Developing bearing steels combining hydrogen resistance and improved hardness

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Abstract

Thermodynamic and kinetic computational modelling are combined to conceive a hydrogen resistant bearing steel. Existing hydrogen resistant steels are not appropriate for bearings due to their low hardness. The proposed microstructure combines a martensitic matrix in which fine cementite precipitates impart strength, and $V_4C_3$ nano-scaled particles acting as hydrogen traps. It is demonstrated that the conflicting objectives of ultra-hardness and hydrogen resistance can be concealed by: (1) Adding 0.5 wt% V to 100Cr6, which allows to preserve existing steel production technology. (2) Following a novel heat treatment procedure consisting of austenitisation (and a subsequent temperature spike to dissolve coarse $V_4C_3$), followed by tempering at 600 °C where $V_4C_3$ particles form (and a subsequent temperature spike to dissolve coarse cementite), followed by quench and tempering at 215 °C, where fine cementite strengthening particles form. The enhanced trapping capacity of the new steel is demonstrated via thermal desorption; the presence of the desired microstructure after heat treatment is proved via transmission electron microscopy. Concomitant with the trapping ability, a significant hardness increase was observed; this was ascribed to the controlled $V_4C_3$ precipitation.

Keywords: hydrogen embrittlement; precipitation; steel; nanostructured materials.

1. Introduction
Bearing steels must be able to withstand extreme cyclic and static loads. This is achieved via carefully balancing composition and heat treatment, resulting in a microstructure ensuring good rolling contact fatigue (RCF) resistance, a property of paramount importance when appraising bearing steels quality. There are three essential parameters that influence RCF: hardness, inclusion and hydrogen content. The first is usually attained by a high carbon concentration in the alloy (typically around 1 wt%), and by following appropriate heat treatments [1]. Inclusion content is controlled during the steelmaking process; the last decades have seen significant improvements in this direction. Nowadays, the oxygen content is limited to 10 ppmw [2] and the sulphur content is around 0.012 wt% in 100Cr6 [3]. Steelmaking companies have been effective in lowering the hydrogen content during casting, since this element can noticeably decrease rolling contact fatigue life as shown by Ciruna [4] (Figure 1). Even if, the hydrogen content is very low in the as-produced bearing, its amount is likely to increase during service, for example due to oil decomposition [5], water in the lubricant, static and fretting corrosion or electric current breaking through the layer of oil [6]. During these processes free hydrogen can form and ingress into the bulk. Although hydrogen embrittlement is a well recognised phenomenon in ultra-strong steels such as wires [7], in mid-carbon steels [8] and multiphase steels [9], there are no reported bearing steels meeting simultaneously improved hardness and hydrogen resistance.

Embrittlement is likely to occur when the steel contains mobile hydrogen. Many theories attempt to explain this phenomenon, but no consensus has been reached as yet. A strongly supported hypothesis is hydrogen enhanced localised plasticity (HELP). This assumes that mobile hydrogen increases dislocation mobility and slip planarity, causing the heterogeneous localised plastic strain and stress concentrations resulting in subcritical crack growth [10]. Another proposed explanation is that hydrogen increases the mobility of crystal defects. The studies of Nagumo et al. show that hydrogen embrittlement is related to vacancies where clustering is induced by deformation, and become stabilised by hydrogen [11]. There is consensus in that mobile hydrogen causes degradation; for that reason there have been many attempts to immobilise it in the microstructure.
Hydrogen immobilisation is possible through the introduction of microstructural traps; these have been classified in numerous studies, and their characteristic activation energy obtained. Pressouyre [12] classified the traps into attractive, physical and a mixture of the two. In the case of attractive traps, hydrogen atoms are attracted by forces due to: electrical fields, stress fields or temperature gradients. A typical example of an electrical field is an electronegative impurity atom, which electron excess 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 immobilise or release hydrogen. Their desorption temperatures ($T_E$) and characteristic activation energy ($E_A$) are relatively low. A trap is considered to be reversible if its activation energy is less than $\sim 50 \text{ kJ/mol}$ [13]. Typical activation energies and temperature peaks for reversible traps are listed in the Table 1.

Physical traps are those in which diffusible hydrogen falls as a result of a random walk. This group includes irreversible hydrogen traps that capture hydrogen until their saturation, and which further release becomes very difficult or in most the cases impossible [13]. 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 ascribes it to a certain group. 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 [14].

The steel proposed in this study contains nanometre-scaled $V_4C_3$ traps. Existing hydrogen embrittlement resistant steels display too low hardness making them not suitable for bearing applications, whereas the bearing steel proposed here displays very high hardness. This is achieved via combining vanadium additions to 100Cr6 with a novel heat treatment.
2. Methods

2.1. Material

100Cr6 is employed as a baseline, and a modified version of it with an intended addition of 0.5 wt% V was cast, the latter will be referred to as 100Cr6+V. The composition of both grades are shown in Table 2, these were determined using a glow discharge atomic emission spectrometer, LECO GDS850A.

Both grades were spheroidised according to a heat treatment schedule reported elsewhere [15], and then heat treated according to the schedules shown in Figure 2. The sample was cut into rods of 4 and 8 mm diameter and 12 mm length, and heat treated in vacuum on a Thermecmaster dilatometer with helium quenching gas at a cooling rate of 25 °C s⁻¹.

2.2. Optical microscopy

Heat treated 8 mm diameter samples were 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 optical microscope was used.

2.3. Transmission electron microscopy

After each heat treatment step in Figure 2b, discs of 3 mm diameter and 0.5 mm thickness were cut in order to produce thin foils. They were mechanically polished to ~50 μm 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 ~130 mA and ~20.5 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.

2.4. Hardness measurement

Hardness tests were carried out by using a Vickers hardness testing machine with a 30 kg load. Each quoted value represents an average of 10 readings with the lowest, and highest single values considered for calculating the mean.
2.5. Thermodynamic modelling

Thermodynamic modelling was conducted with the aid of MTDATA employing TCFE database version 1.0, and Thermocalc with TCFE v.6 database. In performing the calculations, the phases allowed to thermodynamically co-exist were: cementite, ferrite, \( \text{M}_2\text{C} \), \( \text{M}_4\text{C}_3 \), \( \text{M}_7\text{C}_3 \), \( \text{M}_{23}\text{C}_6 \) and \( \text{M}_6\text{C} \). The base steel used for calculation was 100Cr6 (Table 2).

2.6. Precipitation kinetics modelling

MATCALC software with mc\_fe\_tdb thermodynamic database, and with mc\_sample\_fe\_ddb database for the precipitation of cementite and \( \text{V}_4\text{C}_3 \), was employed. The thermodynamically allowed phases to co-exist were the same as for MTDATA and Thermocalc.

2.7. Thermal desorption

Heat treated samples were cut in 4 mm diameter and 6 mm length cylinders. Hydrogen was introduced into the specimens with cathodic electrolysis using an electrolyte solution of 1 dm\(^3\) distilled \( \text{H}_2\text{O} \), 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 a current source of 8 mA. The charging process took 24 h and the electrolyte was stirred and kept at a stable temperature of 80 °C during the whole process. After charging, the samples were gently polished and ultrasonically cleaned with petroleum ether and acetone, respectively. The hydrogen content was measured by means of thermal desorption analysis with pulsed discharge detector with helium carrier gas and the samples were heated up by a Pyroprobe 5000 unit at a rate of 2.6 °C/min. The samples were analysed in subsequent 3 minutes intervals, which allows for the separation of peaks due to hydrogen, oxygen and nitrogen. For the needs of this experiment, hydrogen desorption peak positions for investigating a type of trapping site and the peak areas for estimating the amount of trapped hydrogen, were analysed. 100Cr6 and 100Cr6+V were tested in two conditions: just after H-charging and 24 hours after it.
3. Equilibrium thermodynamics

Thermodynamic computations show that the microstructure of the baseline steel, 100Cr6, consists of ferrite, austenite, cementite and an FCC phase rich in Cu. The expected mass fractions of these phases are shown in Figure 3a. Among the many possible traps, $V_4C_3$ was chosen due to its demonstrated ability to trap hydrogen effectively [16].

Taking as a starting point for this analysis a steel grade that has been reported to effectively display hydrogen resistance, the elements that have the strongest influence on $V_4C_3$ formation were investigated. The composition of that grade is 0.10C-2.00Mn-1.59Mo-0.56V (wt%) [16]; the elements that alter $V_4C_3$ occurrence and composition are primarily vanadium and molybdenum [16]. Iterative calculations on 100Cr6-based alloys indicated that a small addition of vanadium (0.5 wt%) makes thermodynamically possible to produce $V_4C_3$ particles in 100Cr6 steel. The thermodynamic calculations of a modified 100Cr6 steel with $V_4C_3$ traps (100Cr6+V) are shown in Figure 3. However, although it is thermodynamically possible to produce $V_4C_3$ particles, their sole presence does not make them able to trap hydrogen, matrix/precipitate coherency is required for effective trapping; such coherency induces lattice strains to which hydrogen atoms become attracted [16]. The size of $V_4C_3$ might therefore be tailored by adjusting the heat treatment temperature and time.

Bearing steels are spheroidised and further transformed into martensite or bainite to maximise hardness. Following spheroidisation the steel is austenitised around 860 °C; however this temperature is too low for dissolving the $V_4C_3$ particles formed on solidification, which may display an incoherent precipitate/matrix interface. $V_4C_3$ may be stable up to 1200 °C (Figure 4), a temperature strongly dependent on the amount of vanadium and carbon. In order to dissolve the large $V_4C_3$ particles, a one minute temperature spike to 1200 °C was applied following the austenisation step (Figure 2b), the duration of this spike was estimated on the basis of kinetic calculations.

The temperature for the controlled growth of $V_4C_3$, is estimated from thermodynamic calculations to be 600 °C (Figure 3b). At such temperature three phases are present: ferrite (matrix), $V_4C_3$ (trapping precipitates) and cementite. The presence of cementite is undesired
at such temperature as it decreases hardenability. Due to the application of a 1 min spike prior to 600 °C ageing, the controlled formation of $\text{V}_4\text{C}_3$ precipitates is assumed to take place at such temperature, but once it is formed it is necessary for cementite to dissolve so that the hardenability is achieved on further tempering at a lower temperature. Thermodynamic modelling showed that the most important elements influencing cementite at 600 °C are carbon and chromium. By decreasing carbon cementite may not form, but hardenability is decreased; by increasing chromium cementite becomes unstable but other phases such as $\text{M}_{23}\text{C}_6$ or $\text{M}_7\text{C}_3$ may form. It was therefore decided to apply a second (3 min) spike at 860 °C to dissolve the cementite formed at 600 °C (Figure 2b).

4. Precipitation kinetics

The heat treatment schedule 100Cr6+V (Figure 2) and the associated kinetics computed for $\text{V}_4\text{C}_3$ and cementite are shown in Figure 5. It can be seen that during the first stage of heat treatment, austenitisation, the growth of both $\text{V}_4\text{C}_3$ and cementite occurs. The molar phase fraction of $\text{V}_4\text{C}_3$ increases displaying a particle radius growing from 25 nm to 75 nm, whilst the molar phase fraction of cementite decreases and its radius increases from approximately 200 nm to around 400 nm. The first temperature spike dissolves both precipitate phases within $\sim 30$ s; this ensures the controlled growth of $\text{V}_4\text{C}_3$ particles during ageing at 600 °C (which is also shown on the charts), where $\text{V}_4\text{C}_3$ molar fraction increases to 0.0017 and the particles radius grows to around $\sim 4$ nm. At 600 °C there is also an undesired concomitant growth of cementite to be dissolved during the second temperature spike at 860 °C during which there is a monotonic $\text{V}_4\text{C}_3$ particle growth up to a radius of $\sim 7$ nm and a molar fraction approaching 0.007. Quenching after the second spike results in a carbon-supersaturated martensitic structure on which fine cementite particles can form in paraequilibrium at temperatures around 200 °C [17]. At the last stage of heat treatment, tempering at 200 °C, fine cementite growth takes place, which ensures hardenability, whilst fine $\text{V}_4\text{C}_3$ remains unchanged.
5. Experimental results

5.1. Optical microscopy and hardness

Figure 6 shows optical microscopy micrographs for 100Cr6 and 100Cr6+V after the heat treatments prescribed in Figures 2a and 2b, respectively. 100Cr6+V does not show the coarse cementite particles visible in 100Cr6 steel. The hardness of the newly designed steel is higher, 804 HV30, in comparison to 785 HV30 displayed by 100Cr6.

5.2. Transmission electron microscopy

Transmission electron microscopy was employed to verify whether the microstructure predicted by thermodynamic and kinetic modelling were obtained. The two spikes heat treatment was interrupted after selected heat treatment stages to verify the presence and size of V$_4$C$_3$ and cementite.

100Cr6 is spheroidised before hardening heat treatment to enhance machinability. Figure 7a shows 100Cr6+V after spheroidisation; large and evenly distributed cementite particles with a radius around 200-500 nm are observed. 200 nm has been assumed as starting radius for cementite dissolution modelling (Figure 5). The microphotographs taken after the first temperature spike (Figure 7b) show ferritic laths without cementite and V$_4$C$_3$ particles. The diffraction pattern shows additional spots believed to be epsilon carbides, which can form at room temperature [18] as the TEM investigations were carried out approximately two weeks after heat treatment. The tempering stage at 600 °C shows the undesired large cementite particles and confirms the necessity of a second temperature spike for its dissolution (Figure 7c). The growth of V$_4$C$_3$, which is expected to appear at this stage, is difficult to confirm because of the small amount and size of V$_4$C$_3$ in contrast with the large amount of comparably coarse cementite, which makes the diffraction patterns difficult to analyse. Nevertheless, Figure 8a confirms the presence of V$_4$C$_3$ following cementite dissolution, making the diffraction patterns easier to analyse by lowering the amount of diffraction spots so that they become easily identifiable. The TEM microphotographs after the full heat treatment (Figure 8b) show fine cementite and V$_4$C$_3$ particles. Their presence was confirmed by electron
diffraction. The phases predicted via modelling were therefore confirmed by the transmission electron microscopy observations in Figure 7 and 8.

5.3. Thermal desorption analysis

Because the hydrogen traps become activated at certain temperatures [19], thermal desorption analysis was conducted at a constant heating rate to investigate the type of traps present in the microstructure. The thermal desorption charts of the 100Cr6+V display a very high trapping capacity compared to the baseline steel, 100Cr6 (Figure 9). The temperature peaks for 100Cr6+V (which contains V$_4$C$_3$ traps) show a maximum desorption rate at 219 °C, very close to the peaks achieved by Yamasaki, ∼220 °C in 0.10C-2.00Mn-0.40Mo-0.56V and 0.10C-2.00Mn-0.40Mo-0.30V for V$_4$C$_3$ traps [16]. The temperature peaks of 100Cr6 occur at a lower temperature, 188 °C, suggesting that these peaks correspond to dislocations, as shown by Choo [20].

6. Discussion

6.1. A novel hydrogen resistant bearing steel

Newly designed 100Cr6+V opens a new trend in developing hydrogen embrittlement resistant steels. 100Cr6+V combines ultra-hardness with an exceptional hydrogen trapping capacity. According to Yamasaki et al. [21] steels with trapping capacity in excess of 3 ppmw (parts per million by weight) can be claimed to display high resistance to hydrogen embrittlement. The microstructures displaying hydrogen trapping and ultra-hardness were carefully designed via thermodynamic and kinetic modelling. The desired microstructures were confirmed by transmission electron microscopy and thermal desorption analysis, respectively. The heat treatment temperatures and steel composition were tailored to obtain fine V$_4$C$_3$ precipitates and cementite; however, the changes in widely used 100Cr6 (baseline) were aimed to be exiguous and therefore cost-effective for manufacturing companies. The results show that a small addition of vanadium (0.5 wt%) makes V$_4$C$_3$ formation thermodynamically possible (Figure 3b) at 600 °C. This temperature was also estimated on purpose to produce fine V$_4$C$_3$ [22] in a relatively short time, but also was chosen to form the precipitates with the
Baker and Nutting orientation relationship \( \{100\}_\alpha \parallel \{100\}_{V_4C_3}, \{011\}_\alpha \parallel \{001\}_{V_4C_3} \), which shows \( \sim 3\% \) misfit between the ferritic matrix \( \{110\}_\alpha \) and the \( \{011\}_{V_4C_3} \) precipitate [23].

The most important elements influencing the formation and dissolution of \( V_4C_3 \) are vanadium and carbon (Figure 4). A great influence of Mo on \( V_4C_3 \) coherency was confirmed by Yamasaki [16] and related to the higher trapping capacity in steels with higher Mo content due to more favourable coherency strains. That is why it is believed that the addition of Mo could result in even higher trapping capacity in 100Cr6+V. The influence of molybdenum on the dissolution and formation of \( V_4C_3 \) was also observed in this study, however its amount in the baseline steel is believed to be sufficient for influencing coherency strains and no further addition were considered. It is worth noting that the 0.5 wt% addition of vanadium to 100Cr6 might also be beneficial for delaying grain growth during austenitisation [23].

Exceptional hardenability was achieved via the formation of fine cementite particles at \( \sim 200^\circ C \). This follows the cementite dissolution due to the second temperature spike at 860 \( ^\circ C \) (Figure 2). If this had been omitted, the large cementite particles (Figure 7c) would have depleted carbon from ferritic matrix and cause a hardness decline. Large cementite particles may also act as irreversible traps where hydrogen could become permanently trapped until saturation [13]. The first spike (1200 \( ^\circ C \)) was also necessary in order to dissolve coarse \( V_4C_3 \) formed on austenitisation. Due to the two spikes, 100Cr6+V heat treatment (Figure 2b) is more complex than that of 100Cr6; nevertheless, it may be simplified by austenitizing at higher temperatures (up to 1200 \( ^\circ C \)), possibly eliminating the first spike.

6.2. Improved hardness

Referring to the improved hardness displayed by 100Cr6+V, it must be born in mind that the fine \( V_4C_3 \) precipitates also contribute to strengthening, and may well be responsible for the associated \( \sim 20 \) HV30 improvement. Although this may seem as a modest improvement at first, it is quite relevant for bearing applications, where through-hardened bearings rarely exhibit values in excess of 800 HV30, and 100Cr6+V is still subject to improvement as the proposed heat treatment in Figure 5a was the first attempt for the new alloy. The selection of \( V_4C_3 \) may also bring additional benefits to trapping. Such species is stable at higher
temperatures than \( \epsilon \) and cementite, this may aid in ensuring the stability of mechanical properties at temperatures higher than 50 °C, which is a typical temperature for bearing operation. Therefore the alloy may potentially be employed for high temperature bearing and/or gear applications, which demand operation temperatures in excess of 100 °C.

The amount of hydrogen immobilised by a trap can vary as it strongly depends on the hydrogen charging process, where the type of electrolyte solution plays a prominent role. Hagihara [24] proved that the hydrogen charged after around 24 h of electrochemical charging, at the same current density and the exact sample geometry, could vary from \( \sim 1 \) mass ppm (0.1 N NaOH) to \( \sim 4 \) mass ppm (3 % NaCl + 0.3 g/L NH\(_4\)SCN) or to even to \( \sim 8 \) mass ppm (3 % NaCl + 3 g/L NH\(_4\)SCN).

6.3. Hydrogen charging, desorption and trapping

Referring to the thermal desorption technique, a literature review indicates that many factors influence the peak area and position. The peak temperature is likely to shift to higher temperatures if the desorption experiment is conducted long after charging [25], or if the heating rate rises [26]. The peaks shift to lower temperatures as time of electrochemical charging increases [24]. The size of the peak depends on hydrogen content as well as on carbon content in case of dislocation traps. Carbon was reported to have a great influence on a peak height for dislocation traps, and its broadening was reported to be affected by the density of the trap sites [27]. In spite of this, the peaks observed in 100Cr6+V are extremely close to all values reported in the literature (220 °C), but the peak displayed by 100Cr6 is somewhat lower (188 °C vs. 215 °C), which is consistent with its high carbon content [27]. This work seems to confirm that carbon content has a significant influence not only on the hydrogen content in a trap but also on the peak position. In Choo’s studies, the characteristic peak temperature for hydrogen trapped by dislocations in pure iron is 215 °C [19], and in medium carbon steel (0.12 and 0.49 wt% C) is 205 °C [20]; this trend is consistent with the hydrogen desorption peaks presented here (188 °C for 100Cr6), which were obtained from similar thermal desorption conditions.

Another benefit of having \( V_4C_3 \) traps stems from comparing the amount of desorbed
hydrogen immediately after charging, and 24 h after it. By integrating the area under the curve, the amount of hydrogen trapped can be obtained (Figure 9). In 100Cr6+V it was $\sim6$ ppmw in samples just after hydrogen charging; and $\sim4.5$ ppmw 24 hours after hydrogen charging. As expected, the hydrogen amount decreased after 24 h highlighting the trapped hydrogen, while the hydrogen desorbed just after charging displays a mixture of both diffusible and trapped. Referring to the baseline steel (100Cr6), the hydrogen trapped by dislocations decreased strongly from $\sim1$ ppmw to $\sim0.12$ ppmw, immediately and 24 h after charging, respectively. That clearly shows that 100Cr6 does not intrinsically possess good hydrogen trapping capacity, and that a small change in its composition (0.5 wt% of V) and heat treatment increases the trapping capacity by over two orders of magnitude.

6.4. Comparison to other steels in the literature

The originality of the research reported here stems both from the method for alloy design and the resulting combined properties. The method for alloy design was purely computational; as opposed to developments stemming from experience, the proposed grade 100Cr6+V was the result of combining thermodynamic modelling for predicting the temperature windows within which the desired phases form, and kinetics modelling to estimate the duration of the associated heat treatments. The multi-step heat treatment proposed incorporates temperatures at which three conflicting principles can be met:

1. A high temperature austenitisation step to provide an initial homogeneous matrix on which supersaturated C and interstitials are expected to lay. The undesired associated effect is the formation of coarse $V_4C_3$ particles, which are then removed by a high temperature spike to dissolve them.

2. An intermediate temperature tempering step to provide nanometre-scale $V_4C_3$ for hydrogen trapping. The undesired associated effect is the formation of bulky cementite, which can be removed by a high temperature spike to dissolve it.

3. A low temperature tempering step to provide fine cementite particles for ultra strength.

The authors are not aware of a similar heat treatment process in the literature. This is directly responsible for the combined enhanced strength and hydrogen trapping. Devising
heat treatments wherein conflicting principles have been incorporated is a concept that has been exploited by one of the authors for the computational design of ultra–strong steels displaying excellent corrosion resistance, as illustrated in earlier work [28, 29]. It is worth highlighting that previous developments on hydrogen resistant steels have been achieved with significantly lower strength than that of bearing steels. Not only $V_4C_3$ has been employed for hydrogen trapping in steels [16], but also $TiC$ [30] and $NbC$ [25]; in all previous trapping solutions the developed steels display considerable lower strength due to the absence of the multi–step tempering that concomitantly allows for nanoprecipitate traps and hardening nanoprecipitates.

7. Conclusions

The hydrogen trapping capacity of 100Cr6+V steel, which was designed via thermodynamic and kinetic modelling, was evaluated by transmission electron microscopy and thermal desorption analysis. The trapping character and factors influencing it were studied and discussed. The obtained results are summarised as follows:

1. It is possible to conceive a steel that combines both improved hardness and hydrogen trapping capacity, resulting in a grade suitable for bearing applications.

2. Thermodynamic and kinetic modelling show good agreement with the transmission electron microscopy and diffraction investigations. The presence of the desired carbides at various heat treatment stages was proven.

3. Thermal desorption analysis of 100Cr6 displayed a peak at 188 °C, believed to appear due to dislocation trapping, whereas a peak at 219 °C in 100Cr6+V is ascribed to hydrogen trapped by $V_4C_3$.

4. The hydrogen trapped immediately and 24 h after hydrogen charging respectively was $\sim1$ ppmw and $\sim0.12$ ppmw, for 100Cr6, and $\sim6$ ppmw and $\sim4.5$ ppmw for 100Cr6+V. These are consistent with previously reported trapping capacities under similar test conditions.
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References


List of Table captions

1. Types of reversible and irreversible hydrogen traps.
2. Chemical composition of the characterised steels (wt%).
List of Figure captions

1. The influence of hydrogen on fatigue life of X105CrMo17 and 100Cr6 bearing balls, adapted from Ciruna [4].

2. Heat treatment schedules of a) 100Cr6 and b) 100Cr6+V.

3. Phase fraction change with temperature for a) 100Cr6 and b) 100Cr6+V.

4. Dissolution temperature change in 100Cr6+V for different a) carbon and b) vanadium content.

5. Kinetic calculation results for the heat treatment of the proposed steel. (a) Heat treatment schedule. (b) Progress in $V_4C_3$ volume fraction. (c) $V_4C_3$ radius variation with time. (d) Progress in cementite volume fraction. (e) Cementite radius variation with time. Note that the time scales vary for the subsequent stages, but the units is min in all cases.

6. Optical microphotograph of a) 100Cr3 and b) 100Cr6+V.

7. Transmission electron microphotographs of 100Cr6+V: a) bright field image after spheroidisation and a diffraction pattern of spheroidised 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 $^\circ$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 $[3 \bar{1} 1]$.

8. Transmission electron microphotographs of 100Cr6+V: 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 $[0 \bar{1} 1]$; b) diffraction pattern and bright field image after completed two spikes heat treatment, diffraction pattern taken from $[1 \bar{3} 2]$ cementite spot.

9. Thermal desorption analysis results of 100Cr6 and 100Cr6+V a) just after H-charging and b) 24h after H-charging.
### Table 1: Types of reversible and irreversible hydrogen traps.

<table>
<thead>
<tr>
<th>Type of trap</th>
<th>Peak temperature $^\circ$C</th>
<th>Activation energy kJ/mol</th>
<th>Material</th>
<th>Reference</th>
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<tr>
<td>Reversible hydrogen traps:</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Grain boundaries</td>
<td>112</td>
<td>17.2</td>
<td>Pure iron</td>
<td>[19]</td>
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<tr>
<td>Dislocations</td>
<td>215</td>
<td>26.8</td>
<td>Pure iron</td>
<td>[19]</td>
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<tr>
<td>Microvoids</td>
<td>305</td>
<td>35.2</td>
<td>Pure iron</td>
<td>[19]</td>
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<tr>
<td>$V_4C_3$ (coherent)</td>
<td>$\sim 220$</td>
<td>30</td>
<td>Low carbon steel</td>
<td>[16]</td>
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<tr>
<td>TiC (semi-coherent)</td>
<td>$\sim 230$</td>
<td>-</td>
<td>Low carbon steel</td>
<td>[30, 25]</td>
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<td>Ferrite/Fe$_3$C interface</td>
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<td>18.4</td>
<td>Medium carbon steel</td>
<td>[20, 31]</td>
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<td>Dislocations</td>
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<td>[20]</td>
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<td>Irreversible hydrogen traps:</td>
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<td>55</td>
<td>Dual Phase Steel</td>
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</tbody>
</table>

### Table 2: Chemical composition of the characterised steels (wt%).

<table>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>P</th>
<th>S</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>0.974</td>
<td>0.282</td>
<td>0.276</td>
<td>0.056</td>
<td>1.384</td>
<td>0.184</td>
<td>0.042</td>
<td>0.21</td>
<td>0.01</td>
<td>0.017</td>
<td>0.00</td>
</tr>
<tr>
<td>100Cr6+V</td>
<td>0.994</td>
<td>0.272</td>
<td>0.282</td>
<td>0.093</td>
<td>1.42</td>
<td>0.01</td>
<td>0.003</td>
<td>0.247</td>
<td>0.004</td>
<td>0.003</td>
<td>0.549</td>
</tr>
</tbody>
</table>
Figure 1: The influence of hydrogen on fatigue life of X105CrMo17 and 100Cr6 bearing balls, adapted from Ciruna [4].

Figure 2: Heat treatment schedules of a) 100Cr6 and b) 100Cr6+V.
Figure 3: Phase fraction change with temperature for a) 100Cr6 and b) 100Cr6+V.

Figure 4: Dissolution temperature change in 100Cr6+V for different a) carbon and b) vanadium content.
Figure 5: Kinetic calculation results for the heat treatment of the proposed steel. (a) Heat treatment schedule. (b) Progress in $V_4C_3$ volume fraction. (c) $V_4C_3$ radius variation with time. (d) Progress in cementite volume fraction. (e) Cementite radius variation with time. Note that the time scales vary for the subsequent stages, but the units is min in all cases.
Figure 6: Optical microphotograph of a) 100Cr3 and b) 100Cr6+V.
Figure 7: Transmission electron microphotographs of 100Cr6+V: a) bright field image after spheroidisation and a diffraction pattern of spheroidised 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 $600^\circ$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 8: Transmission electron microphotographs of 100Cr6+V: a) bright field and dark field image after second temperature spike, the diffraction pattern is taken from the V$_4$C$_3$ particle indicated by the arrow, the zone axis of V$_4$C$_3$ is [0 ¯1 1]; b) diffraction pattern and bright field image after completed two spikes heat treatment, diffraction pattern taken from [1 3 2] cementite spot.
Figure 9: Thermal desorption analysis results of 100Cr6 and 100Cr6+V a) just after H-charging and b) 24h after H-charging.