Effects of boron modifications on phase nucleation and dissolution temperatures and mechanical properties in 9%Cr steels: sensitivity and stability

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Abstract
Effects of boron modifications in 9%Cr steels were investigated by considering design parameters, i.e., sensitivity and stability with the help of analytical equations as reported previously. The interference of phase temperature(s) for a phase on the rest of the phases was discussed. Overlapping of phase temperature for two distinct phases was observed. Invariability, an invariable composition(s), and susceptibility for phase temperatures were determined. Full stability, partial stability, and no stability for phase/property were analytically discussed. In this respect, boron modification only delayed the formation of detrimental phases. A mixture of positive, negative, and transient sensitivity was observed for some phases. However, a few phases showed both negative and transient sensitivities. Nevertheless, only negative sensitivity and only positive sensitivity found in some phases and properties. At last, the self-changing capability of linear and non-linear functions was found to confirm the nature of boron (i.e., minimization or maximization or point of inflexion). A decrease in a phase/property band was observed for designed boundary condition (DBC) as regards studied boundary condition (SBC). For phases and properties, the band of variation decreased by ∼52% and ∼32%, respectively, for the DBC as regard SBC and verified upper limit of 350 ppm boron modification as optimized structure-property in 9%Cr steels.

Nomenclature and definitions

| Symbol   | Description                                      |
|----------|--------------------------------------------------|
| α0°C     | Dissolution temperature of ferrite               |
| α0°C     | Nucleation temperature of Cr-rich Martensite     |
| DBC PPM  | Design boundary condition, 0–350 ppm             |
| δ°C      | Nucleation temperature of δ-ferrite              |
| δ°C      | Dissolution temperature of δ-ferrite             |
| %El      | Linear elongation                                |
| γ0°C     | Nucleation temperature of austenite              |
| γ0°C     | Dissolution temperature of austenite             |
| GB       | Grain Boundary                                   |
| HRC      | Rockwell Hardness at C-scale                    |
| Invariability — | A condition, when a phase/property does not change with unit boron modification. |
| Ia°C     | Nucleation temperature of liquid                 |
| L0100°C  | Saturation temperature of liquid                 |
| n        | Strain hardening exponent                        |
| Nb3°C    | Dissolution temperature of Nb(C,N)              |
1. Introduction

Structural instabilities have been a primary issue in ferritic/martensitic 9%Cr steels having superior properties and resistance to corrosion from their inception. These instabilities were due to stringent demand to increase the operating temperature and pressure of thermal and nuclear power plants leading to severe thermo-mechanical loading. This demand is being fulfilled by tailoring a more stable microstructure via both microalloying elements and heat treatments [1–3]. Carbon is a key element to enhance mechanical properties by allowing distinct types of precipitates at and around grain boundaries (GBs). Its fraction was kept at a maximum limit for 9%Cr due to (i) allowing maximum carbides formation as their coarsening to be controlled and (ii) to delay nucleation of Z-phase [1].

The previous study reported Z-phase formation in 9%Cr steel [4]. To keep the minimum susceptibility of Z-phase formation by keeping in mind the Fe–Cr phase diagram and ASTM recommended fraction, Cr concentration was kept minimum, i.e., 8.5% as this fraction allows enough precipitation of M23C6 carbides and high-temperature oxidation in 9%Cr steels [5]. Mo is one of the essential macro-alloying elements needed to increase solid solution strengthening and elevated temperature strength and delays temper embrittlement. But enough Mo causes creep-strength breakdown due to (i) coarsening of M23C6 carbides and (ii) formation of lave phase by depleting Mo from solid solution [1]. Mn addition was kept below 0.5% to keep wider transformation temperatures (\(A_1\) and \(A_3\)) and to suppress the risk of retained austenite on cooling. Si was added minimum to suppress susceptibility of lave formation, and to maintain high-temperature corrosion resistance, which was reduced due to the addition of a minimum fraction of Cr as discussed, earlier. In this respect, these materials were optimized by adding V/Nb to form MX type carbides/carbo-nitrides [1, 6]. Ti addition was preferred very low as it forms thermodynamically more stable Ti carbides/carbo-nitrides, whose uniform dispersion in microstructure has been worried for metallurgists [3]. But Ti concentration was kept slightly higher than the concentration of nitrogen so that only stable TiN would form than BN. The concentration of Ni and segregating elements like Cu, P, S, etc, were controlled by modern steel making technologies to provide additional microstructural stability and resistance to GB embrittlement in 9%Cr steels, respectively [1, 6, 7]. However, it was reported that controlled nitrogen and boron modified 9%Cr steels show better performance in terms of properties than both boron-nitrogen free and only boron modified steels [8–11]. Also, welding of 9%Cr steels provides soft and fine grains that fail in type IV manner. This failure can be delayed or altered either by manipulating welding parameters or by modifying with boron [12, 13]. The boron modification in 9%Cr steels has both delayed and altered the failure modes [14]. Boron is known to segregate around prior austenite grain boundaries (PAGBs) and giving GB hardening under controlled concentrations [8, 15, 16]. It is reported that segregation of enough concentration of boron brings GB embrittlement [7]. Such catastrophic structural instability needs to be predicted and analyzed before putting boron modified 9%Cr steels into service. This knowledge would delay structural instabilities, and would prolong its service life. In this regard, preliminary investigations on the effects of boron modifications in 9%Cr steels were presented in alloy design, where optimal alloy design from the analytical modeling as derived from computational software packages was discussed [17]. These software packages included

| Negative sensitivity | [°C or MPa]/PPM | Decrease in phase/property as regards per unit of boron modification. |
|----------------------|----------------|------------------------------------------------------------------|
| NMNNM                | —              | Neither maximizing nor minimizing                                   |
| PAGB                 | —              | Prior austenite grain boundary                                       |
| Positive sensitivity | [°C or MPa]/PPM | An increase in phase/property as regards per unit of boron modification. |
| SBC                  | PPM            | Studied boundary condition, i.e., 0–2000 ppm                       |
| Hv                   | PPM            | Half (median) value                                                  |
| PI                   | PPM or MPa     | Point of inflexion known as NMNM                                     |
| Sensitivity          | [°C or MPa]/PPM | Instantaneous rate change in temperature/property as regards per unit ppm of boron modification. |
| Stability            | —              | A condition, when there is not much susceptibility and the flow behavior of curve moved into fixed direction, i.e., gradient is either positive or negative. |
| Susceptibility       | —              | A condition, when too high sensitivity of phase/property with per unit boron modification at given composition. |
| \(T_{\text{io-o}}\)  | °C             | Dissolution temperature of Ti(N,C)                                   |
| Transient sensitivity| PPM            | Occurs at a point and in the range, where nature of sensitivity changes. |
| TS                   | MPa            | Tensile strength                                                    |
| \(V_{\text{a-o}}\)  | °C             | Dissolution temperature of V(N,C)                                   |
| VHN                  | VHN            | Vickers Hardness Number                                             |
| YS                   | MPa            | Yield strength                                                      |
| \(Z_{\text{a-o}}\)  | °C             | Dissolution temperature of Z-phase                                  |

(Continued.)
thermocalc and JMatPro, which were used to predict nucleation and dissolution temperatures of phases and properties in SBC by pre-screening of all micro- and macro-alloying elements in 9%Cr steels. The alloy design started from an explicit prediction of phases/properties by using thermocalc/JMatPro, where these were examined within SBC (0–2000 ppm) and concluded it as DBC (0–350 ppm). However, alloy design did not cover the effects of boron modifications for structural sensitivity and stability, which is drawn in the current paper from the previously developed analytical models. The archival literature has been handicapping in delineating the effect of per unit ppm of boron in a wide range of phases/properties [12, 14–16, 18, 19]. Hence, this paper continues the in-depth effects of boron modifications to its maximum limit. To interpret the same, modeling parameters like sensitivity and stability were selected. It is essential to understand how boron affects phase/property (sensitivity), while alloy designing of 9% Cr steels by boron for a particular application. Especially, when the phase/property follows exponential decay/growth and other non-linear behavior rather than linear decay/growth as concluded in alloy design. The definition of all functions was reported in alloy design [17]. Furthermore, it becomes more interesting to know the direction and magnitude of the flow behavior of phase/property to decide full stability or partial stability or no stability. Based on the discussion, the goal of this study was to divulge the fundamental knowledge on the effects of the unit ppm of boron in 9%Cr steel in the 0–2000 ppm boron range (i.e., SBC) by using design parameters, i.e., sensitivity and stability. By using these design parameters, structural stability and instability were also predicted. The concept of stability and sensitivity of phase/property was finally used to define the concept of invariability, invariable composition, and susceptibility.

2. Materials and methods

The studied chemical composition and heat treatment history of 9%Cr steel is given in table 1. While the previously developed equations and their significance, which are required to understand this section can be found in alloy design [17]. The effects and importance of each micro- and macro-alloying elements have already been discussed in introduction of this manuscript. However, boron was varied from 0–2000 ppm (SBC) for analytical modeling at 0, 5, 10, 20, 50, 80, 100, 150, 300, 500, 800, 1000, 1500, and 2000 ppm. The reason behind studying such large variation was to minimise the computation error as discussed in alloy design. A detailed summary of experimentation involved, and their validation was reported in alloy design. With the help of thermocalc and JMatPro, nucleation and dissolution temperatures and properties were found and analytically modeled in alloy design. By using linear and non-linear equations reported in alloy design, sensitivity and stability were evaluated, which was found by first differentiation. These parameters were further used to find special conditions of phase/property. Based on an algorithm of alloy design on boron modifications (figure 1), the upper design limit was fixed as 350 ppm. This algorithm briefly depicts the steps involved in alloy design of phase/property. First, phase nucleation and dissolution temperatures were successfully found. These phase temperatures were logically deduced towards optimal boron modification with the help of half values of boron calculated in alloy design. Whereas, property optimization with similar procedures was done. This process showed the scope of further improving mechanical properties. This failure led to gradient-based optimization of properties and the upper limit for boron modification was limited as 350 ppm (figure 1). Hence, the calculation for sensitivity and stability was done in the range of 5–350 ppm. A sensitivity of boron infers that by how much nucleation and dissolution temperatures, and properties changed instantaneously with modification of per unit ppm of boron as regards boron-free 9%Cr steels, i.e., describing ‘rate of change in phase/property’ (found by first differentiation of equations reported in alloy design). Negative sensitivity (negative gradient) means, the modification of the unit ppm of boron decreases the phase/property, while positive sensitivity (positive gradient) means, it increases phases/property. Whereas, transient sensitivity refers to a point or a range of boron modifications, where the nature of sensitivity changes. Susceptibility is the special condition, where too high sensitivity of phase/property with unit ppm of boron modification at given composition meets, i.e., gradient change was very high and it was usually observed at a point or in the range. Besides, the stability of phase/property comes, when there is not much susceptibility and the flow behavior of the curve moved into fixed direction, i.e., gradient was either positive or negative, i.e., not following both. Invariability comes, when a phase/property does not react with boron modification and the concentration is called invariable composition. However, it does not frequently meet throughout DBC rather than occurred in small intervals or high boron modification. Such parameters would make alloy design more attractive and easier as it helps in distinguishing various phase/property behavior.
Table 1. Chemical composition (in wt., normalizing, and tempering conditions of 9%Cr steel.

| Element | C  | Cr  | Mo  | Mn  | Si  | V   | Nb  | Al  | Ni  | Ti  | N   | W   | B   | Fe  | Normalizing | tempering |
|---------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|--------------|-----------|
| Wt.     | 0.11| 8.50| 0.85| 0.39| 0.33| 0.23| 0.08| 0.02| 0.01| 0.0065| 0.0045| 0.0039| 0–0.2| Bal.| 1050 °C/0.5 h| 760 °C/3 h |
3. Results and discussion

3.1. Interferences of nucleation and dissolution temperatures of one phase on other phases

The overall effect of boron on nucleation and dissolution temperatures is shown in figure 2(a). Dissolution temperature of M$_2$B (M$_2$B) was severely affected by boron modification, which interfered with dissolution temperature of lave phase (lave), dissolution temperature of Z$_o$-phase (Z$_o$), nucleation temperature of austenite ($\gamma_0$), dissolution temperature of ferrite ($\alpha_0$), dissolution temperature of M$_2$C$_{6}$ (M$_2$C$_{6}$), dissolution temperature of V$_0$-phase (V$_0$), dissolution temperature of Nb$_0$-phase (Nb$_0$), nucleation temperature of liquid (L$_0$), up to 50 ppm of boron modification (figure 2(b)). However, it interfered with Ti$_0$-phase at 900 ppm of boron modification (figure 2(b)). L$_0$ was found the second most affected phase after M$_2$B by boron modification up to 100 ppm. It interfered with austenite dissolution temperature ($\gamma_0$), dissolution temperature of Ti(N,C) (Ti$_0$), nucleation temperature of $\delta$-ferrite ($\delta_0$), and dissolution temperature of M$_2$B (M$_2$B) at boron modification up to 100 ppm (figure 2(b)). Ti$_0$ was observed to interfere with Nb$_0$ and $\delta_0$ at 10 ppm of boron modification. Whereas, it again interfered with $\delta_0$ at 500 ppm of boron modification.

One of the possible mechanisms of interference could be the partitioning effect of boron at a particular concentration and temperature. $\delta_0$ was the second nucleating phase after L$_0$ to be affected by 20 ppm boron modification. After adding more than 10 ppm of boron modification, $\gamma_0$ showed the third most affected nucleating phase. Whereas, the nucleation temperature of martensite ($\alpha_0$) showed the next dependent on boron modification and saturation temperature of liquid (L$_{100}$) showed the least affected. It was also observed that the dissolution temperature of $\delta$-ferrite ($\delta_0$) and L$_{100}$ were overlapped throughout boron modification, which means $\delta$-ferrite was the last solid phase to be dissolved. Similar to previous, overlapping of $\alpha_0$ and M$_2$C$_{6}$ phases was observed (figure 2(c)), which confirmed that the dissolution of ferrite would suppress grain.
refinement and would reduce boundary hardening produced by M23C6 upon boron modification in 9%Cr steels. Figure 2(c) also showed the closeness of \( \alpha_0 \) and the dissolution temperature of MB (MB).

### 3.2. Sensitivity and stability of phase/property by boron modification

In this section, the sensitivity and stability of the phases/properties with itself changing capability are briefly discussed to rationalize the dominancy of one phase/property with respect to others. Analytically, the gradient obtained from the given phase/property equation would provide gradient at boron-free (0 ppm). But physically it cannot be adopted as the value referred to calculate such gradient for boron-free does not lie in the SBC. Hence, a calculation was done from 5 ppm to upper design limit, i.e., 350 ppm of boron modification.

#### 3.2.1. On phases

The sensitivity of boron modification on nucleation and dissolution temperatures of different phases is shown in figure 3. For \( \alpha_0 \), negative sensitivity occurred between 0–5 ppm and 80–300 ppm. While positive sensitivity met between 10–50 ppm and transient sensitivity met at 10 ppm and 50–80 ppm. 10 ppm was the special point for \( \alpha_0 \), where invariability occurred. No susceptibility was observed whereas, full stability of martensite was observed with boron modification, which could be due to the presence of MB at \( \alpha_0 \).

For \( \gamma_0 \), invariability was found between 0–10 ppm after adding more than 10 ppm of boron modification. It showed negative sensitivity till 300 ppm with transient sensitivity between 10–20 ppm. Whereas, no positive sensitivity was found (figure 3). Full Stability of \( \gamma_0 \) found due to the absence of susceptibility. The possible mechanism of such behavior could be the presence of keying capability of different precipitates.

For \( \delta_0 \), negative sensitivity was found between 0–50 ppm and 80–100 ppm. Whereas positive sensitivity was found between 100–200 ppm and transient sensitivity was found between 50–80 ppm and 200–300 ppm.
100 ppm was an invariable point. Due to the mixed nature of sensitivity between intermediate points, δ₀ can be considered as partly stabilized. The possible mechanism for this behavior was the engulfing of MX types precipitates by nucleation of δ-ferrite [20].

For L₀, no positive and transient sensitivities were found, hence, it followed negative sensitivity throughout DBC (figure 3). Whereas, between 20–80 ppm, susceptibility occurred, i.e., at 50 ppm. In our previous study, we observed GB dissolution in 100 ppm steel, hence, this would be called GB susceptibility [21]. After 50 ppm of boron modification, sensitivity continuously deceased, i.e., meeting horizontal asymptote simply called limiting value of L₀. Due to susceptibility, L₀ had no stability after 20 ppm. The possible behavior for this nature was the presence of enough free-boron. It was also reported that 100 ppm was enough to occupy GBs [22]. Hence, GBs were prone to the formation of liquid.

For L₁₀₀, invariability met between 0–5 ppm with positive sensitivity in DBC (figure 3). Instead, negative sensitivity was found between 5–10 ppm and 50–300 ppm and transient sensitivity was found between 10–20 ppm and 20–50 ppm. This mixed sensitivity caused partial stability of L₁₀₀. No susceptibility was observed here. The possible mechanism behind this was variation in the solubility behavior of boron in liquid iron.

For α₀–₀, negative sensitivity was observed between 0–10 ppm and 50–300 ppm with no positive sensitivity (figure 4). Whereas, transient sensitivity was observed between 10–50 ppm. The presence of this transient sensitivity partly disturbed the stability of α₀–₀. For α₀–₀, no invariability and susceptibility were observed. This could be due to the stability of M23C6 carbides, which enhanced with boron modification as it delayed coarsening of M23C6 carbides by replacing carbon atom in its sub-lattice position [8, 23] and resulted in a change in sensitivity thereby leaving partial stability of α₀–₀.

For γ₀–₀, negative sensitivity was observed between 0–50 ppm and 150–300 ppm with no positive sensitivity (figure 4). While transient sensitivity was observed between 50–80 ppm and 100–150 ppm. Hence stability lost temporarily at some ranges. Invariability observed between 80–100 ppm. This effect confirmed the solubility limit of boron in austenite [7, 24], increasing from this modification, borides formation depleted boron from both GBs and γ-matrix.

For δ₀–₀, negative sensitivity was observed between 0–300 ppm with no positive and transient sensitivity (figure 4). Similar signs of sensitivity caused full stability throughout DBC due to the last dissolving phase, hence, no susceptibility and no invariability were encountered.

For M₂₃C₆, negative sensitivity was observed throughout DBC with no positive and transient sensitivity, this effect brought full stability of M₂₃C₆ (figure 4). Hence susceptibility was absent. The possible mechanism behind
this was the partial replacement of carbon atoms in $M_{23}C_6$ carbides, which enriched it with both chromium and boron [14, 16, 25].

For $V_{0.0}$, loss in stability was observed due to the presence of positive and negative sensitivity in DBC (figure 4). Negative sensitivity was observed between 20–50 ppm. Whereas, positive sensitivity was observed between 5–10 ppm and 80–150 ppm. However, transient sensitivity was observed between 10–20 ppm, 50–80 ppm, 150–200 ppm, and 200–300 ppm. Invariability was encountered between 0–5 ppm. It has been discussed in alloy design that it is essential to keep a lower amount of nitrogen contents to get properties better than nitrogen-free 9%Cr steels. This nitrogen content was 45 ppm. But again, it is postulated that TiN is a more thermodynamically stable phase than any other nitride [26]. Hence, this effect caused no stability in V(N,C).

For $Nb_{0.0}$, negative sensitivity was observed between 0–10 ppm (figure 4), whereas, transient sensitivity was found between 10–20 ppm, 50–80 ppm, 150–200 ppm, and 200–300 ppm and positive sensitivity was observed between 50–100 ppm. Invariability was observed between 20–50 ppm. Hence, it caused no stability. The loss of stability is primarily due to boron segregation to PAGBs and its enrichment in $M_{23}C_6$ carbides, which resulted in the non-availability of boron in its sub-lattice.

For $Z_{0.0}$, negative sensitivity was found throughout DBC with an invariable composition between 0–20 ppm, Hence, full stability was retained (figure 4). Such behavior described its strong thermodynamic stability.

For $Ti_{0.0}$, negative sensitivity was observed between 0–5 ppm, and 50–300 ppm. While positive sensitivity was observed between 10–20 ppm (figure 4). Whereas, transient sensitivity was observed in between 5–10 ppm and 20–50 ppm. Hence, stability was disturbed up to 50 ppm as discussed for V(N,C). Susceptibility observed at both 5 ppm and 10 ppm, at these two points, susceptibility in terms of grain-coarsening and grain-refinement would proceed, respectively.

For the lave phase, negative sensitivity was observed throughout DBC with no invariability and susceptibility (figure 4). Hence full stability was retained. For the sigma phase, negative sensitivity was observed with no invariability and no susceptibility throughout DBC, which maintained full stability (figure 4). Based on this behavior, it is concluded that boron does not alter thermodynamic stability of the Z-phase, lave phase, and sigma phase rather than, it was only effective to delay them.

For $M_2B$, positive sensitivity was observed in DBC (figure 4). In this respect, the susceptibility of sustaining high dissolution behavior of $M_2B$ increased between 0–50 ppm, which increased much rapidly at 5 ppm and 10 ppm. At 10 ppm, it increased slightly lesser than 5 ppm and so on. Hence it provided full stability to $M_2B$.

For $M_2B_3$, no negative and transient sensitivity were found (figure 4), instead of former, positive sensitivity was observed between 0–20 ppm. The magnitude of this positive sensitivity decreased at each step and from 50 to 300 ppm, it met with the condition of invariability. Hence, full stability retained through DBC. Such behavior could be due to the availability of free-boron to form borides, which were increased with boron modifications.

For MB, mixed sensitivity was observed, hence, it caused no stability and invariability occurred at 5 ppm (figure 4). In this respect, negative sensitivity was observed between 5–10 ppm. While positive sensitivity was observed between 20–50 ppm and transient sensitivity was observed between 10–20, 50–80, 80–100, 100–150, 150–200, and 200 ppm. This is possible due to interference of $\alpha'_0$ with MB at the initial level of boron modification. With increased boron modification, MB temperature increased, but, it non-linearly provided full martensite stability as discussed.

### 3.2.2. On properties

For both yield strength (YS) and tensile strength (TS), positive sensitivity was observed from 0–300 ppm with no invariability, and no susceptibility (figure 5(a)). Hence, boron modification provided full stability. However, the increment in strength decreased at each step as regards the previous one. But the increment in strength was higher for TS than YS and this difference became weak as boron modification increased. Similar to YS/TS, positive sensitivity was marked for both Vickers hardness number (VHN) and Rockwell hardness at C-scale (HRC) and their magnitude also decreased with an increase in boron. Hence, full stability was also maintained. But the difference in magnitude of VHN and HRC did not meet and maintained a certain difference throughout DBC. This kind of behavior indicated the linear relation between YS/TS and hardness, which was also discussed in alloy design.

Negative sensitivity was observed for linear elongation (%EL) and strain hardening exponent (n) at the absence of both invariability and susceptibility throughout DBC (figure 5(b)). For %EL, the magnitude of sensitivity reduced at each step as the concentration increased. Whereas, for n, the magnitude decreased fast till 20 ppm, after that magnitude decrease was $2.5 \times$ less than the magnitude at 20 ppm and finally magnitude decreased. From this discussion, it can be stated that full stability was retained for %EL. While, stability lost between 20–50 ppm for n and at this point, susceptibility was observed.

The sensitivity of phases/properties was discussed, which is more sensitive towards boron modification for nucleation and dissolution temperature. It can be marked that some of the gradients, i.e., sensitivity
(exponential/power-law/parabolic laws) are still the function of boron and but, for linear, it is not. Each one tells us about the rate of change of the previous function, i.e., change in phase/property. But its second derivative, i.e., change in sensitivity tells how fast the tangent is moving, i.e., how the rate of phase/property change is itself changing, i.e., change of slope, i.e., how uncertainty in phase/property output of the alloy design model attributed different uncertainty source of boron modification (figures 5(c)–(d)). For the linear function, the second gradient is zero, i.e., no change by itself. Whereas, for others, it existed. It helps in determining and optimizing the nature of half-life ($H_v$) and DBC (maximizing, minimizing or points of inflection). The definition of half-value was reported in alloy design.

The effects of boron/VHN/HRC on minimizing/maximizing the phase/property behavior based on their second derivative are shown in table 2. In this table, some of the phase/property was neither maximizing nor minimizing (NMNM), i.e., point of inflexion (PI) existed throughout DBC. These phases were $\alpha_0$, L$_{100}$, $\delta_0$, Z-phase, and sigma phase, their values in DBC confirmed their minimization as regards boron modification. The properties were YS/TS, which were found to be a case of maximization as regards boron, HRC, and HVN. Similar to YS/TS, VHN, and HRC showed maximization as regards boron, whereas, $%\text{El}$ and n showed minimization as regards boron. But the magnitude for n was weak.

For $\gamma_0$, it decreased for 20 ppm and came back to PI at 50 ppm and remained constant. For $\xi_0$, no definite behavior was observed rather than tangent movement reduced after 80 ppm. For $L_0$, a tangent movement was observed between 10–100 ppm. Before and after this range, PI was observed. For, $\alpha_{0.0}$, tangent movement increased/decreased up to 80 ppm and remained constant after that. For $\gamma_{0.0}$, a tangent movement dominated till 80 ppm and tried to minimize after that. For $M_2\text{C}_6$, a tangent movement decreased till DBC, but, never reached to PI. For $V_{0.0}$, a large tangent movement was observed throughout DBC. For $Nb_{0.0}$, it increased up to 20 ppm, then decreased till 80 ppm, after that, it became almost constant, i.e., tending to PI. Whereas, for $Ti_{0.0}$, tangent movement decreased till 50 ppm, after that, it came to PI. For both $M_1B_2/M_3B$, it started increasing from 5 ppm to 80 ppm, after that, change was zero (PI). For MB, a high tangent movement was observed, which was reduced with an increase in boron modification.

For YS/TS/VHN/HRC, it was observed that tangent movement increased with boron modification, but, never reached to PI in the DBC. It could be possible as all these properties represent the strength of phases in 9%
Cr steels. Whereas for %El and n, the tangent movement suddenly dropped till 50 ppm, after that, it slowly dropped till 100 ppm and finally reached to PI.

Furthermore, in many phases/properties, an increase in boron modification caused less effectiveness or zero effectiveness on tangent movement, i.e., self-changing capability of phase/property. This could be explained by observing figure 6, which showed that band of phase nucleation/dissolution temperatures drastically reduced for the DBC as regard SBC (∼52%). Whereas, for properties, the reduction was ∼32% for the DBC as regard SBC and ∼39% reduction as regards phase temperatures. It means that only 350 ppm boron modification was enough to alter the above numbers for phase/properties. Hence, it can be concluded that high boron modification was somewhat effective in altering phase temperatures, but, it was not much helpful for properties. Before this work, there was a need to limit boron modification, which has now been fulfilled. Based on the above

Figure 6. Plots of (a) percent change in nucleation/dissolution temperature of phases and (b) percent change in properties as regards boron free 9%Cr steels at an upper limit of SBC and DBC (computational data).

Table 2. Implicit nature of boron, HRC, and VHN for different phases/properties.

| Phase     | Boron Nature     |
|-----------|------------------|
| δ_{0-0}   | NMNM + minimizing |
| L_{100}   | NMNM             |
| α'_{0}    | NMNM             |
| Z-Phase   | NMNM             |
| Sigma     | NMNM             |
| δ_{0}     | Minimizing + Maximizing |
| Lave phase| Minimizing       |
| M_{23}C_{6}| Minimizing      |
| γ_{0-0}   | Minimizing       |
| Ti(N,C)   | Minimizing       |
| δ_{α_{0}} | Minimizing       |
| L_{α}     | Minimizing       |
| M_{2B}    | Maximizing       |
| M_{3B2}   | Maximizing       |

| Properties | Boron Nature |
|------------|--------------|
| VHN        | Maximizing   |
| YS         | Maximizing   |
| TS         | Maximizing   |
| HRC        | Maximizing   |
| n          | Minimizing   |
| %El        | Minimizing   |

| Properties | HRC Nature |
|------------|------------|
| %El        | Minimizing |
| YS         | NMNM       |
| TS         | NMNM       |

| Properties | VHN Nature |
|------------|------------|
| %El        | Minimizing |
| YS         | NMNM       |
| TS         | NMNM       |
analyses, it is confirmed that boron modification in 9%Cr steels provided an optimum sandwich of phase-strength between DBC.

4. Conclusions

The effects of boron modifications in the 9%Cr steels in terms of sensitivity and stability were continued and briefly described. In this respect, the various analytical equations as reported in alloy design were used to evaluate sensitivity/stability. As the upper design limit of boron was fixed as 350 ppm, hence, DBC was adopted for this calculation. In addition to previous, interference of nucleation or dissolution temperature of one phase on the rest of phases was discussed. At last, the self-changing or slope of the slope was found to confirm optimum structure-property for 9%Cr steels. The following conclusions were succinctly drawn as regards boron modifications.

- $M_2B$ was a most affected phase, which interfered with nine phases at 50 ppm of boron modification, whereas, it interfered with $Ti_{0.0}$ at 900 ppm of boron modification. $L_0$ was second most affected followed by $\delta_0$ and $\gamma_0$ by interfering with four phases up to 100 ppm of boron modification. $Ti_{0.0}$ interfered with two phases up to 10 ppm of boron modification and with phase at 500 ppm of boron modification. $L_{100}$ showed the least dependency. Overlapping of $\delta_{0.0}/L_{100}$ and $\alpha_{0.0}/M_{23}C_6$ were observed. $\delta$-ferrite was the last solid phase to be dissolved.

- Positive/negative/transient sensitivity found in $\alpha'_{0.0}$, $\delta_0$, $L_{100}$, $V_{0.0}$, $Nb_{0.0}$, $Ti_{0.0}$, and MB, followed by negative/transient sensitivity found in $\gamma_0$, $\alpha_{0.0}$, $\gamma_{0.0}$. Whereas, only negative sensitivity found in $L_0$, $\delta_{0.0}$, $M_{23}C_6$, $Z_{0.0}$, lave phase, sigma phase, %El, and n and only positive sensitivity was found in $M_2B$, $M_3B_2$, $YS$, $TS$, $VHN$, and HRC.

- Invariability observed with an invariable composition(s) in $\alpha'_{0.0}$ (10 ppm), $\gamma_0$ (0–10 ppm), $\delta_0$ (100 ppm), $L_{100}$ (0–5 ppm), $\gamma_{0.0}$ (80–100 ppm), $V_{0.0}$ (0–5 ppm), $Nb_{0.0}$ (20–50 ppm), $Z_{0.0}$ (0–20 ppm), and $M_3B_2$, (50–300 ppm). Whereas, susceptibility met in $L_0$ (20–80 ppm), $Ti_{0.0}$ (5–10 ppm), $M_2B$, (0–50 ppm), and MB (5 ppm).

- Full stability encountered for $\alpha'_{0.0}$, $\gamma_0$, $Z_{0.0}$, $M_2B$, lave, $M_3B_2$, sigma, $YS$, $TS$, $VHN$, $HRC$, and %El. Nevertheless, partial stability witnessed for $\delta_0$, $L_0$, $L_{100}$, $\alpha_{0.0}$, $\gamma_{0.0}$, $Ti_{0.0}$, and n. Whereas, no stability noticed for $V_{0.0}$, $Nb_{0.0}$, and MB. Boron modification did alter the stability of detrimental phases rather than delayed their formations.

- Tangent movement calculation by the second derivative of phase/property was used to further understand the optimizing nature of Hv and DBC (i.e., maximizing, minimizing or PI) and succinctly discussed. Its value was nil for linear function, and for others, existed.

- Minimization observed for $\alpha'_{0.0}$, $\gamma_0$, $L_{100}$, $\alpha_{0.0}$, $\gamma_{0.0}$, $\delta_{0.0}$, $L_{100}$, $M_{23}C_6$, $Z_{0.0}$, $Ti_{0.0}$, lave, sigma phase, %El, and n in DBC. While maximization observed for $M_2B$, $M_3B_2$, $HRC$, $VHN$, $YS$, and TS and mixed for $\delta_0$, $V_{0.0}$, $Nb_{0.0}$, and MB.

- Band of phase/property decreased by ~52%/32%, respectively, for the DBC as regard SBC and verified upper limit of 350 ppm boron modification was best for 9%Cr steels.

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Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.
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