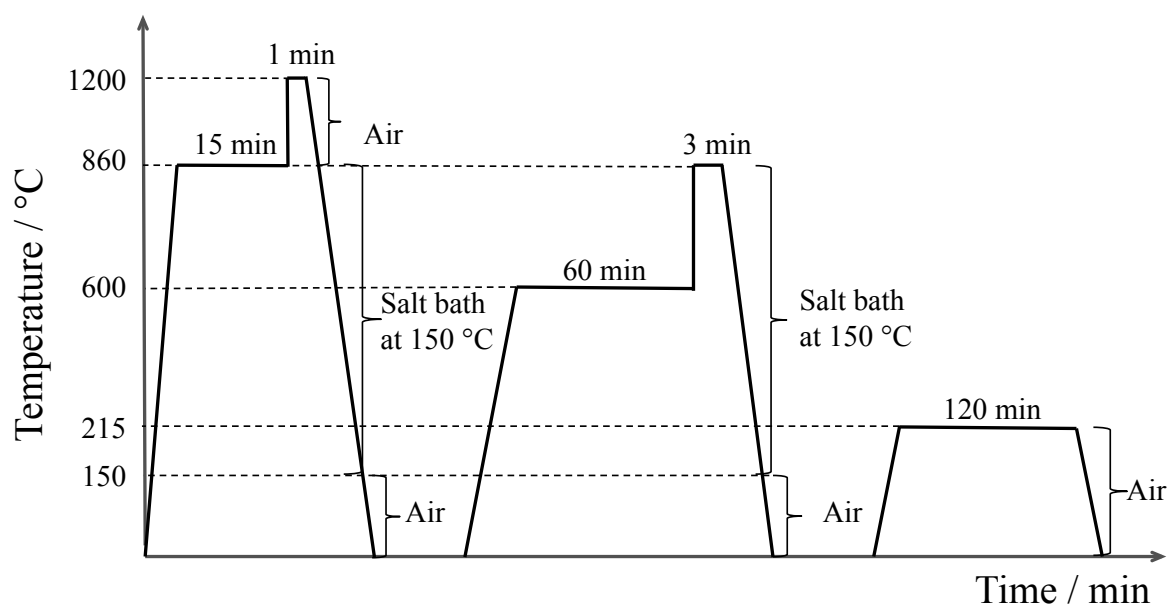


Figure 5.4: Heat treatment schedule of 100Cr6+0.5V performed in the salt bath furnaces.

5.2 Optical, scanning electron microscopy and hardness

The 8 mm diameter samples were heat treatment in the dilatometer and cut in half, hot mounted in conductive bakelite, ground using 1200 grit SiC paper and polished with 6 μm and 1 μm diamond paste. The samples were etched in 2% nital (2% Nitric acid and 98% Methanol). Zeiss Axioplan2 and Leica DM6000 optical microscopes were used. For hardness testing, a Vickers hardness testing machine with a 30 kg load was employed. Each quoted value represents an average of 10 readings with the lowest, and highest single values not considered for calculating the mean. A 15×15 mm cube was cut from the 8 kg 100Cr6+0.5V hot-rolled plate, and its microstructure and hardness were examined; a pearlitic microstructure with 305 HV30 (~ 31 HRC) hardness was obtained. Figure 5.5a shows the associated microstructure. A typical optical microscopy image of 100Cr6+0.5V after spheroidization (Figure 5.1) is shown in Figure 5.5b. The hardness after this treatment was 232 HV30 (20 HRC).

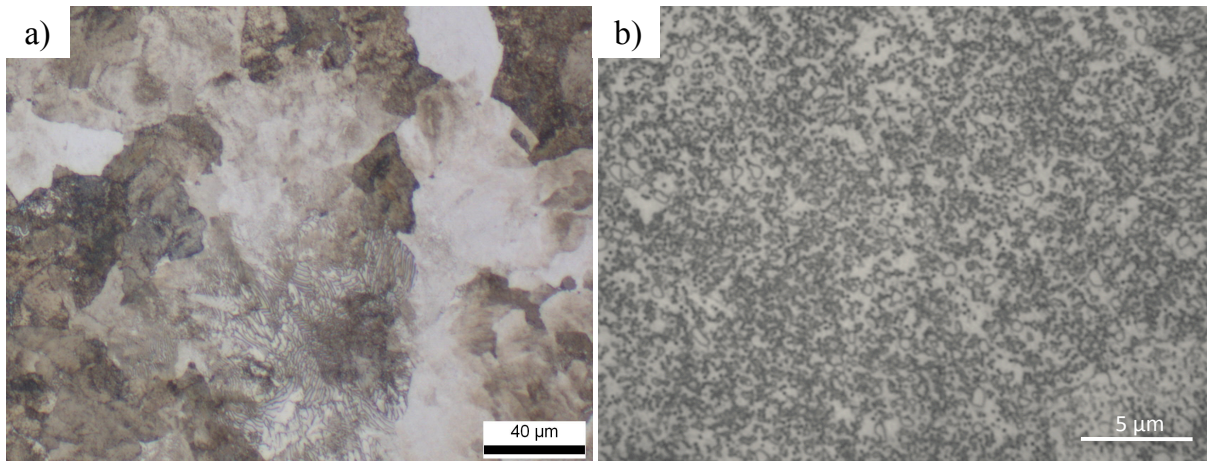


Figure 5.5: The microstructure of 100Cr6+0.5V after a) casting and hot rolling and b) after spheroidization.

100Cr6+0.5V(G) was also spheroidized according to the treatment prescribed in Figure 5.1 and the resulting microstructure resembled that of Figure 5.5b. The hardness after this treatment was also the same 232 HV30 (20 HRC). The microstructures after hardening are shown in Figure 5.6a and Figure 5.6b, for 100Cr6 and 100Cr6+0.5V, respectively. These heat treatments resulted in hardnesses of 804 HV30 (~ 63 HRC) for 100Cr6+0.5V and 785 HV30 (~ 62 HRC) for 100Cr6. After hardening the samples were machined to the final shape required by test specifications.

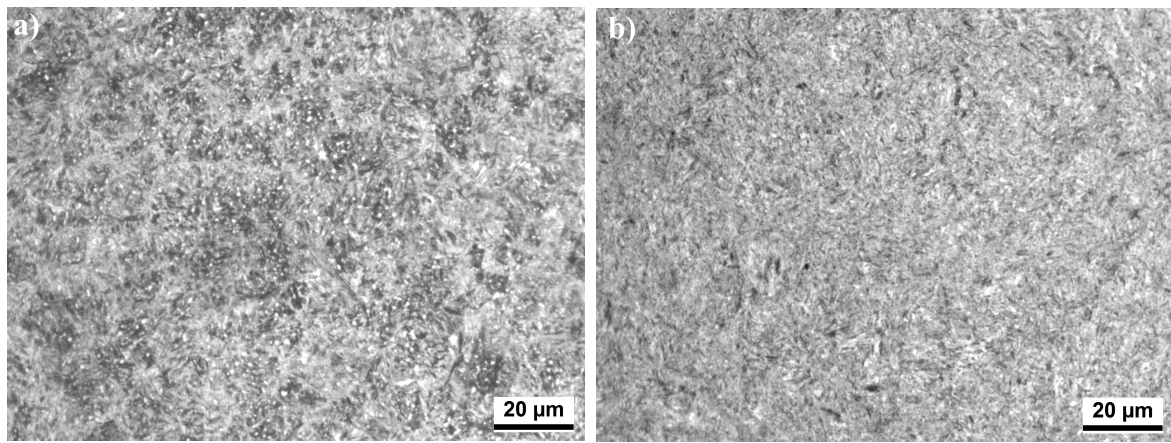


Figure 5.6: Optical microphotographs of a) 100Cr6 and b) 100Cr6+0.5V after hardening.

Further investigation of 100Cr6+0.5V(G) showed large primary carbides and significant segregation as shown in Figure 5.7.

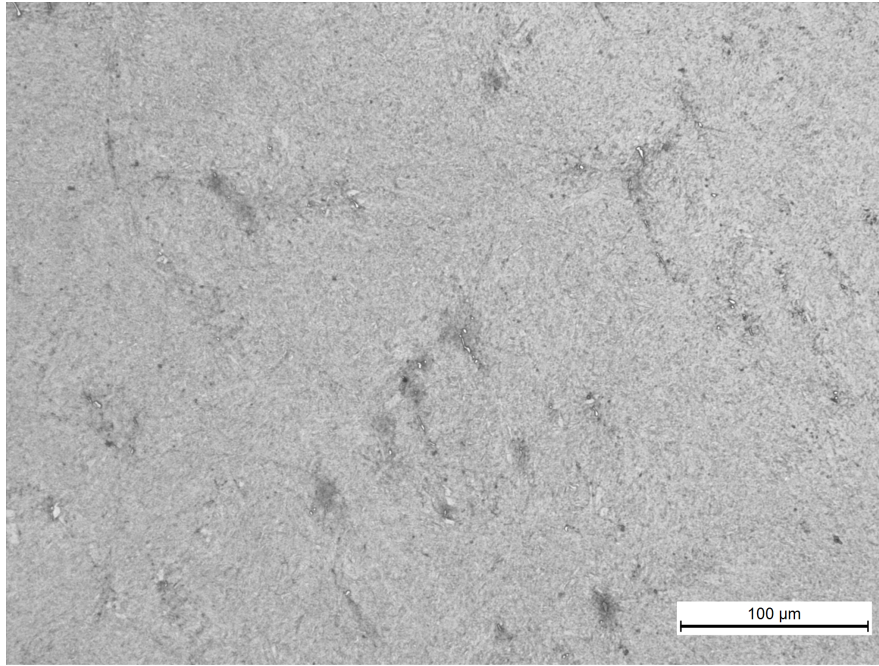


Figure 5.7: Optical microphotographs of 100Cr6+0.5V(G) experimental cast with observed primary carbides and segregations.

The carbide characterisation was done by using Energy Dispersive X-Ray Spectroscopy (EDS) used in conjunction with Zeiss Supra 55 Scanning Electron Microscope (SEM) with a 20kV electron beam voltage in the secondary electron mode, showing that the investigated carbides are high in chromium and vanadium (Figure 5.8).

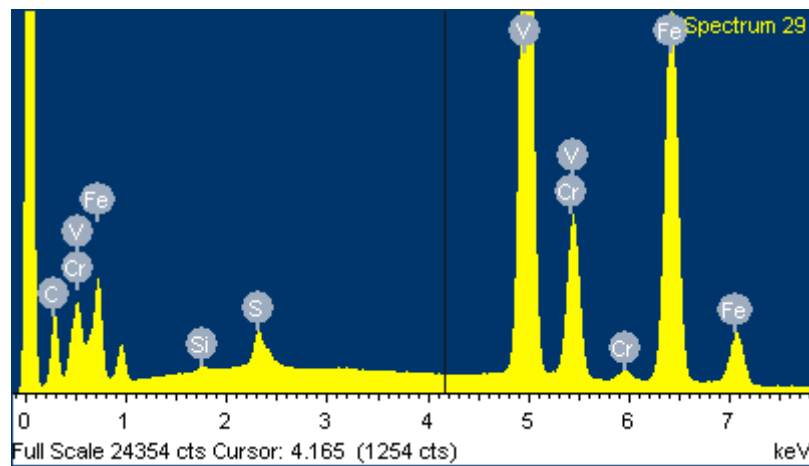
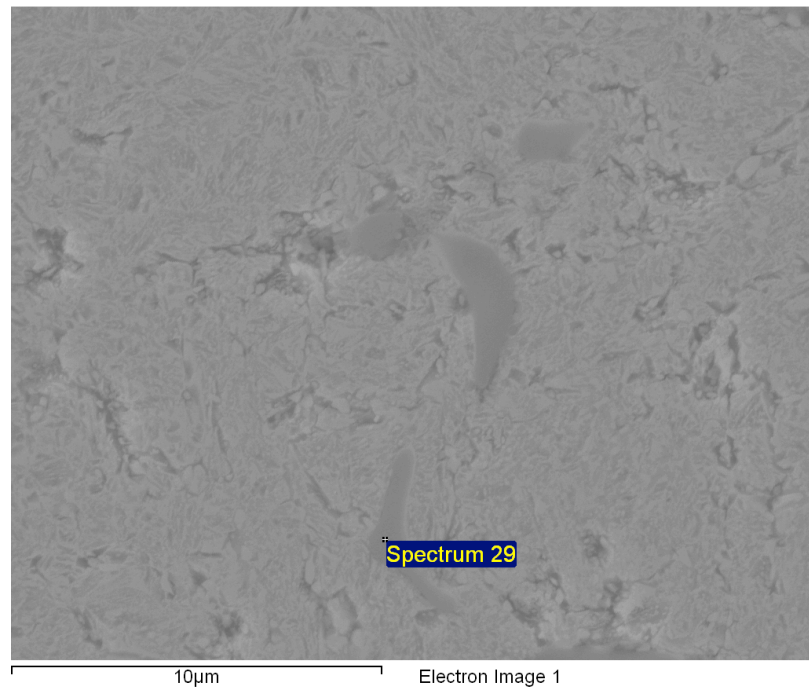


Figure 5.8: Scanning electron microscopy with energy dispersive X-Ray spectroscopy results for inclusions found in 100Cr6+0.5V(G) experimental cast.

The specimens machined for Charpy, rolling contact fatigue and hydro-hardness testing displayed long seams, sometimes even visible to the naked eye. Such are the results of folding over of surface metal generated during hot rolling, and are considered to be hot rolling defects [140] (Figure 5.9). These seams are perpendicular to the plate surface and follow the hot-working axis. Those defects have a strong influence on all mechanical properties of 100Cr6+0.5V(G), and have to be taken into consideration when analysing these results.

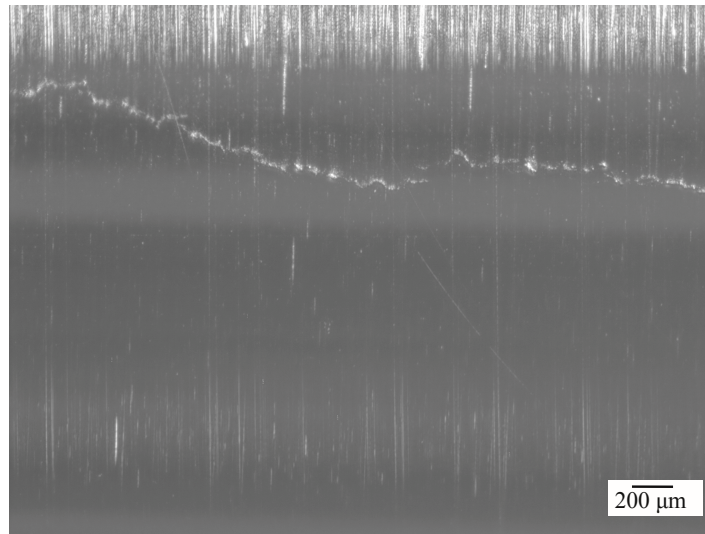


Figure 5.9: Seam observed in the 8 kg 100Cr6+0.5V(G) after machining a rolling contact fatigue sample from the hot-rolled plate.

5.3 Transmission electron microscopy

After each heat treatment step in Figure 3.14b, discs of 3 mm diameter and 0.5 mm thickness were cut in order to produce thin foils. They were mechanically polished to $\sim 50\text{ }\mu\text{m}$ by using 1200 grit SiC paper and cleaned in acetone, and further electropolished in 15% perchloric acid and 85% ethanol solution by using a Struers Tenupol 5 electropolisher. A current of $\sim 130\text{ mA}$ and $\sim 20.5\text{ V}$ resulted in samples of sufficient thickness for transmission electron microscopy (TEM). JEOL 2000FX (200 kV) and Philips CM30 (300 kV) transmission electron microscopes were employed to verify that the desired microstructure

were obtained. 100Cr6+0.5V heat treatment (Figure 3.14) was interrupted at selected heat treatment stages to verify the presence and size of V_4C_3 and cementite. Figure 5.10a shows 100Cr6+0.5V after spheroidization, cementite particles with a radius around 200-500 nm are observed. After the first temperature spike (Figure 5.10b), ferritic laths without cementite and V_4C_3 particles were detected. After high temperature tempering at 600 °C the undesired large cementite particles are shown in (Figure 5.10c). Along with cementite formation, the growth of V_4C_3 is expected; however, this is difficult to confirm because of the small amount and size of V_4C_3 in contrast with the large amount of coarse cementite making the diffraction patterns difficult to analyse.

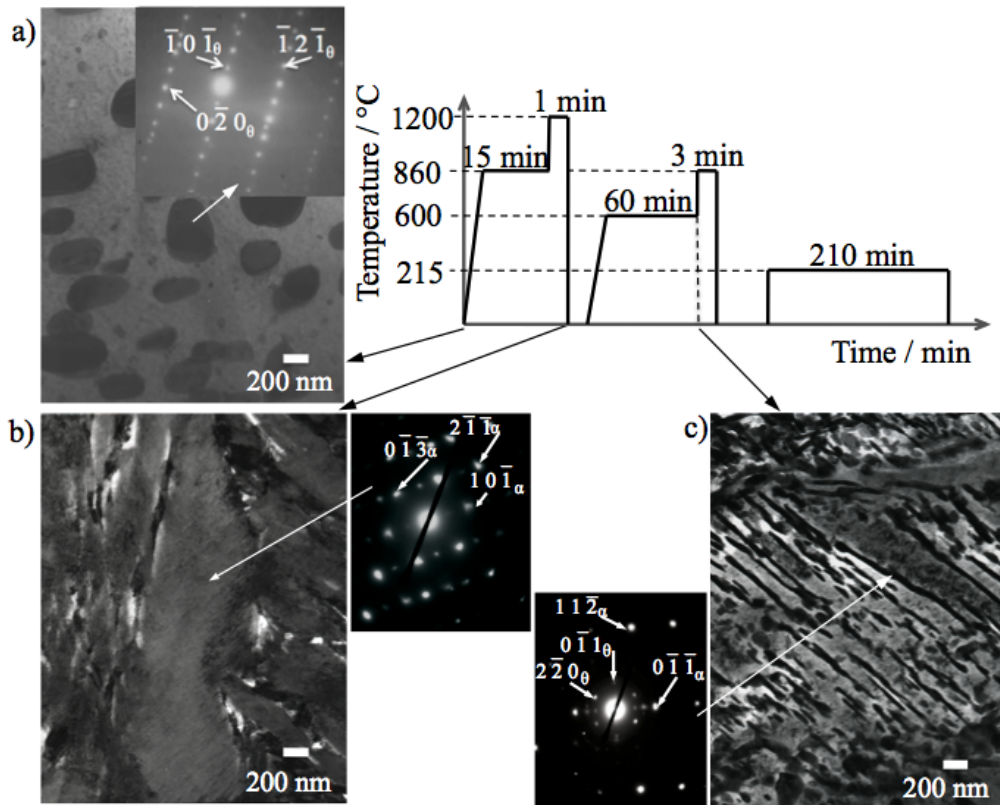


Figure 5.10: Transmission electron microphotographs of 100Cr6+0.5V: a) bright field image after spheroidization and a diffraction pattern of spheroidized cementite indicated by arrow, the zone axis is $[\bar{1} 0 1]$; b) bright field image after the first temperature spike and a diffraction pattern taken from the ferritic lath visible on the image, the zone axis is $[\bar{1} \bar{1} 1]$; c) bright field image after the first temperature spike followed by tempering at 600 °C for 1 h, the diffraction pattern is taken from the elongated cementite particle indicated by the arrow, the zone axis of cementite is $[1 1 1]$ and of ferrite is $[3 \bar{1} 1]$.

Figure 5.11a proves the presence of V_4C_3 following cementite dissolution, which makes the diffraction patterns easier to analyse. The full heat treatment microphotograph is shown in Figure 5.11b, showing fine cementite and V_4C_3 particles, with their presence confirmed by electron diffraction.

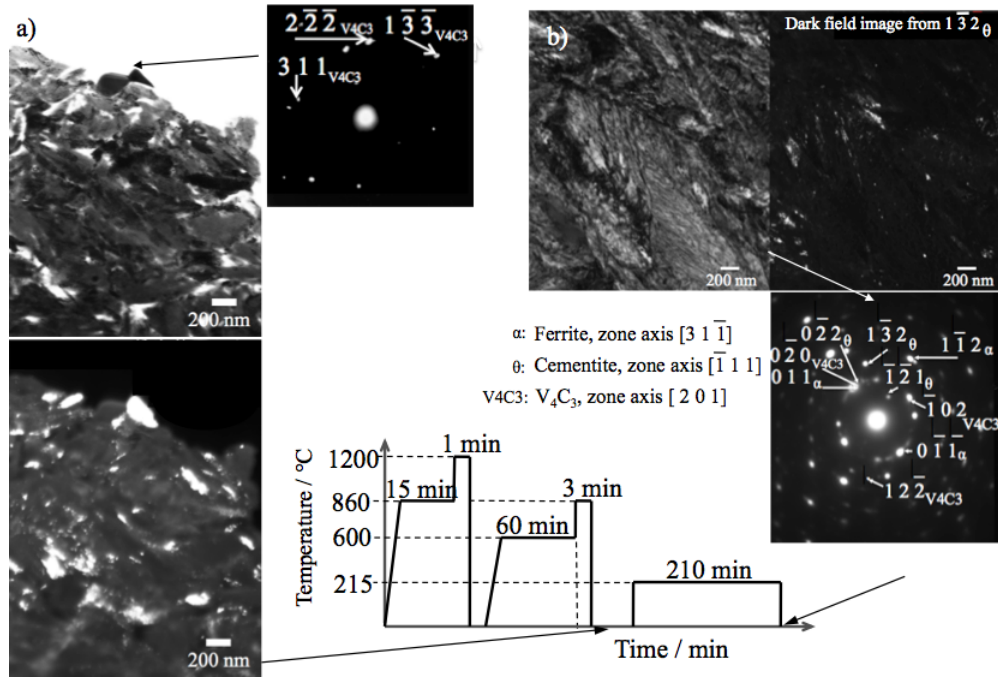


Figure 5.11: Transmission electron microphotographs of 100Cr6+0.5V: a) bright field and dark field image after second temperature spike, the diffraction pattern is taken from the V_4C_3 particle indicated by the arrow, the zone axis of V_4C_3 is $[0\bar{1}\bar{1}]$; b) diffraction pattern and bright field image after completed two spikes heat treatment, diffraction pattern taken from $[1\bar{3}\bar{2}]$ cementite spot.

5.4 Impact testing

Impact testing was conducted on an MFL PSW 300 impact testing machine with 300 J capacity. The samples were cut from the 100Cr6+0.5V(G) plate and a 100Cr6 steel bar with the notch being perpendicular to the rolling direction. The sample geometry can be seen in Figure 5.12.

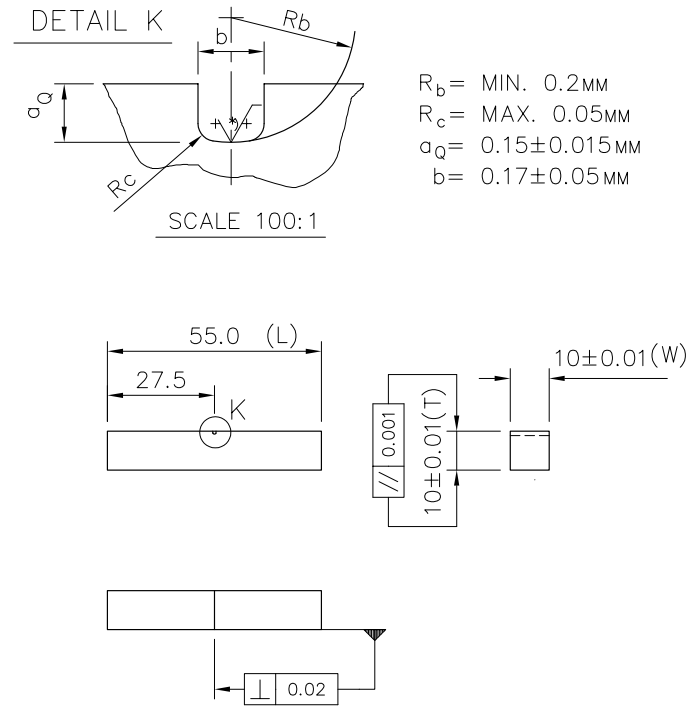


Figure 5.12: Charpy impact sample used in these studies.

The samples before impact testing were charged with 5 ppm of hydrogen, the hydrogen amount was estimated and checked by MET. The hydrogen charging of Charpy specimens is described in Section 4.2 with its charging conditions listed in Table 4.3. After charging all the samples (including the hydrogen-free samples) were stored in a freezer at $-80\text{ }^{\circ}\text{C}$ for avoiding hydrogen desorption. However, before the impact test the samples were allowed to reach room temperature before testing. The samples were tested under three conditions: hydrogen-free, just after charging and 24 h after charging; every condition was tested on a set of five individual samples. After Charpy impact testing, the fracture surface was investigated by a Zeiss Supra 55 Scanning Electron Microscope (SEM) with a 10kV electron beam voltage in the secondary electron mode. The fracture surface was examined at the crack initiation point and at the centre of the sample. The fracture microphotographs of 100Cr6 are shown: in Figure 5.13 (hydrogen-free), Figure 5.14 (just after charging) and Figure 5.15 (24 h after charging). The obtained absorbed energy was 11.33 J, 10 J and 10.33 J for hydrogen-free, just after charging and 24 h after charging 100Cr6, respectively.

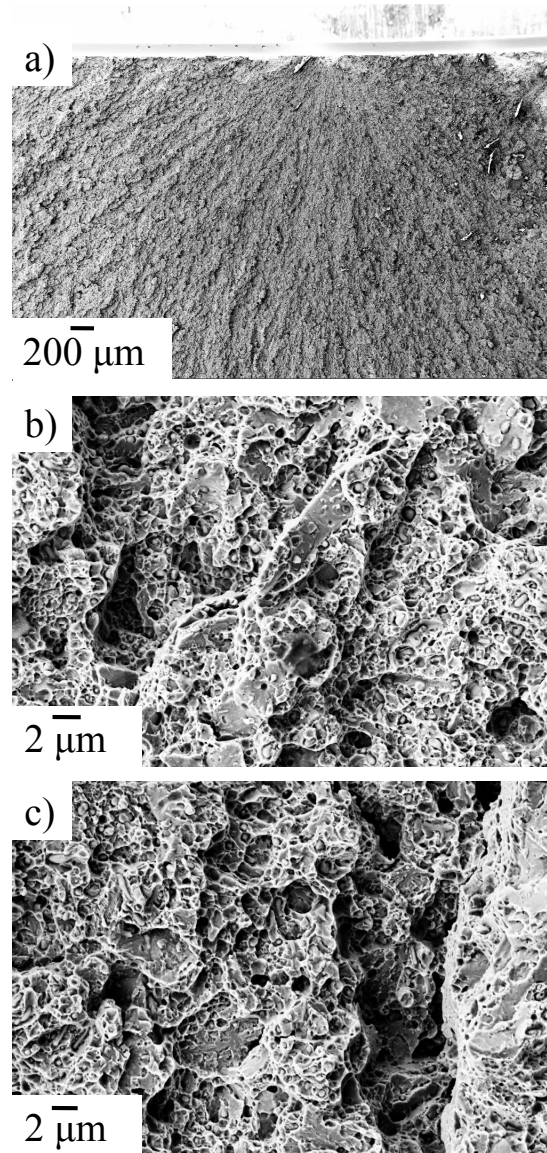


Figure 5.13: Representative scanning electron microphotographs of fractured surface of 100Cr6 samples after Charpy impact testing showing a) the overall fracture surface, b) the microstructure just under the crack initiation point and c) in the middle of the sample; the samples were not subjected to hydrogen charging. Absorbed energy 11.33 J.

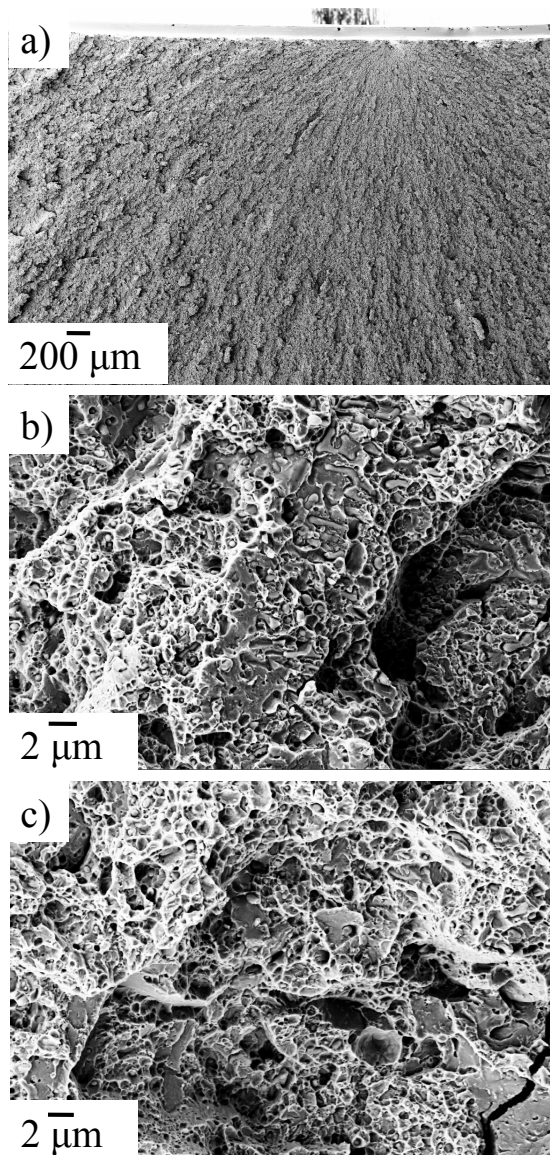


Figure 5.14: Representative scanning electron microphotographs of fractured surface of 100Cr6 samples after Charpy impact testing showing a) the overall fracture surface, b) the microstructure just under the crack initiation point and c) in the middle of the sample; the samples were tested just after hydrogen charging. Absorbed energy 10 J.

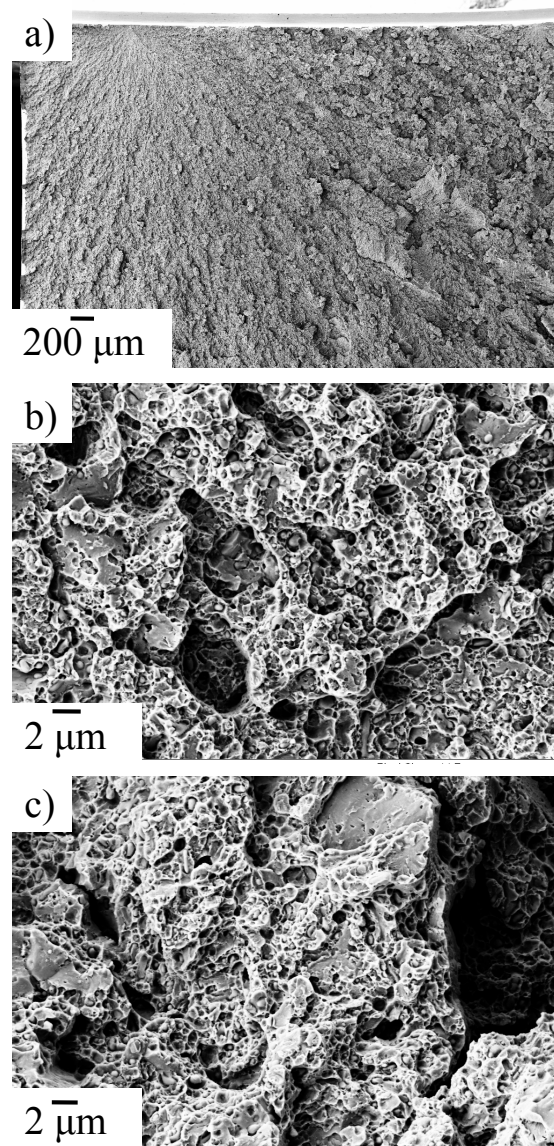


Figure 5.15: Representative scanning electron microphotographs of fractured surface of 100Cr6 samples after Charpy impact testing showing a) the overall fracture surface, b) the microstructure just under the crack initiation point and c) in the middle of the sample; the samples were tested 24 h after hydrogen charging. Absorbed energy 10.33 J.

The fracture microphotographs of 100Cr6+0.5V(G) are shown in Figure 5.16 (hydrogen-free), Figure 5.17 (just after charging) and in Figure 5.18 (24 h after charging). The obtained absorbed energy was 4.83 J, 5.33 J and 4.83 J for hydrogen-free, just after charging and 24 h after charging, respectively.

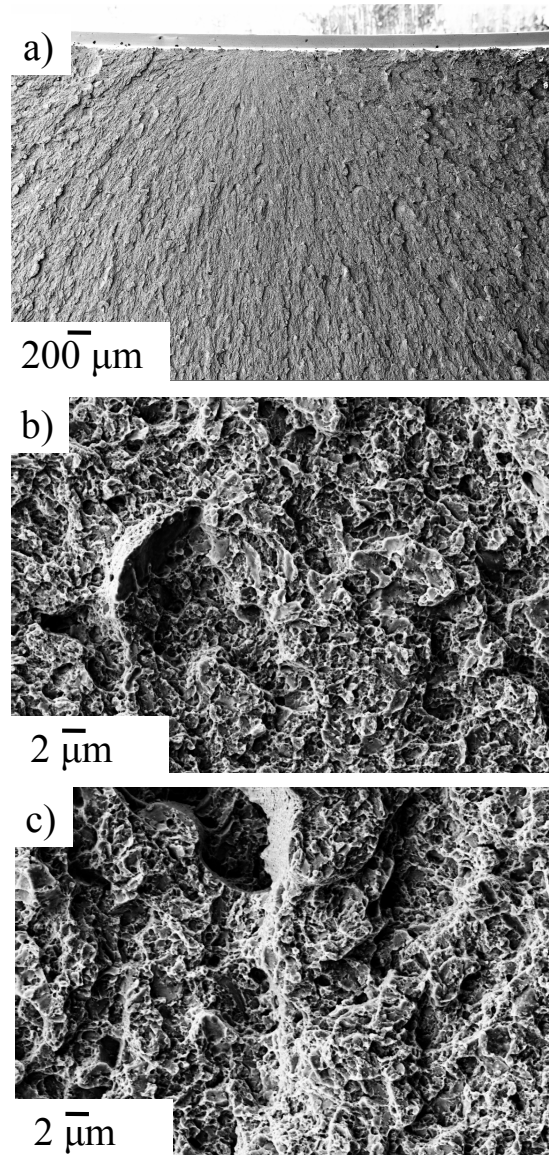


Figure 5.16: Representative scanning electron microphotographs of fractured surface of 100Cr6+0.5V(G) samples after Charpy impact testing showing a) the overall fracture surface, b) the microstructure just under the crack initiation point and c) in the middle of the sample; the samples were not subjected to hydrogen charging. Absorbed energy 4.83 J.

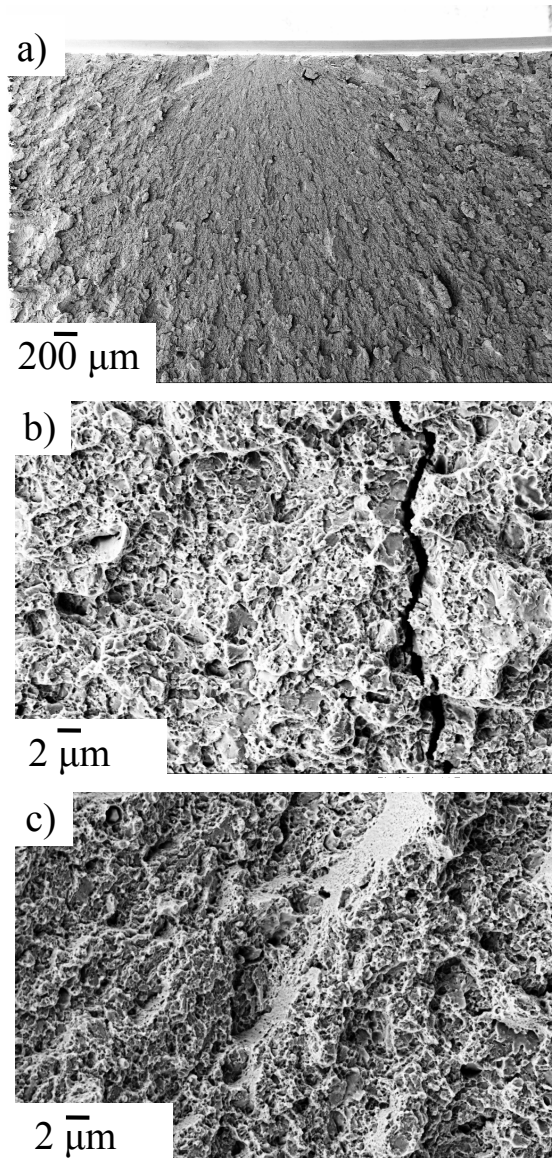


Figure 5.17: Representative scanning electron microphotographs of fractured surface of 100Cr6+0.5V(G) samples after Charpy impact testing showing a) the overall fracture surface, b) the microstructure just under the crack initiation point and c) in the middle of the sample; the samples were tested just after hydrogen charging. Absorbed energy 5.33 J.

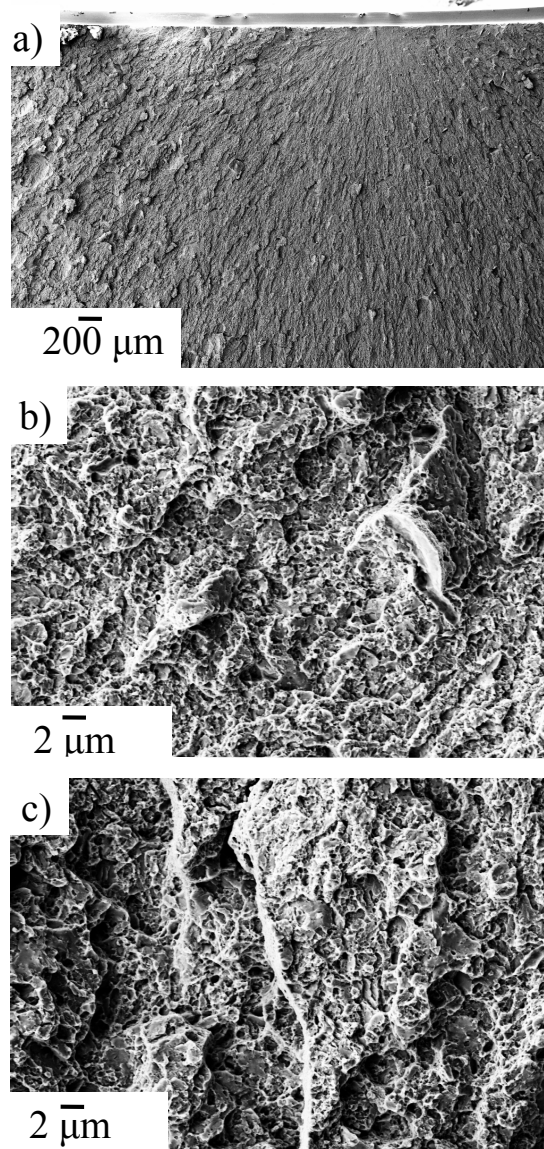


Figure 5.18: Representative scanning electron microphotographs of fractured surface of 100Cr6+0.5V(G) samples after Charpy impact testing showing a) the overall fracture surface, b) the microstructure just under the crack initiation point and c) in the middle of the sample; the samples were tested 24 h after hydrogen charging. Absorbed energy 4.83 J.

5.5 Hydro-Hardness test

Hydro-Hardness is a new technique proposed here to examine the nature of crack propagation and hydrogen embrittlement mechanisms in 100Cr6, 100Cr6+0.5V(G), SB200 and SB300. Hydrogen has been reported to decrease the yield strength and ultimate tensile strength in various materials [141, 142, 143]. Yield strength and Young's modulus are related to the subsurface stresses induced by Vickers indentation [144]. A high yield strength to Young's modulus ratio in brittle materials results in the cracking originated from the indentation. Therefore, the indentation and subsequent crack observations are commonly used in studying embrittlement in brittle materials such as ceramics. However, without hydrogen presence in the metallic materials the indentation induced tensile stress is not able to reach the tensile strength, and the indentations do not cause cracking [145]. For hydrogen-rich steels, a critical tensile strength for crack nucleation during the Vickers indentation is reduced [145], and the indentations induce the cracking, thus the crack length and appearance investigations might provide a useful information for hydrogen embrittlement in metallic materials, similar to in embrittlement studies of hydrogen-free ceramics.

Vickers indentation was used to induce cracks propagating from the indentation in samples immediately after hydrogen charging. The specimens were charged with ~ 50 ppm of hydrogen as this amount was reported to be sufficient for causing cracking by indentation [145]. Immediately after the indentation, the cracks originating from it were observed by using Zeiss Axioplan2 optical microscope, and a drop of the thin immersol (TM) 518F oil for optical microscope Zeiss was put on the top of the sample. The oil drop fostered the formation of hydrogen bubbles around cracks. The combination of crack formation by indentation of hydrogen rich samples, and the subsequent filming of bubbles emitted from the crack is termed *hydro – hardness analysis*. A schematic illustration showing the hydrogen entry and egress during the hydro-hardness analysis is shown in Figure 5.19.

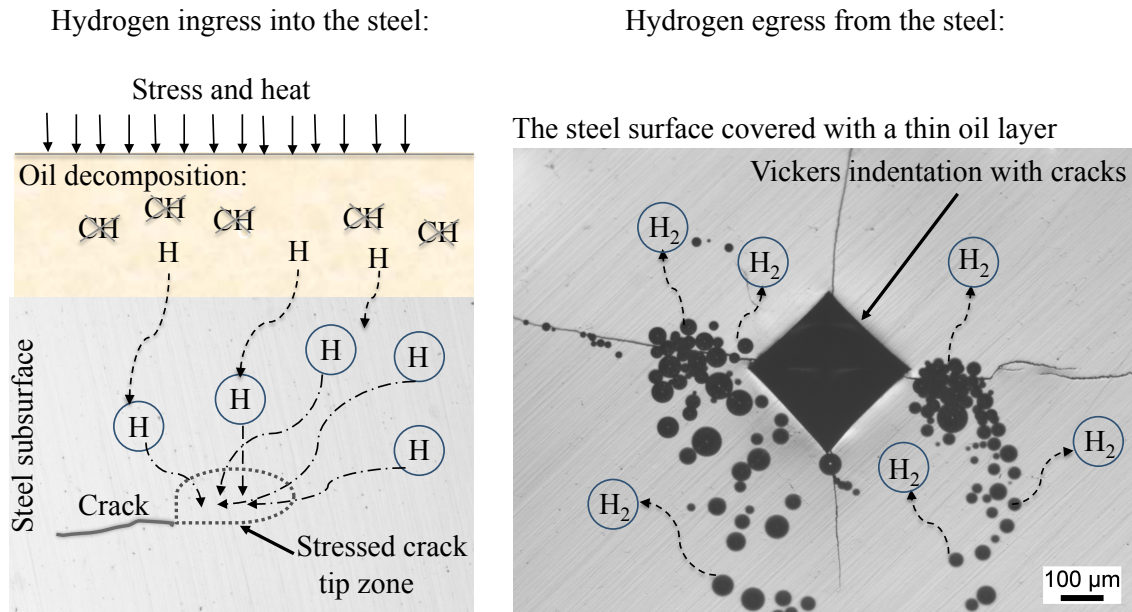


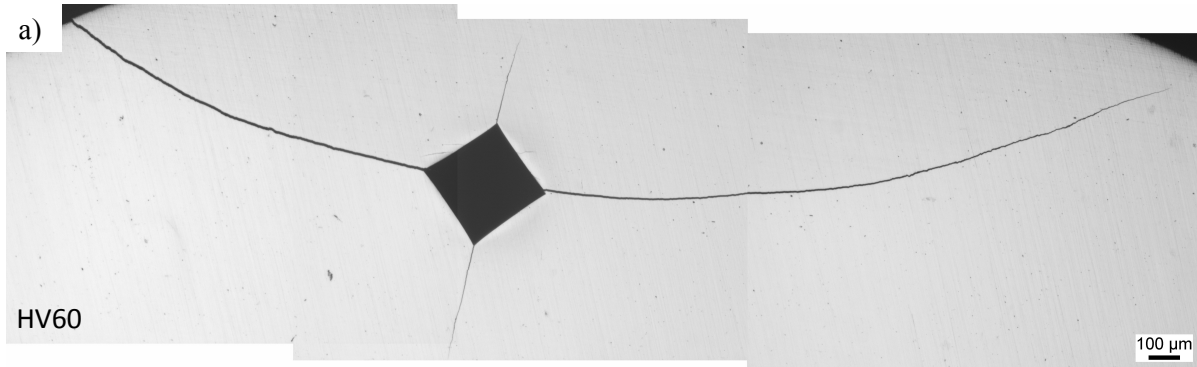
Figure 5.19: Schematic illustration of hydro-hardness method. Note that oil decomposition can be replaced by electrolyte decomposition in hydrogen charging.

The tested samples were cut in 8 mm diameter and 20 mm rods. The bottom surface of the samples was ground using 1200 grit SiC paper and then polished with 6 μm and 3 μm diamond paste. All the samples were hydrogen charged as described in Table 4.3. After hydrogen charging, the bottom surface of the sample was re-polished with 3 μm diamond paste and cleaned with ethanol. It can be seen that as hydrogen enters the microstructure it tends to diffuse to the stressed crack tip area, and it diffuses out of the bulk after gathering at the stressed cracks areas around the indentation. In the hydrogen embrittlement studies, Vickers hardness testing with 60, 120 and 250 kg loads was performed. An average hardness was calculated from 10 readings with the lowest and highest values not considered for estimating the average.

For investigating the principles behind this method, first 100Cr6 was tested in three conditions: immediately after hydrogen charging (Figure 5.20a), without hydrogen charging (Figure 5.20b), with hydrogen charging and a drop of the immersion oil leading to the formation of hydrogen bubbles (Figure 5.20c) and without hydrogen charging (Figure 5.20d), but immediately after storing the samples at $-80\text{ }^{\circ}\text{C}$ for promoting crack formation. The hardness tested in all the samples did not change and was $\sim 780\text{ HV60}$ ($\sim 61.7\text{ HRC}$).

A video showing hydrogen escaping from the metal surface (Figure 5.20c) can be downloaded from <http://www.msm.cam.ac.uk/skf/hh/technique.avi>.

Sample not-covered with immersion oil:



Samples covered with immersion oil:

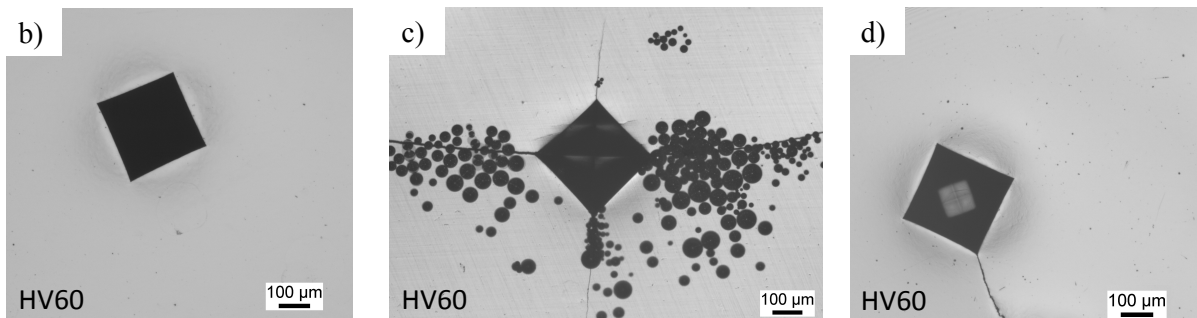


Figure 5.20: Hydro-hardness results for 100Cr6 sample a) just after H-charging, b) without H-charging, c) just after H-charging and covering with immersion oil, and d) without H-charging but after keeping the sample in the freezer at $-80\text{ }^{\circ}\text{C}$ and covering with immersion oil.

Applying exactly the same charging conditions, the rest of the steels were tested with the hydro-hardness method. 100Cr6+0.5V(G) showed much shorter cracks compared to 100Cr6 (Figure 5.21a). Similarly, when covering the indentation with immersion oil, bub-

bles desorbed out from cracks (Figure 5.21b), seams and pores (Figure 5.21c and 5.21d). Due to the continuous desorption of the hydrogen bubbles from these discontinuities, some of them might appear fuzzy and out of focus, as shown in Figure 5.21d. Porosity in 100Cr6+0.5V(G) experimental cast is shown in Figure 5.21c and 5.21d, and needs to be noted as it has a significant influence on rolling contact fatigue performance and impact testing results. Also here the hardness was not altered in the presence of hydrogen, showing ~ 800 HV60 (~ 62.5 HRC) for all the conditions.

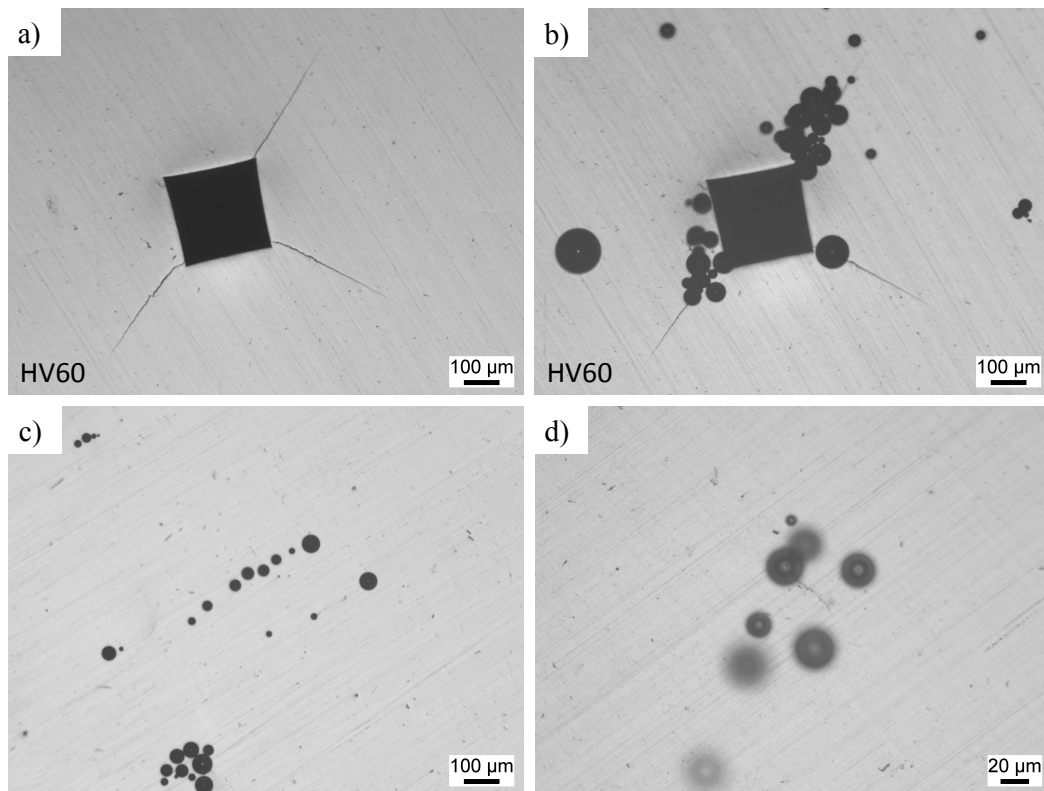


Figure 5.21: Hydro-hardness results for 100Cr6+0.5V(G) sample a) just after H-charging (not covered with oil), b) after H-charging (covered with oil), c) and d) hydrogen bubbles desorbing from seam (covered with oil).

Subsequently, SB200 and SB300 were hydrogen charged and subjected to hydro-hardness analysis. Out of a total of 10 indentations, SB200 showed 7 indentations without crack propagation (Figure 5.22a) and three with tinny cracks around the indentations (Figure 5.22b) when using 60 kg load. For a higher load (125 kg) 8 per 10 indentations showed cracking as shown in Figure 5.22c and 5.22d. The sample in Figure 5.22d is additionally

covered with the immersion oil showing the hydrogen bubbles desorbing out from the crack. The hardness was not influenced by hydrogen showing ~ 625 HV60 (~ 55.5 HRC) for all the conditions.

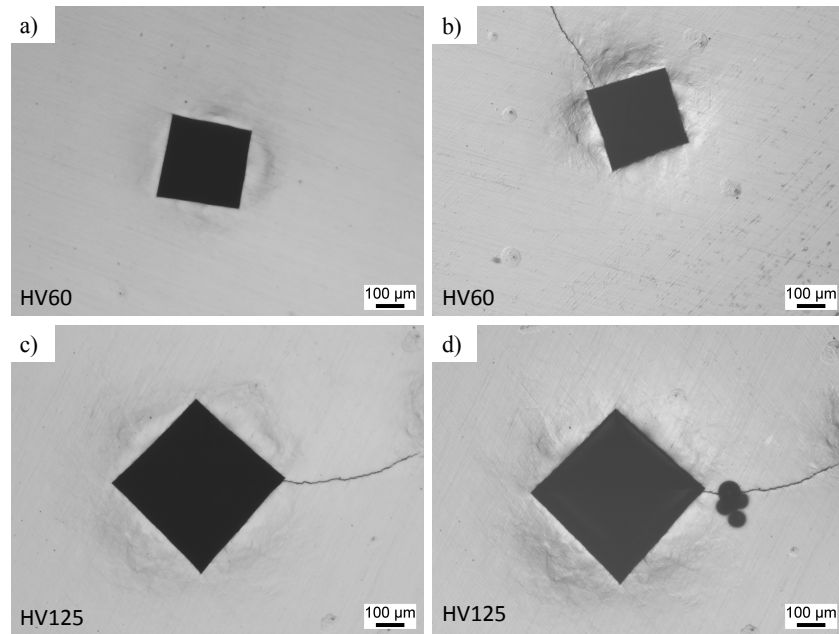


Figure 5.22: Hydro-hardness results for SB200 after H-charging a) no cracks observed from the indentation (60 kg load), b) tiny crack observed from the indentation (60 kg load), c) a crack observed from the indentation (125 kg load) and d) the same indentation as in picture “c”, but covered with oil; samples a, b, c are not covered with oil.

SB300 after charging did not show cracks propagated from the indentation when testing with 60 kg (Figure 5.23a) and even with 250 kg load (Figure 5.23b). Measured hardness showed ~ 535 HV60 (~ 51.8 HRC) for all the conditions.

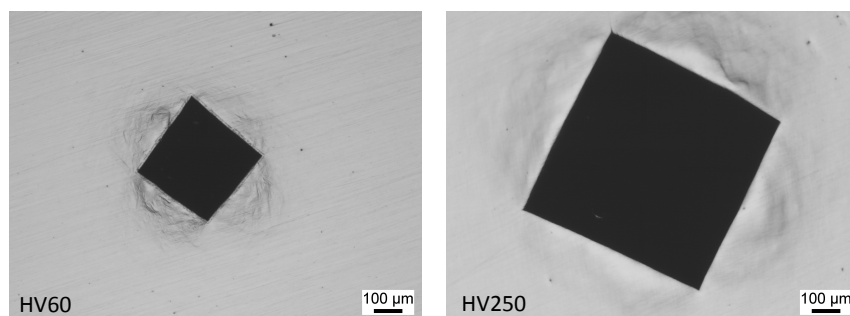


Figure 5.23: Hydro-hardness results for SB300 sample when using a) 60 kg and b) 250 kg load. Both the indentations are covered with oil.

5.6 Rolling contact fatigue

Rolling contact fatigue (RCF) experiments were conducted on 100Cr6 and 100Cr6+0.5V(G) samples in two conditions, hydrogen-free and 24 h after hydrogen charging. Hydrogenised samples were charged to 5 ppm of hydrogen. This content was measured on dummy samples and investigated by melt extraction technique; the charging conditions are shown in Table 4.3. All tested specimens were stored in the freezer at $-80\text{ }^{\circ}\text{C}$ for avoiding hydrogen desorption. Before testing, the samples were allowed to reach room temperature. A rolling contact fatigue tester by Delta Research Corporation Model BR-4 was used; a detailed description of the equipment has been reported by Glover [146]. The specimen geometry is shown in Figure 5.24. The maximum contact stress used was 3.75 GPa, the speed of rotation 3600 rpm and BP2380 turbine oil was used as a lubricant at 10 drops/min.

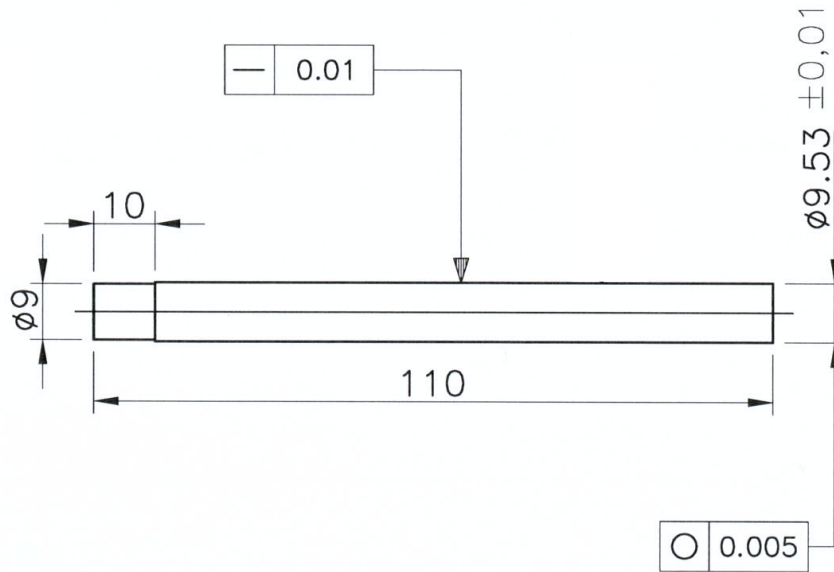


Figure 5.24: Rolling contact fatigue sample geometry used for RCF testing.

The results obtained from RCF testing for hydrogen-free and hydrogen-charged samples are shown in Table 5.2 and 5.3, respectively. These results are also illustrated in Figure 5.25 for easier comparison.

Table 5.2: Rolling contact fatigue results for hydrogen-free 100Cr6 and 100Cr6+0.5V.

Designation	Alloy	Time / hour	Number of cycles $\times 10^6$	Comments
G3-1	100Cr6	~309	159	suspended
G3-2		~309	159	suspended
GB-1	100Cr6+0.5V	~309	159	suspended
GB-2		~309	159	failed (seam initiated)

Table 5.3: Rolling contact fatigue results for hydrogen-charged 100Cr6 and 100Cr6+0.5V.

Designation	Alloy	Time / hour	Number of cycles $\times 10^6$	Comments
G3-1_H	100Cr6	~39.5	20.3	failed (hydrogen)
G3-2_H		~10.5	5.33	failed (hydrogen)
G3-3_H		~1.5	0.80	failed (surface initiated)
GB-1_H	100Cr6+0.5V	~10.0	5.02	failed (seam initiated)
GB-2_H		~9.5	4.87	
GB-3_H		~6.0	3.16	
GB-4_H		~4.0	2.11	
GB-5_H		~3.0	1.48	
GB-6_H		~3.0	1.43	
GB-7_H		~3.0	1.36	
GB-8_H		~1.0	0.44	
GB-9_H		~0.5	0.36	

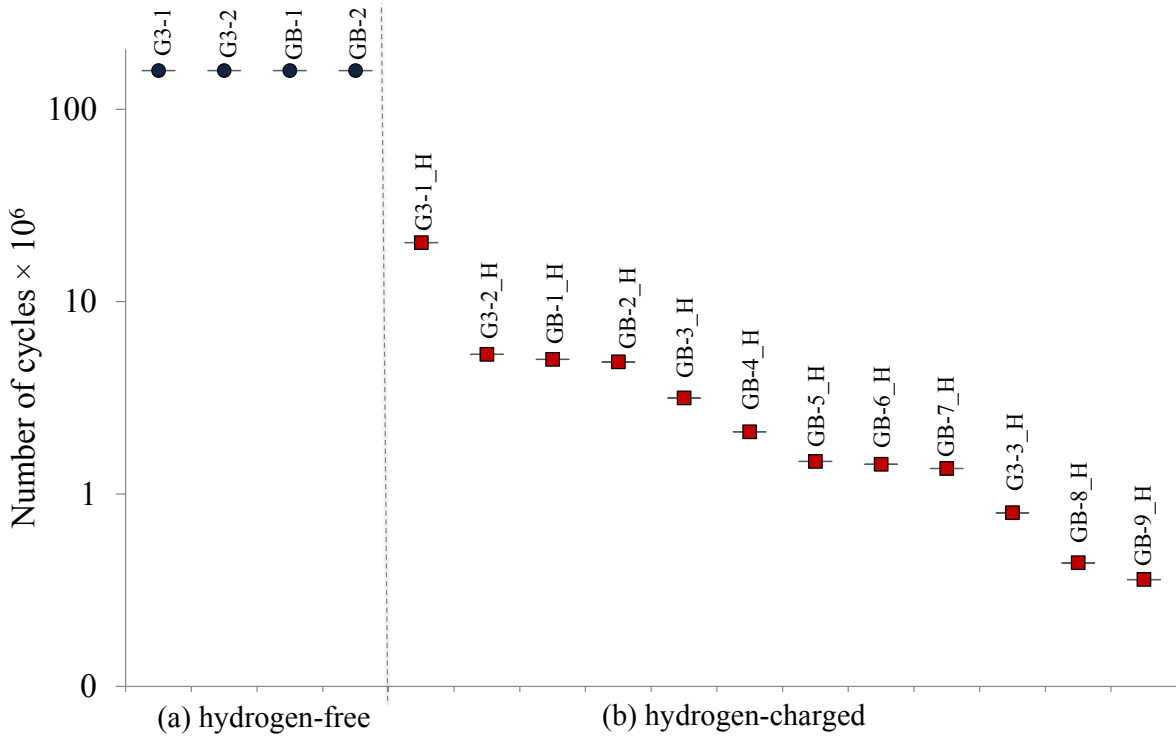


Figure 5.25: The illustration of RCF results presented in Table 5.2 and 5.3 for 100Cr6 and 100Cr6+0.5V in a) hydrogen-free and b) hydrogen-charged condition.

All the samples that ran under $\sim 5.33 \times 10^6$ cycles (11 hours), surface (100Cr6) or seam (100Cr6+0.5V(G)) initiated failure, increased their vibration level making further sample analysis impossible. The RCF tester stops when a sensor detects a vibration level in excess of $100 G_{\text{rms}}^1$ (root-mean-square acceleration). Further microstructural investigations of both 100Cr6 and 100Cr6+0.5V(G) in hydrogen-free condition (Table 5.2) did not show microstructural changes under the raceway surface such as white etching areas or butterflies.

100Cr6 charged samples (MET indicated ~ 5 ppm) failed after 2.3×10^7 cycles (~ 2 days), compared to non-charged samples (MET indicated ~ 0.70 ppm), which did not fail even after 1.59×10^8 cycles (~ 13 days), after which the test was stopped. Optical microscopy observations of 100Cr6 showed spalls on the raceway of 100Cr6 charged sample in Figure 5.26a (G3-1_H) and 5.26b (G3-2_H), and no signs of damage on the raceway of

¹ G_{rms} is a square root of the area under the acceleration spectral density (g^2/Hz) vs frequency (Hz) curve; “g” is a measure of acceleration.

hydrogen-free sample in Figure 5.26c (G3-1).

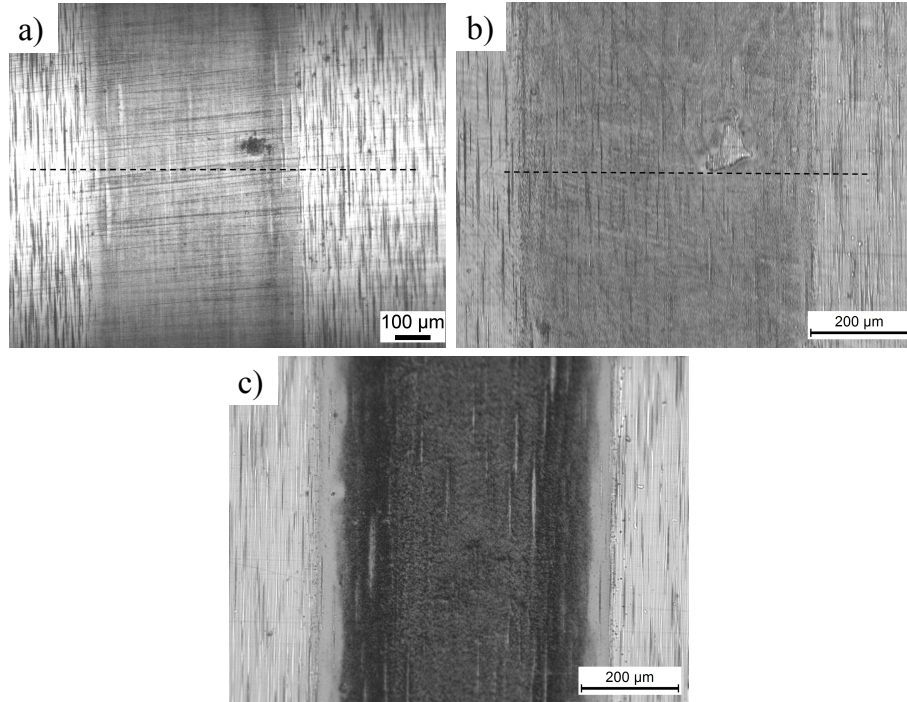


Figure 5.26: Raceways of 100Cr6 after rolling contact fatigue showing sample a) G3-1_H, b) G3-2_H tested after hydrogen charging and c) G3-1 hydrogen-free specimen. The broken line indicates the cutting section for subsequent subsurface investigations.

White etching areas formed under the raceway in charged samples (Figure 5.27), while no such microstructural change was observed in the non-charged sample. These results demonstrate that hydrogen charged samples do display a much reduced fatigue life, which is accompanied by early damage in the form of white etching areas in 100Cr6.

100Cr6+0.5V(G) non-charged specimen run also for 1.59×10^8 (~ 13 days), but GB-2 sample (Table 5.2) failed at the end of the planned running time. Optical microscopy observations of the raceway showed that spalling started from a seam (Figure 5.28). Spalling was a reason for almost all 100Cr6+0.5V(G) RCF sample failures. No microstructural changes such as dark etching, white etching areas or butterflies were observed in charged 100Cr6+0.5V(G) after 5.02×10^6 cycles (~ 10 h, GB-1_H) under the raceway surface while the highly developed white etching areas were found in 100Cr6 after 5.33×10^6 (~ 10 h, G3-2_H).

Charged 100Cr6+0.5V(G) (Figure 5.25) did not reach more than 5.02×10^6 cycles and

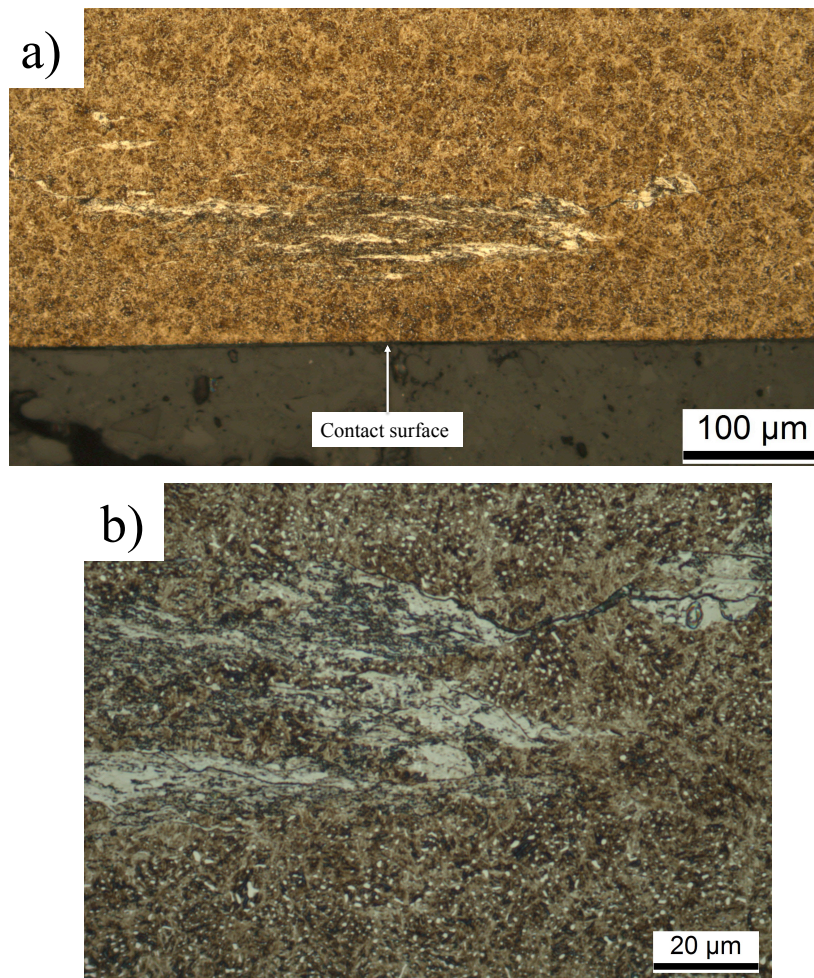


Figure 5.27: 100Cr6 after H-charging showing the subsurface under the spalling caused by RCF and accelerated by hydrogen in a) lower magnification and b) higher magnification. Etched in 1.5 wt% Nital.

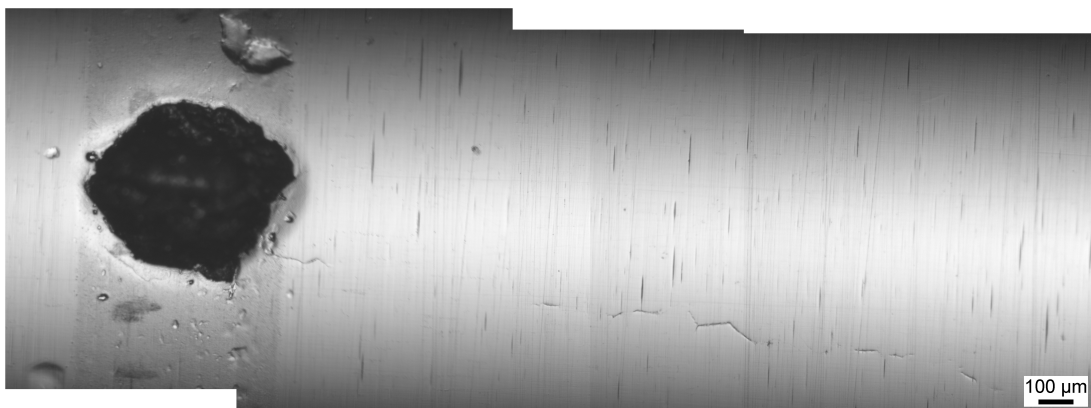


Figure 5.28: The raceway of 100Cr6+0.5V(G) (GB-2) in hydrogen-free condition showing the spalling originated from seam.

the optical microscopy observations of the raceways of the filed samples showed a seam on the raceway surface. Figure 5.29a is an example of seam failure in sample GB-1_H; and the experiment was stopped as it caused an unacceptable vibration level. Optical microscopy observations showed the cracks present in the raceway subsurface (Figure 5.29b).

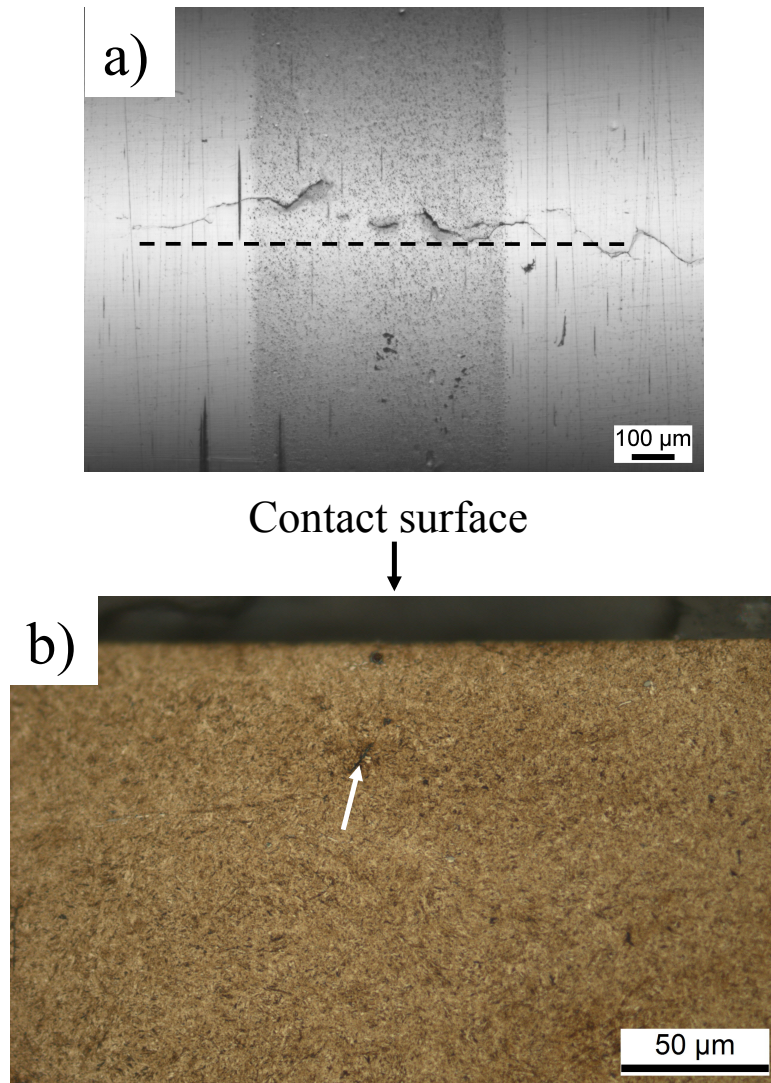


Figure 5.29: An example of a) a raceway and b) the subsurface under the raceway, for all 100Cr6+0.5V(G) (GB-1_H) in hydrogen charged condition. The white arrow indicates a crack.

5.7 Discussion

I. Microstructural analysis

The first series of experiments were performed on small samples in a dilatometer; this aimed at determining whether the desired microstructures can be achieved. Since the machinability is very important for bearing steels, spheroidization was conducted on 100Cr6+0.5V adopting the same schedule employed for 100Cr6 (Figure 5.1). Optical microphotography showed the 100Cr6+0.5V can be spheroidized (Figure 5.5b) and achieve a level of hardness favourable for steel machinability (~ 232 HV30). The same spheroidization process was reproduced on the big 100Cr6+0.5V(G) cast before the salt bath heat treatment, resulting in the same microstructure and hardness. First, the heat treatments on 100Cr6 and 100Cr6+0.5V were studied by dilatometry (Figure 5.2 and 5.3, respectively). The dilatometry curves of 100Cr6+0.5V show that 15 minutes austenitization completes the process and can be shortened from 20 min, 100Cr6, (Figure 5.3, stage I). A subsequent temperature spike of $1200\text{ }^{\circ}\text{C}$ for V_4C_3 dissolution followed by cooling to room temperature at $25\text{ }^{\circ}\text{C s}^{-1}$ resulted in hard martensite of 910 HV30 (67 HRC). This hardness decreased during V_4C_3 reprecipitation and the further coarse cementite dissolution by a second temperature spike of $860\text{ }^{\circ}\text{C}$ (Figure 5.3, stage II), which finished with martensite of a lower hardness of 790 HV30 (62 HRC). Stage II in Figure 5.3 is different than for 100Cr6, since it ensures that the desired precipitates are formed at the nanometre scale for hydrogen trapping capacity. The last stage of 100Cr6+0.5V heat treatment (Figure 5.3, stage III) was the same as for 100Cr6 in Figure 5.2 (stage II). This leads to cementite which was observed to be in a finer form than in 100Cr6 (Figure 5.6). The hardness after the completed heat treatment was 804 HV30 (~ 63 HRC) for 100Cr6+0.5V and 785 HV30 (~ 62 HRC) for 100Cr6. Although heat treatment on dilatometer is simple to perform, bigger samples such as rolling contact fatigue and impact testing specimens are impossible to produce in a dilatometer because of their dimensions. Therefore, an industrial-type heat treatment was considered. The most difficult challenge was achiev-

ing the desired heating and cooling rate, which are crucial for avoiding the cracking and high temperature grain growth. The most suitable from the foreseen industrial heat treatment opportunities, was the salt bath heat treatment. As pointed out, the cooling rate is very important for avoiding the cracking during high temperature thermal shock from relatively high temperature, and the salt bath was useful in controlling this. Few quenchants were tested, such as water, oil, salt bath and their combinations, with the air and the subsequent salt bath quenching bringing the best results. The salt bath temperature was chosen to be 150 °C in order to avoid martensite cracking caused by the temperature shock, and the martensite recovery at a higher temperature [147]. An 8 kg cast was produced in Germany, the chemical analysis after casting showed that the obtained cast reached the planned chemical composition; however, hot rolling (which resulted in hardness of 305 HV30 and the microstructure shown in Figure 5.5a) did not reach a sufficient reduction ratio so that pores were closed. Due to the insufficient reduction ratio, seams were present after the samples were machined; this significantly reduced the number of the samples for testing, because the seams spread throughout the samples. Even though the sample was oversized before heat treatment, the seam present inside them often caused cracking during heat treatment what further decreased the number of specimens for testing. The samples that survived showed seams present after the final machining. In Figure 5.9 the seam on the sample surface after a final machining can be observed. It is very important that bearing steels are seam-free and free of surface cracks, which reduce mechanical properties. The 100Cr6+0.5V(G), experimental cast performed in Germany, was of a much lower quality when compared to 100Cr6 received from SKF subjected to tight microstructural quality control specified in accordance with ISO 9443 [148], and decarburization in accordance with ISO 3887 [149]. Therefore, the mechanical properties and rolling contact fatigue performance of experimental cast 100Cr6+0.5V(G) cannot be directly compared with 100Cr6 industrial cast; rolling contact fatigue life and mechanical properties are very sensitive to surface quality, inclusions and primary carbides content. Primary carbides observed in 100Cr6+0.5V(G) are shown in Figure 5.7. SEM investigations showed that

these carbides are high in chromium and vanadium, therefore they have high hardness and are undesired for good rolling contact fatigue performance accordingly to ISO 4967 method A, where tight micro-inclusions limits are specified [150]. Therefore it should be born in mind that 100Cr6 meets all the requirements, however the 100Cr6+0.5V(G) experimental melt is far from meeting them. In spite of this, 100Cr6+0.5V(G) is very helpful for understanding the influence of pre-cracking in a hydrogen-rich environment.

II. Formation of submicrometre phases

Referring to the transmission electron microscopy study, the modelled heat treatment was interrupted after each heat treatment stage as shown in Figure 5.10 and 5.11 and the presence of desired and undesired phases at certain stages was analysed by TEM using diffraction analysis. TEM analysis of 100Cr6+V started from spheroidization (Figure 5.10a). The large and evenly distributed $\sim 200\text{-}500$ nm cementite particles were observed. Note that 200 nm has been estimated as the starting radius for cementite dissolution modelling discussed in Section 3.1.3.5, (Figure 3.12). Figure 5.10b shows microphotographs taken after the first temperature spike, the microstructure contains ferritic laths without cementite and V_4C_3 . The diffraction pattern shows additional spots, they are believed to belong to epsilon carbides, which forms at room temperature [151], as the TEM investigations were conducted approximately two weeks after heat treatment. The TEM observations after high tempering stage at 600 °C showed undesired elongated cementite particles and confirmed the necessity of a second temperature spike for their dissolution (Figure 5.10c). The formation of V_4C_3 , which was predicted to appear at the high temperature tempering stage, is difficult to confirm because of the small amount and size of V_4C_3 compared to the large amount of coarse cementite; the diffraction patterns are difficult to analyse due to the numerous diffraction spots. Figure 5.11a confirms that V_4C_3 was formed after the subsequent cementite dissolution (induced by the second spike), which made the diffraction patterns possible to analyse by lowering the amount

of the diffraction spots. The TEM microphotographs and diffraction after the full heat treatment (Figure 5.11b) show the presence of both cementite and V_4C_3 particles. The transmission electron microscopy observations in Figure 5.10 and 5.11 therefore confirm the accuracy of the thermodynamic and kinetic modelling predictions (Chapter 3).

III. Charpy impact results and hydrogen ingress during charging

Impact testing on both 100Cr6 and 100Cr6+0.5V(G) show no significant difference in fracture appearance between the samples tested in three conditions: non-charged, immediately after charging and 24 h after charging. The density of dimples was similar and their appearance seemed not to be affected by hydrogen. However, there was a slight difference in absorption energy, since it decreased from 11.33 to 10 and 10.33 J, for 100Cr6 tested in the following conditions, respectively: hydrogen-free, just after and 24 h after charging. The absorption energy for 100Cr6+0.5V(G) showed lower values 4.83, 5.33 and 4.83 J for hydrogen-free, just after charging and 24 h after charging, respectively. But as mentioned above, these results cannot be directly compared as the real absorption energy values for 100Cr6+0.5V(G) due to the seam occurrence in the samples (Figure 5.30), significantly lowered the impact toughness. The lower absorption energy values of 100Cr6+0.5V(G) compared to 100Cr6 were predicted during the heat treatment of 100Cr6+0.5V(G) already, since the presence of porosity and seam was observed on the machined to heat treatment Charpy as well as rolling contact fatigue samples. Some of these samples were lost during the process, because of the cracks spreading throughout the specimens. This happened likely due to the thermal stresses occurring during the heat treatment. Therefore, as 100Cr6+0.5V(G) microstructure with the numerous discontinuities was heat treated the pores and seams most probably became crack nucleation sites from which further crack growth was easier to follow either during the heat treatment or in the later stage during the Charpy testing. Moreover, all the samples were notched before charging which may have masked the increased brittleness due to the hydrogen charging.

a) Hydrogen charging cell:

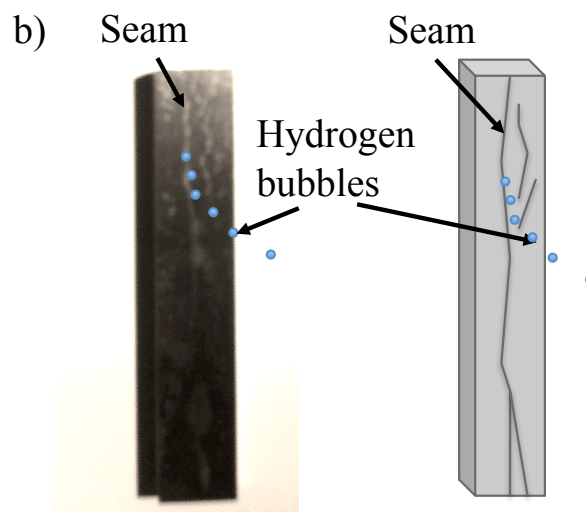
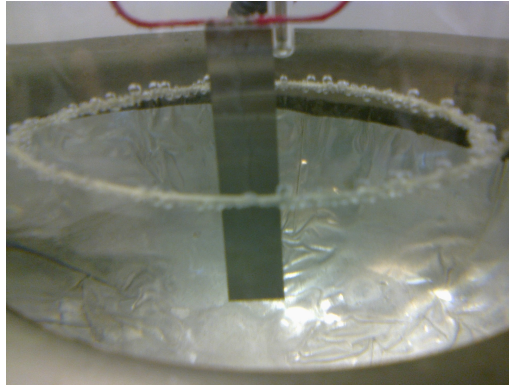


Figure 5.30: Hydrogen charging process of a) 100Cr6+0.5V(G) Charpy sample showing b) the way of hydrogen bubbles generated during the charging and they diffusion through the seam to the sample interior observed during the whole process; due to the low photograph resolution a schematic drawing on the right side is presenting the seam distribution in the real sample from the left side.

In addition, the lower absorption energy of the experimental melt is probably caused because of the higher inclusions and oxygen content in 100Cr6+0.5V(G), that have a strong influence on impact toughness [152, 153]. Moreover the presence of seams make the sample brittle on itself, making hydrogen diffusion easier. It was observed during charging that hydrogen bubbles entered 100Cr6+0.5V(G) sample through the seams (Figure 5.30). In the samples without seams (100Cr6) there was no preferential diffusion. SEM microphotographs showed cracks growing from seams during charging. Figure 5.31 shows a crack developing around a seam running alongside the sample (red arrow), and far away from the notch.

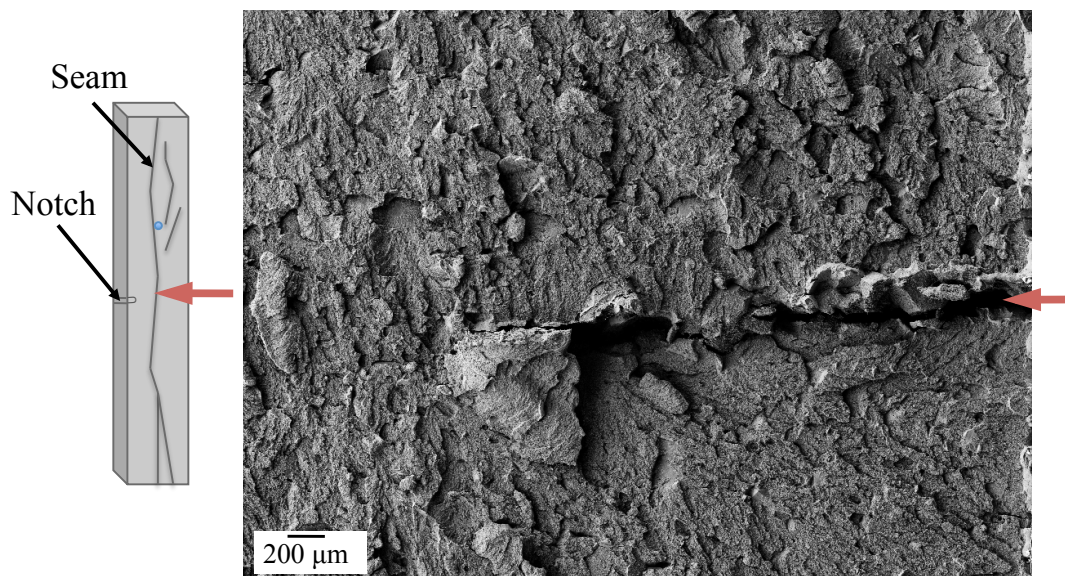


Figure 5.31: Seam causing the cracking during the charging of the 100Cr6+0.5V(G) sample. The red arrows show the crack along the side of the sample with the crack originating from the seam.

Further SEM images show that hydrogen tends to travel to grain boundaries and cause cracking in such areas. Therefore, microstructural traps such as V_4C_3 in 100Cr6+0.5V, or phases such as retained austenite in superbainite microstructure, can either delay or block hydrogen diffusion to grain boundaries. Complex microstructures with a large ratio of interfaces per unit volume are more prone to hydrogen embrittlement. This view is supported by the hydrogen absorption experiment performed on coarse-grained pure iron (Figure 4.10) which showed surprisingly low hydrogen content after subjecting it to the

same hydrogen charging conditions as 100Cr6 and superbainite (Figure 4.11).

The seams spreading in 100Cr6+0.5V(G) charged samples appear to allow hydrogen to travel from the electrolyte (Figure 5.30) directly to the grain boundaries (Figure 5.31), short-cutting the diffusion through non-coherent interfaces. This suggest that hydrogen tends to diffuse through grain boundaries that are predicted to be amongst the most favourable for hydrogen places to reside and cause decohesion [1, 138]. Grain boundary cracking observed in 100Cr6+0.5V(G) hydrogen charged samples is seen in Figure 5.32. The grain boundaries cracking was observed just in the hydrogen charged samples close to the notch or a seam. This supports the view that pre-cracked bearing steels are more prone to hydrogen-related failure, with the cracks accelerating hydrogen diffusion towards weak interfaces leading to early fatigue failure.

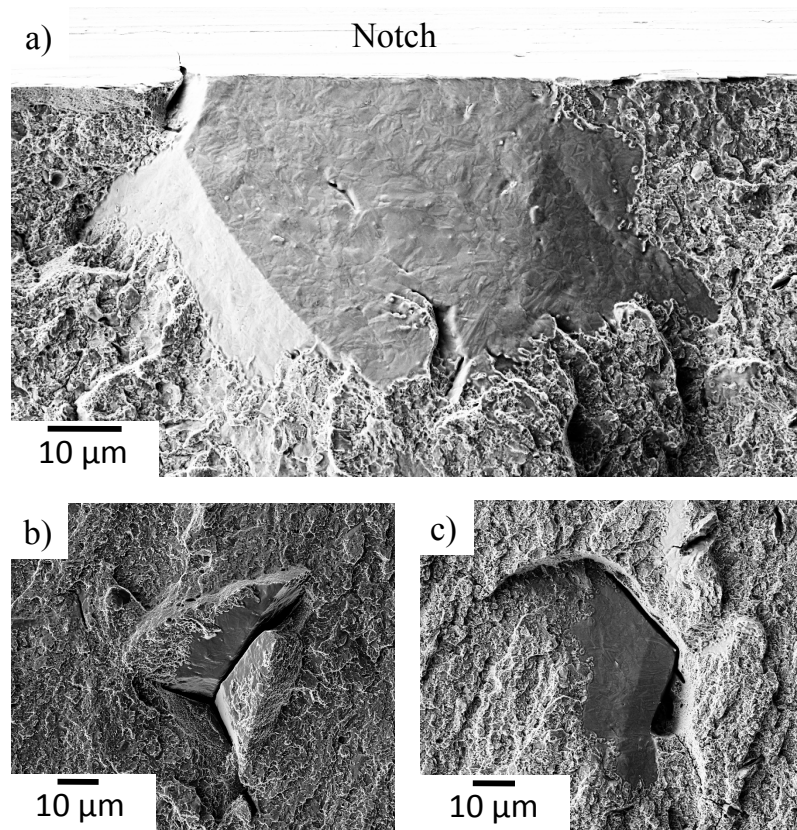


Figure 5.32: Grain boundary cracking observed in 100Cr6+0.5V(G) after charging and Charpy impact testing, where the large seam net was observed already during charging; a) the cracking starting from the grain boundary in the notch area, b) and c) show the grain boundaries decohesion located close to b) the seam c) the notch.

IV. Hydro – hardness results and hydrogen egress from the sample during testing

Figure 5.21 shows the results of hydro-hardness test for 100Cr6+0.5V(G). These results show much shorter cracks induced by the Vickers indenter, which proves that 100Cr6+0.5V(G) is more hydrogen embrittlement resistant when a localised load is applied (Figure 5.21a and 5.21b). Additional observations showed hydrogen desorbing from the seam (Figure 5.21c) and a small crack (Figure 5.21d) proving that hydrogen tends to diffuse to strained areas in the microstructure. The hardness of the samples in different conditions did not change and showed ~ 800 HV60 (~ 62.5 HRC).

The results for SB200 shown in Figure 5.22, provide another argument supporting that superbainite is a hydrogen embrittlement (yet softer) resistant microstructure. After the sample was charged and hydro-hardness tested, almost no cracking caused by the indentation was observed during testing with a 60 kg load (Figure 5.22a and 5.22b). After increasing the load to 125 kg, the number of indentation with cracks increased, but still they were much shorter when comparing to 100Cr6. The hardness of the sample was ~ 625 HV60 (~ 55.5 HRC) in all the conditions.

Hydro-hardness test on SB300 showed no cracking, even when testing with a 250 kg load (Figure 5.23a and 5.23b), supporting also the results from melt extraction technique (Figure 4.20), which showed that SB300 is the most promising grade for working in a hydrogen environment. However, it needs to be mentioned that this steel has also the lowest hardness from the previously described steels, what can be the reason for the cracks not to be caused by indentation [145]. The excellent performance of SB300 is consistent with the thermal desorption analysis results, which show that the desorption peak for SB300 appeared at 227 °C, indicating that the retained austenite-ferrite interface trap hydrogen more effectively than SB200 and 100Cr6+0.5V(G) (TDA peak at 219 °C). Additionally, impact testing and melt extraction results also showed that purer microstructures with a lower amount of grain boundaries (pure iron like microstructure) appear to be more resistant to hydrogen.

Hydro-hardness method allows to observe the hydrogen desorbing from the sample in real time; these results point out that Hydrogen Enhanced Localised Plasticity (HELP) is the prevailing mechanism in bearing steels. The hydrogen bubbles produced around the cracks (Figure 5.20c, 5.21b and 5.22d) show that hydrogen tends to diffuse to the highly stressed area, the crack tip, and subsequently egresses. Hydrogen escapes from the sample for a few hours after the indentation was performed. Additionally, it was noticed that the cracks are longer in the sample edge area when comparing to their middle section, this indicates that edges are more susceptible to hydrogen cracking; likely more hydrogen was located in those areas.

The newly developed H-H method shows that diffusible hydrogen can be visualised in the macro-scale and used for further analysis. A similar method based in mercury wherein diffusible hydrogen is collected in a capillary tube has been proposed earlier [154]. The collection of hydrogen by mercury is more complex and has been avoided due to health hazards. The developed H-H method could be used for quantitative analysis, for example for a given crack size and hydrogen content, the number and volume of hydrogen bubbles around the crack could be recorded. This would lead to the time and temperature dependence of hydrogen migration towards the crack determination, from which the activation energy for hydrogen diffusion towards the crack tip could be determined, and valuable information for HELP crack growth modelling could be drawn.

V. RCF and hydrogen damage evaluation

Rolling contact fatigue results on 100Cr6 (Figure 5.27) confirm that hydrogen, when present in large quantities in the microstructure, is a serious problem in bearing steels. Hydrogen-rich 100Cr6 displays a life approximately an order of magnitude shorter. Other tests showed that 100Cr6 without hydrogen charging and under similar pressure can run for much longer time without failure [103]. It was shown that 5 ppm of hydrogen is sufficient to dramatically decrease the number of cycles to failure. White etching areas

appeared on the 100Cr6 hydrogen-charged sample (Figure 5.27), and early damage can be associated to them; they appeared along with dark shadows around them as reported by Tamada *et al.* [155], who argued that hydrogen is responsible for the formation of early white etching areas. No white etching areas were observed in 100Cr6+0.5V(G) after similar number of cycles (~ 10 h of running), which suggests that 100Cr6+0.5V(G) even with surface discontinuities and seams present in the microstructure may not be prone to hydrogen embrittlement (Figure 5.29).

5.8 Summary

Microstructural investigations showed that the computer designed 100Cr6+0.5V grade can be heat treated in a dilatometer or in salt bath furnaces achieving the desired microstructure and hardness. However, the cast quality 100Cr6+0.5V(G) performed so far needs improvement to attain bearing steel requirements on tensile and impact properties; rolling contact fatigue endurance also requires further evaluations. Additionally, 100Cr6+0.5V displays the nanoprecipitate traps as confirmed by TEM analysis.

Impact testing results showed that the absorption energy slightly decreased in the presence of hydrogen in 100Cr6 and 100Cr6+0.5V(G), but the fractography observation under SEM did not show a significant difference in the structure of the crack. The undesired seams present in 100Cr6+0.5V(G) revealed that hydrogen tends to travel to the stressed areas and further to microstructurally weak regions (such as grain boundary edges and corners), causing their decohesion. These observations support hydrogen enhanced localised plasticity mechanism, since the hydrogen is observed to travel to the stress concentrated areas such as grain boundaries or crack surroundings, likely increasing dislocation movement and cracking in these highly dislocated places. This is consistent with previous research [31, 30, 32, 38].

Hydro-hardness results support the prevalence of the HELP mechanism, since hydrogen was found to diffuse and then escape from the sample through the cracks caused

by indentation. 100Cr6+0.5V(G) showed much shorter cracks spreading from the indentations suggesting that this steel is more resistant to hydrogen embrittlement when comparing to 100Cr6. SB300 showed the best results, with no cracks appearing close to the indentations further supporting its good performance in the presence of hydrogen. Hardness tested in this experiment was not affected by hydrogen. The newly developed H-H method can be successfully used for hydrogen diffusion studies, and is likely to have a significant impact in HELP mechanism studies.

Rolling contact fatigue results demonstrate that hydrogen accelerates damage via the formation of white etching areas in 100Cr6, where early failure is observed. White etching areas were not observed in 100Cr6+0.5V(G) after a similar number of cycles ($\sim 5 \times 10^6$). However, a higher quality 100Cr6+0.5V cast will likely result in much longer bearing life in the hydrogen-charged condition, since although 100Cr6+0.5V(G) showed surface discontinuities such as hot rolling defects (seams), it did not develop the white etching areas, which were noticed in the 100Cr6 industrial cast after H-charging and RCF testing for a similar number of cycles.

Chapter 6

Conclusions

The microstructure of 100Cr6+0.5V was designed via thermodynamic and kinetic modelling; TEM investigations proved that the desired nanoprecipitate hydrogen traps were achieved. MET analysis showed that this microstructure has a low hydrogen absorption, and a high efficiency for hydrogen trapping, above two orders of magnitude higher than the baseline steel (100Cr6) as measured by TDA. These results show that it is possible to accurately design a desired microstructure via computer modelling, suggesting that other precipitate species with hydrogen trapping potential could be explored, such as TiC, Mo₂C or NbC.

The rolling contact fatigue response of 100Cr6+0.5V(G) and of a commercial 100Cr6 in non-charged condition was equivalent; and similar behaviour was also observed in some of the samples in hydrogen-charged condition. However, due to the seam and porosity present in 100Cr6+0.5V(G), which were likely saturated with hydrogen, the assessment of the actual rolling contact fatigue life of proposed 100Cr6+0.5V steel was hindered.

Superbainite samples were tested for better understanding of the hydrogen response of bainitic microstructures, showing interestingly low hydrogen absorption. Hydro-hardness analysis showed short or no cracking around the indentations, suggesting superior resistance to hydrogen embrittlement. TDA and MET investigations showed that the active hydrogen trapping sites in superbainite are retained austenite/ferrite interfaces, which

may be semi-coherent or coherent.

It was noticed that TDA and MET analysis should always be conducted simultaneously and subsequently compared to each other, since these results combined can provide a better indication of hydrogen influence on a tested microstructure.

The observations from the hydrogen charging process of the samples with seams showed that the preferential way of hydrogen entry into the bulk is through the surface discontinuities, which proved that the pre-cracked surface is more prone to the hydrogen damage. Moreover, hydrogen entering through defects such as seams tends to diffuse directly to grain boundaries and cause decohesion.

Additionally, the H-H results suggest that HELP mechanism might prevail in bearing steels, since it was shown that hydrogen tends to diffuse to the damaged areas in the pre-charged specimens, the crack tip, and subsequently desorbs through cracks spread around the indentations. Hydrogen desorbs from the sample for a few hours after the indentation was performed.

The hydro-hardness technique is a novel method and it is believed that it can help to determine the nature of hydrogen embrittlement, as well as the hydrogen distribution at the engineering scale. This may be particularly useful for components in complex shapes.

Chapter 7

Future work

The suggested future work is divided in two parts. The first part is devoted to improvements and further research closely related to designed and tested steels as well as techniques used and described in this thesis. In the second part the main problems faced are summarised and some possible ways of broadening the understanding of hydrogen embrittlement are presented.

It would be recommended to investigate the resistance of 100Cr6+0.5V to rolling contact fatigue after hydrogen charging in an actual bearing test. It is important that a high quality cast is employed, without seams and pores.

100Cr6+2.75V should also be cast, thermomechanically treated, heat treated and analysed via TEM, MET and TDA, as well as hydro-hardness tested, paying special attention to the crack length, and comparing this to the other microstructures. In terms of the heat treatment of 100Cr6+0.5V and 100Cr6+2.75V, the induction heat treatment or precipitate formation on cooling from hot rolling temperature (~ 1250 °C) could be examined, as this could be easier to perform cost-effectively in industry.

For further testing of hydrogen trapping in superbainite microstructure employing atom probe tomography after deuterium charging can be conducted, in order to visualise the nature of the hydrogen trapping sites in nano-scale, and evaluate if hydrogen is trapped by the retained austenite/ferrite interfaces or whether it is stored in the retained

austenite interior.

In terms of the equipment used, there could be many improvements in H-charging, MET and TDA. In addition to electrochemical charging, oil decomposition leading to free hydrogen in RCF testing should be evaluated.

For improving TDA, a pyroprobe unit suitable for bigger samples is advised to be employed. The pyroprobe should be able to sustain long time at high temperature such as 1200 °C, which would enable the examination of irreversible traps.

The TDA peak shift should be studied in order to investigate any activation energy change associated with the chemical composition, hydrogen content and strains present in the tested microstructure variations. All these studies could be used for determining the coherency and interactions between different phases in the microstructure. These results could also be combined with first principle calculations for producing energy maps indicating the most favourable places for hydrogen places to migrate in a given system.

The Hydro-Hardness can be further useful for quantitative analysis; for a given crack size and hydrogen content, the number and volume of hydrogen bubbles around the crack can be recorded. This recording would allow to evaluate the temperature and time dependence of hydrogen diffusion towards the crack. The obtained results could help in determining the activation energy for hydrogen diffusion towards the crack tip, and important information for HELP crack propagation modelling can be drawn.

It is suggested to combine the tests that allow crack propagation observations, such as K_{IC} or stretch flange formability, with hydrogen studies on oil decomposition. Charging can be conducted in different oil types and temperatures for better understanding of hydrogen ingress into the bulk.

In future studies it is important to standardise the type of tests and their conditions; this would help in hydrogen embrittlement mechanism evaluations, and in comparisons between different trap types, their trapping energies and the different microstructural responses to hydrogen attack.

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