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

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Abstract
This paper was dedicated to rationalizing the effect of boron modifications in alloy design of 9%Cr steels. It acquired the values of nucleation and dissolution temperatures, and mechanical properties (further referred to as properties) from computational software. Subsequently, properties were validated for five different boron modifications and were used to analytically model the behavior of boron with their computationally evaluated values. Different mathematical functions were designated for phases/properties. All phases revealed decay behavior except borides, which depicted growth behavior and no relationship for V(N,C)/Nb(C,N)/MB. Whereas, properties exhibited growth behavior, except for linear elongation and strain hardening coefficient. Besides, some phases/properties showed piecewise behavior. For an in-depth understanding of the effects of boron modifications, saddle point(s) and zone of saturation(s) were determined. A decrease in nitrogen contents as per ASTM recommendations to ppm level was found effective to increase boron concentration. This combination avoided BN and concurrently improved properties. Boron in small amounts was found effective due to the decreasing nature of multiplication factors of analytical models. Half value as a design parameter was selected. For phase and property considerations, it was 346–468 ppm and 204–239 ppm, respectively. Due to the scope of improving properties, the gradient-based optimization approach was adopted, and the upper design limit of boron was fixed as 350 ppm.

Nomenclature and definitions

| Symbol | Description |
|--------|-------------|
| Ac1 | °C | Lower critical temperature |
| Ac3 | °C | Upper critical temperature |
| α | — | Ferrite |
| α0-0 | °C | Dissolution temperature of ferrite |
| α′ | — | Cr-rich Martensite |
| α0 | °C | Nucleation temperature of Cr-rich Martensite |
| CALPHAD | — | Calculations of Phase Diagrams |
| CDT | [PPM]–1 | The decay constant for dissolution temperature |
| CNT | [PPM]–1 | The decay constant for nucleation temperature |
| DBC | PPM | Design boundary condition, 0–350 ppm |
| εδ | °C | Nucleation temperature of δ-ferrite |
| εδ-0 | °C | Dissolution temperature of δ-ferrite |
| %EL | % | Linear elongation |
1. Introduction

P91 steel is ferritic/martensitic steel having excellent properties and corrosion resistance. Its prime usage is in the thermal and nuclear energy industries in steam carrying pipes and pressure vessels. The perpetual demand to increase the efficiency of power-plants with less CO₂ emissions has increased the operating temperature from 650 °C to 760 °C [1]. The operating temperature has been increased, but ferritic/martensitic steels like 9%Cr steels are still promising in both technological and economic perspectives at lower temperature range, i.e., 570 °C–625 °C [2, 3]. During service, these steels experience harsh thermo-mechanical conditions in power-plants, which enable microstructural instability [4, 5]. Attempts have been given to reduce this instability by alloy design and optimizing heat treatment processes [6]. Various microalloying elements in 9%Cr steels play a key role in high-temperature properties [7]. It has been optimized with V/Nb, which form MX type carbides/carbo-nitrides to enhance properties during service [8]. The concentration of Ti is kept low as Ti forms highly stable nitride, but, its carbide deteriorates properties [9]. According to ASTM A335/ A335M−18b (simply referred to as ASTM), Mn addition in 9%Cr steels should not exceed 0.5% to keep wider transformation temperatures, i.e., a large difference between lower transformation temperature (Ac₃) and upper transformation temperature (Ac₁). It also alters martensite start temperature leading to high risk of retained austenite. Ni concentration was reduced to 0.01% to give additional persistency to phases in 9%Cr steels [7]. Segregating elements like phosphorous, sulfur, copper, etc are kept in tramp by adopting modern steel manufacturing methods to avoid grain boundary (GB) embrittlement [10]. However, the effects of boron modifications have still been mysterious and under key investigations due to its both interstitial and substitutional nature [2, 6, 11]. This alloy modification in 9%Cr steels is expected to tolerate enhanced service temperature of the modern power-plant industry [12, 13]. It is well understood that the characterization of boron at the ppm level is difficult rather than
to observe its effect [14]. Such experimentations require high cost (cost associated with controlling composition, phases, and high rolling cost of plates, etc.), which has been handicapping these studies to realize into practice. With the development of high-speed computational modeling and its increased reliability by various software have found minimizing dependency on experimentation. This revolution has attracted not only a high number of research agencies but also the finest minds worldwide. Therefore, there is an enthusiasm to analytically model the metallurgical and mechanical behaviors of 9%Cr steels as regards boron modifications from the values obtained from high-end computation software. This is feasible due to the explicit prediction of phase/property in studied boundary conditions (SBCs), i.e., 0–2000 ppm. Computational software packages like thermocalc and Java-based Materials Properties (JMatPro) were chosen to study the effects of boron modifications in 9%Cr steels by pre-screening a set of compositions. Both of these packages are updated from time to time and validated by many researchers [1, 15–17]. This paper induces an in-depth analysis of the effects of boron modifications in alloy design of 9%Cr steels via nucleation and dissolution behaviors of different phases formed with the help of Thermocalc. Properties were obtained by experimentation, i.e., tensile testing and hardness testing at room temperature for five boron modified 9%Cr steels and they were compared with computed values of JMatPro. However, an evaluation of properties for a higher concentration of boron, i.e., boron >100 ppm was not possible due to the unavailability of these materials. Finally, the values of different phases and properties were analytically modeled to understand the effects of boron modifications in 9%Cr steels.

2. Materials and methods

2.1. Composition and thermal history of materials

The chemical composition and heat treatment history of 9%Cr steels are given in table 1. Heat treatment given to all 9%Cr steels was done as recommended in ASTM, but, this code does not state about time for each heat-treatment process. Time for heat treatment was selected from our previous work [16, 18].

2.2. Computational methodologies

Thermocalc follows the calculation of phase diagrams (CALPHAD) approach to predict various phases that are extrapolated from binary and ternary systems into a multicomponent system. Thermocalc TCFE9 thermodinamic and kinetic databases containing mobility database MOBFE4 have recently updated for various types of steels [19, 20]. TCFE9 is a validated database provided by thermocalc, which also contains a database for boron. During thermocalc calculations, intermediate compounds were ignored to minimize the number of phases and only thermodinamic stable phases were considered. To obtain accurate results, maximum iteration was given as 500 during thermocalc calculation. Nucleation and dissolution behaviors of different phases were computed by Thermocalc. During thermodynamic computations, increment in boron modification was taken as 0 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 80 ppm, 100 ppm, 150 ppm, 300 ppm, 500 ppm, 800 ppm, 1000 ppm, 1500 ppm, and 2000 ppm (referred to as SBC). This variation was kept to analytically model the effects of boron modifications on nucleation and dissolution behaviors of various phases in 9%Cr steels. Analytical modeling based on variation in a small range of boron modifications would mask the effects of boron, which would lead to erroneous results. Such results have been discussed in this work. Rockwell and Vickers hardness values and tensile properties were computed with the help of JMatPro at a strain rate of $1 \times 10^{-2}$ s$^{-1}$ in 0–2000 ppm (SBC). These values were further to compare with experimental observations as stated below.

2.3. Experimental methodologies

To validate properties (tensile/hardness) obtained from JMatPro, mechanical testing of 5 types of 9%Cr steel having 0 ppm, 10 ppm, 20 ppm, 50 ppm, and 100 ppm boron was carried out. Whereas, Rockwell hardness testing was performed at the C scale with 150 kg load. Vickers microhardness testing was done at 50 g load with 15 s of dwell time. To carry out, both the hardness testing, samples were polished by using emery paper (80 to up to 1200grit) followed by cloth polishing. All the hardness results presented in the manuscript were the average hardness value of 10 indentations. Cylindrical samples of five boron modified 9%Cr steels were prepared for uniaxial tensile tests at room temperature as per ASTM E8M. These samples were only polished by using emery paper (0 to 1200grit). Instron 8862 servo–electric universal testing machine having a load–bearing capacity of 100 kN was employed for tensile tests. The linear strain was measured by using an extensometer at a strain rate of $1 \times 10^{-2}$ s$^{-1}$ having gauge length 12.5 mm and the range of travel was ±100%.

After tensile testing, engineering-stress versus engineering-strain diagrams for all boron modified samples were computed with the help of JMatPro at a strain rate of $1 \times 10^{-2}$ s$^{-1}$ and compared with experimental data. A satisfactory match was observed between experimental and predicted data. Therefore, experimental data with predicted data were used to analytically model properties. During modeling, general mathematical functions were adopted as regards boron modification and properties. If a quantity was falling rapidly towards zero,
Table 1. Chemical composition, normalizing, and tempering conditions of 9%Cr steel.

| Element | C  | Cr | Mo | Mn | Si | V  | Nb | Al | Ni | Ti | N  | W  | Fe  | Normalizing | tempering |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|-----|-------------|----------|
| Wt.%    | 0.11 | 8.50 | 0.85 | 0.39 | 0.33 | 0.22 | 0.08 | 0.02 | 0.01 | 0.006 | 0.004 | 0.003 | Bal. | 1050°C/0.5 h | 760°C/3 h |
without even reaching zero, then exponential decay or power-law type model was adopted based on its fitting function.

3. Results and discussion

3.1. Effects of boron modifications on nucleation behavior of phases (Computation approach)

Corresponding values obtained from the effects of boron modification on nucleation temperature of martensite, austenite, δ-ferrite, and liquid phases were analytically modeled in SBC. The nature of the nucleation temperature of these phases followed linear decay, exponential decay, and mixed behavior as discussed below.

3.1.1. Cr-rich Martensite (α′)

Cr-rich martensite (α′) is nothing, but, martensite having high chromium concentration. Martensitic transformation in lower carbon (0.1 wt.%) steel brings BCC type crystal structure rather than BCT [21]. Addition of boron delayed formation of ferrite. But this delay brought an increase in the nucleation temperature of α′ (α′₀) [22–24]. Figure 1(a) showed the persistence of α′₀ by modifying with 50 ppm boron, i.e., martensite nucleation temperature increased till 50 ppm. But further, an increase in boron was cutting-off this effect and α′₀ started reducing as regards boron modification. Zone of saturation (ZOS) is defined as a range of variation in boron modifications, in which either nucleation or dissolution temperature or property does not change appreciably. Whereas, saddle point is the point, where, zero gradient of nucleation or dissolution temperature or property occurs, i.e., a point, from where, the slope of thermodynamic/property curve changes. It can be observed that change in α′₀ was not so high until from 0–50 ppm (figure 1(a)), hence, it might be considered as ZOS, whereas 50 ppm was saddle point. Further, an increase in boron into 9%Cr steels from 50 ppm started decreasing α′₀ linearly till 2000 ppm (equation (1)). In this respect, it followed a negative α′₀ gradient, i.e., the slope was 0.014. Therefore, this reduction phenomenon is referred to as linear decay.

\[ \alpha_0' = 361.5 - 0.014 \times \text{Boron}[\text{PPM}] \]  
\[
(50 \leq \text{Boron}[\text{PPM}] \geq 2000)
\]
3.1.2. Austenite ($\gamma$)

Figure 1 (b) represents the nucleation temperature of austenite (\(\gamma_0\)), which is also called \(\text{Ac}_3\) for steel. This figure showed that boron modifications in 9%Cr steels did influence the \(\text{Ac}_3\) temperature till 20 ppm, i.e., lied in ZOS. With a slight increase in boron concentration from 20 ppm, \(\gamma_0\) started decreasing exponentially (equation (2)). Hence, 20 ppm was a saddle point. Exponential decay is the inverse of exponential growth function, which means, it is driving exponential function in the opposite direction. The decay constant for nucleation temperature (\(C_{\text{NT}}\)) for \(\text{Ac}_3\) was \(1.8 \times 10^{-3}\) with a \(\gamma_0\) amplitude of 11.3. 

\[
\gamma_0 = 820 + 11.3 \exp^{-1.8 \times 10^{-3} \times \text{Boron}[\text{PPM}]}
\]  
\((20 \leq \text{Boron}[\text{PPM}] \geq 2000)\)

3.1.3. $\delta$-ferrite

Figure 1 (c) shows that an addition of boron from 0 to 10 ppm did not influence the nucleation temperature of $\delta$-ferrite ($\delta_0$). However, a slight increase in boron by 10 ppm started decreasing $\delta_0$ until 80 ppm exponentially (equation (3)). \(C_{\text{NT}}\) and $\delta_0$ amplitude were 1.176 and 533280, respectively. From 100 to 200 ppm and 200 to 500 ppm, it followed the asymmetric Gauss function. After 500 ppm, $\delta_0$ reversed its nature and started increasing exponentially with boron having $C_{\text{NT}}$ of \(1.16 \times 10^{-3}\) and a negative $\delta_0$ amplitude of 53 (equation (4)). As exponential function was increasing in this range, it is exponential growth function. But due to mathematical constraint, which arose from saturation tendency of phase/property at higher boron modifications obliged it to show in terms of exponential decay. If the sign of both decay constant and amplitude is negative then the function follows analogous to exponential growth, where, it decays from the uppermost value of dissolution temperature, i.e., opposite of exponential decay. From 0 to 2000 ppm, there were three saddle points, i.e., at 80 ppm, 200 ppm, and 500 ppm. It is noted that from 0 to 10 ppm and 20 to 80 ppm, the boron effect was nil on $\delta_0$, and these ranges were called ZOS. Such behavior was referred to as mixed behavior and combined function is called a piecewise function. This kind of function is defined by sub-functions as functional behavior of phase/property switching governed equation at some point of SBC. 

\[
\delta_0 = 1228 + 533280 \exp^{-1.176 \times \text{Boron}[\text{PPM}]}
\]  
\((10 \leq \text{Boron}[\text{PPM}] \geq 80)\)

\[
\delta_0 = 1263 - 53 \exp^{-1.16 \times 10^{-3} \times \text{Boron}[\text{PPM}]}
\]  
\((500 \leq \text{Boron}[\text{PPM}] \geq 2000)\)

3.1.4. Liquid

Figure 1 (d) shows that boron modifications up to 20 ppm reduced the nucleation temperature of the liquid ($L_0$) linearly with a negative gradient of 1.19923 (equation (5)). However, further boron modifications from 20 to 300 ppm reduced $L_0$ behavior from linear decay to an exponential decay (equation (6)). The $L_0$ amplitude and $C_{\text{NT}}$ were 2469 and 0.1154, respectively. At last, $L_0$ returned to its original behavior, i.e., linear decay with a negative gradient and an intercept as $4.4 \times 10^{-3}$ and 1194.7, respectively, (equation (7)). Therefore, this behavior resembled a piecewise function. No ZOS was observed for $L_0$, but, 20 ppm and 300 ppm were marked as saddle points. 

\[
L_0 = 1460 - 1.19923 \times \text{Boron}[\text{PPM}]
\]  
\((0 \leq \text{Boron}[\text{PPM}] \geq 20)\)

\[
L_0 = 1193 + 2469 \exp^{-0.1159 \times \text{Boron}[\text{PPM}]}
\]  
\((20 \leq \text{Boron}[\text{PPM}] \geq 300)\)

\[
L_0 = 1194.7 - 4.4 \times 10^{-3} \times \text{Boron}[\text{PPM}]
\]  
\((300 \leq \text{Boron}[\text{PPM}] \geq 2000)\)

3.2. Effects of boron modifications on dissolution behavior of phases (computational approach)

3.2.1. Ferrite ($\alpha$)

The dissolution temperature of ferrite ($\alpha_{0-3}$) is the \(\text{Ac}_1\) for steel. Figure 2 (a) shows up to 10 ppm, there was no effect of boron on \(\alpha_{0-3}\), i.e., it was in ZOS. But further increased in boron modification by 10 ppm reduced the \(\alpha_{0-3}\) parabolically (equation (8)). The intercept and coefficient of a square of boron were positive, whereas, the coefficient of boron was negative. The value of the square of boron governed the shape/nature of the curve and its coefficient was less than one and close to zero. This leads to a fat and upward curve. Nevertheless, the negative value of boron did not intuit much rather than translating parabola, which did not show dependency on boron modifications, i.e., minimizing its gradient. However, the saddle point for \(\alpha_{0-3}\) was 20 ppm and the ZOS was
0–20 ppm. Negligible drop in $\alpha_{0-0}$ could be due to the segregation of boron around prior austenite GBs (PAGBs), which suppressed the ferrite nucleation at GBs/sub-GBs (SGBs) [25] for 0–20 ppm. But for 50 ppm, $\alpha_{0-0}$ increased, and then, dropped by a further increase in boron. The change in the beneficial effects of boron at PAGBs was altered, because, segregated boron started the formation of different types of borides. Therefore, the unavailability of free-boron and availability of borides made PAGBs more susceptible to the formation of $\alpha$.

\[
\alpha_{0-0} = 876 - 0.37 \times \text{Boron[PPM]} + 1 \times 10^{-5} \times \text{Boron[PPM]}^2
\]  
\[ (20 \leq \text{Boron[PPM]} \leq 2000) \]

3.2.2. Austenite ($\gamma$)
As observed in figure 2(b), up to 10 ppm, boron did not affect the austenite dissolution temperature ($\gamma_{0-0}$). Slight increment in boron from 10 ppm started decreasing $\gamma_{0-0}$ exponentially with a decay constant for dissolution temperature ($C_{DT}$) of 0.135, which saturated upon reaching 100 ppm (figure 2(b)) (equation (9)). $\gamma_{0-0}$ further dropped from 100 ppm to 2000 ppm by following the power-law having a negative exponent 0.0082 (equation (10)). In other words, it followed the piecewise function. In this respect, 100 ppm was saddle point and ZOS was between 0–10 ppm and 50–80 ppm.

\[
\gamma_{0-0} = 1386.5 + 21 \exp^{-0.135 \times \text{Boron[PPM]}}
\]  
\[ (10 \leq \text{Boron[PPM]} \leq 100) \]

\[
\gamma_{0-0} = 1441 \times \text{Boron[PPM]}^{-0.0082}
\]  
\[ (100 \leq \text{Boron[PPM]} \leq 2000) \]

It is also reported that boron modifications suppressed $\gamma_{0}$ and $\gamma_{0-0}$ [26]. Whereas, if the heating rate was increased from slow to high then for fixed boron content, it increased. The reason behind this was an enhancement in boundary stability, which caused a decrease in $\gamma_{0}$ and $\gamma_{0-0}$ temperatures [27].

3.2.3. $\delta$-ferrite
On the variation of boron from 0 to 800 ppm, a dissolution temperature of $\delta$-ferrite ($\delta_{0-0}$) decreased linearly having a negative gradient of 0.0111 (equation (11)). Though, its nature shifted from linear decay to an exponential decay for 800 ppm to 2000 ppm (equation (12)) (figure 2(c)). The $C_{DT}$ and $\delta_{0-0}$ amplitude during

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**Figure 2.** Effects of boron addition on dissolution temperatures of (a) ferrite, (b) austenite, (c) delta-ferrite, and (d) Liquid formation [100%] in 9%Cr steels (computational data).
the exponential decay were $7.1 \times 10^{-3}$ and 3691, respectively. In this respect, 800 ppm was saddle point, and ZOS was absent here.

$$\delta_{0-0} = 1510.5 - 0.0111 \times \text{Boron}[\text{PPM}] \quad (0 \leq \text{Boron}[\text{PPM}] \geq 800)$$

$$\delta_{0-0} = 1489 + 3691 \exp^{-7.1 \times 10^{-3} \times \text{Boron}[\text{PPM}]} \quad (800 \leq \text{Boron}[\text{PPM}] \geq 2000)$$

3.2.4. Liquid [100%]

Figure 2(d) shows the addition of boron up to 20 ppm did not influence the liquid saturation temperature ($L_{100}$), but, further increase in boron linearly decayed liquid saturation temperature in 9%Cr steels with a negative slope of 0.01196 (equation (13)). In this respect, 20 ppm was a saddle point with 0–20 ppm as ZOS.

$$L_{100} = 1510.7 - 0.01196 \times \text{Boron}[\text{PPM}] \quad (20 \leq \text{Boron}[\text{PPM}] \geq 2000)$$

3.2.5. M$_{23}$C$_6$

The dissolution temperature of M$_{23}$C$_6$ dropped exponentially, where 0 to 10 ppm and 20 to 100 ppm were ZOS (figure 3(a)). The CDT and M$_{23}$C$_6$ amplitude during exponential decay were $7 \times 10^{-4}$ and 43, respectively (equation (14)).

$$M_{23}C_6 = 829 + 43 \exp^{-7 \times 10^{-4} \times \text{Boron}[\text{PPM}]} \quad (0 \leq \text{Boron}[\text{PPM}] \geq 2000)$$

The presence of carbon in 9%Cr steels encourages the precipitation of a large amount of Cr-rich M$_{23}$C$_6$ carbides. These carbides provide keying to GBs/SGBs resulting in improved properties [8]. However, during service, the coarsening of M$_{23}$C$_6$ carbides due to high carbon diffusion in them leads to a breakdown in properties [21, 28]. It is reported that fine M$_{23}$C$_6$ carbides were beneficial in improving properties, which were achieved by boron modifications [11]. Figure 3(a) shows that despite modifying boron at the ppm level, the dissolution temperature of M$_{23}$C$_6$ was still higher than service temperature.

3.2.6. V(N,C)

No definite relationship was observed between the dissolution temperature of V(N,C) ($V_{0-0}$) and boron modifications (figure 3(b)). Boron modification up to 20 ppm didn’t affect $V_{0-0}$, but, slightly reduced at 50 ppm, and latter followed an increase in $V_{0-0}$ till 150 ppm. Thereafter, $V_{0-0}$ decreased at 200 ppm and so on, the $V_{0-0}$ behavior kept on changing till 2000 ppm. Formation of MX type V(N,C) is desirable to improve properties in 9%Cr steels. However, Al is preferred due to its deoxidizing nature during the melting practice of 9%Cr steels.
which forms aluminum nitride (AlN) during service at the expense of both dissolved nitrogen from matrix and fine V(N,C). Because Al is a strong nitride forming element that causes a loss in solid solution hardening due to precipitation hardening. [9]. Hence, Al concentration kept in the trace.

3.2.7. Z-phase
The dissolution temperature of Z-phase ($Z_{0.0}$) showed a linear decay behavior with boron modifications (figure 3(c)). It was found that $Z_{0.0}$ was dropped with a negative gradient of 0.0134 (equation (15)). In this behavior, 10 ppm was a saddle point with 0–10 ppm as ZOS.

$$Z_{0.0} = \frac{724 - 0.0134 \times \text{Boron}[PPM]}{0 \leq \text{Boron}[PPM] \leq 10}$$  \hspace{1cm} (15)$$

$$Z_{0.0} = \frac{724 - 0.0134 \times \text{Boron}[PPM]}{0 \leq \text{Boron}[PPM] \geq 2000}$$

It is known that MX type carbo-nitrides improve properties, but, its consumption through Cr diffusion resulted in Z-phase formations that keep on coarsening till all MX exhausted. Hence, degraded properties in 9% Cr steels are due to an absence of MX phases, which finally promoted preferential recovery of martensite [9]. The occurrence of this phase is more predominant in high nitrogen steels. Therefore, nitrogen contents in 9% Cr steels were minimized.

3.2.8. Nb(C,N)
Similarly, no relationship was found between the dissolution temperature of Nb(C,N) ($Nb_{0.0}$) and boron modifications (figure 3(d)). Boron addition decreased $Nb_{0.0}$ till 10 ppm and after that, $Nb_{0.0}$ increased till 100 ppm. At 150 ppm of boron modification, $Nb_{0.0}$ again dropped, and the latter increase at 200 ppm exhibiting cyclic behavior. This behavior was continued, till 2000 ppm. Nb(C,N) is one of those precipitates, which provides keying of GBs during normalizing, leading to grain refinement. Whereas, during service, they retard the movement of GBs/SGBs, resulting in improved properties [9].

3.2.9. Ti(N,C)
As observed in figure 3(e), no relationship between the dissolution temperature of Ti(N,C) ($Ti_{0.0}$) and boron was observed, till 20 ppm. But afterward, $Ti_{0.0}$ decreased by following an exponential decay (equation (16)). In this respect, 20 ppm was the saddle point, and 10–20 ppm was ZOS. However, $C_{Ti}$ and $Ti_{0.0}$ amplitude for this exponential nature were $2.4 \times 10^{-3}$ and 48, respectively.

$$Ti_{0.0} = 1223 + 48 \exp^{-2.4 \times 10^{-3} \times \text{Boron}[PPM]}$$ \hspace{1cm} (16)$$

$Ti$ predominantly forms titanium nitride (TiN) during service, which is similar to AlN. But, the persistence of TiN is up to its melting point as its solubility in $\alpha$-Fe is low. It means that fine TiN is an essential precipitate to enhance properties. However, controlling its dispersion by appropriate heat treatment is difficult due to its highly stable nature [8]. Thus, the formation of AlN is least expected and therefore was excluded from present motivation in the current alloy design.

3.2.10. Lave phase
Lave phase showed two types of dependency, one was linear decay and later was exponential decay. From 0 to 500 ppm, the lave phase showed linear decay with a negative slope of 0.13 (equation (17)) (figure 3(f)). After 500 ppm to 2000 ppm, the lave phase showed exponential decay type dependency with a negative decay rate of $6 \times 10^{-3}$ and amplitude of 1734 (equation (18)). In this respect, 500 ppm was saddle point, and between 1500–2000 ppm was ZOS.

$$Lave = 624 - 0.13 \times \text{Boron}[PPM]$$ \hspace{1cm} (17)$$

$$Lave = 463.4 + 1734 \exp^{-6 \times 10^{-3} \times \text{Boron}[PPM]}$$ \hspace{1cm} (18)$$

Lave phase retards properties during service as it decreases the solid solution of Mo in the ferrite matrix [29]. Hence, carbo-nitrides are essential to resist coarsening and loss of solid solution strengthening during service exposure [28]. However, high nitrogen content forms MX, which ultimately converts into unwanted Z-phase by Cr diffusion [8].

3.2.11. $M_2B$
Figure 4(a) shows 5–10 ppm did not affect the dissolution temperature of $M_2B$. But the further increase from 10 ppm started increasing the dissolution temperature of $M_2B$ by exponential growth having $C_{Ti}$ and negative $M_2B$ amplitude of 0.0769 and 1212, respectively (equation (19)). In this respect, 5–10 ppm was ZOS, and 10 ppm
was the saddle point. This function is exponential growth function as defined, earlier.

\[
\text{M}_2\text{B} = 1225 - 1212e^{-0.0769 \times \text{Boron}[\text{PPM}]}
\]

\((0 \leq \text{Boron}[\text{PPM}] \leq 2000)\)  

3.2.12. M\textsubscript{3}B\textsubscript{2}

Figure 4(b) shows the exponential type relationship between the dissolution temperature of \(\text{M}_3\text{B}_2\) and boron having a negative amplitude of 298 and \(C_{\text{CT}}\) of 0.22 from 5 to 2000 ppm (equation (20)). During 100–2000 ppm, ZOS was observed without a saddle point. This phase also followed exponential growth but shown in terms of exponential decay as explained, earlier.

\[
\text{M}_3\text{B}_2 = 1076 - 298 \exp^{-0.22 \times \text{Boron}[\text{PPM}]}
\]

\((0 \leq \text{Boron}[\text{PPM}] \geq 2000)\)

The formation of borides at GBs/SGBs reduces the availability of free-boron at GBs/SGBs, which caused an increase in GBs energy [2]. This increase in GB energy with boride formations would provide high mechanical strength.

3.2.13. MB

MB type boride did not show any definite relationship between its dissolution temperature and boron (figure 4(c)). However, it can be observed that the dissolution temperature had cyclic nature, which continuously changed from 0 to 200 ppm, 200–1000 ppm, and so on.

3.2.14. Sigma phase

Sigma phase showed a linear decay type dependency between its dissolution temperature and boron modifications (figure 4(d)). However, the dissolution temperature decreased with a negative gradient of 0.0124 (equation (21)).

\[
\Sigma = 411 - 0.0124 \times \text{Boron}[\text{PPM}]
\]
3.3. Properties of boron modified 9%Cr steels

3.3.1. Hardness values of different boron modified 9%Cr steels

(a) Experimental hardness

Rockwell and Vickers hardness of 0, 10, 20, 50, and 100 ppm boron modified 9%Cr steels were experimentally determined, and their average values are collated in table 2. It was observed that hardness increased as the boron modification level increased. The percentage increase in hardness for 10, 20, 50, and 100 ppm boron was 5.65, 6.84, 8.7, and 11.14% as regards boron-free 9%Cr steel, respectively.

(b) Computed hardness

Average Rockwell and Vickers hardness values for 0–2000 ppm were computed by JMatPro and have been shown in table 2 and figure 5. Hardness value for 5, 10, 20, 50, 80, 100, 150, 200, 300, 500, 800, 1000, 1500, and 2000 ppm boron modified 9%Cr steels increased by 1.04, 1.50, 2.45, 4.96, 7.54, 9.30, 12.29, 15.22, 18.42, 23.21, 27.72, 29.48, 29.48, and 28.62% as regards boron-free 9%Cr steel, respectively. The relationship between hardness and boron modifications was found analytically (equations (22)/(23)). The negative hardness amplitude and growth constant for hardness were 7.73/66 and 3.4 × 10^{-3}/2.9 × 10^{-3} for Rockwell and Vickers hardness, respectively.

\[
HRC = 34.6 - 7.73 \exp(-3.4 \times 10^{-3} \times \text{Boron[PPM]}) \quad (22)
\]

\[
VHN = 327.9 - 66 \exp(-2.9 \times 10^{-3} \times \text{Boron[PPM]}) \quad (23)
\]

From table 2 and figure 5, a computational error was calculated for both types of hardness testing. The percent range of this error was 2.84%–6.80%, which was in the acceptable range. Hence, the values obtained computationally were further considered with the reliability factor of 0.93–0.97 for analytical modeling and the hardness values computed for the rest of the boron modified steels. It has been reported that boron addition provided martensite persistence [27]. Moreover, as boron modification increased, boride fraction simultaneously increased, which caused an increase in hardness, because, borides were brittle. Hence their compressive load-bearing capability further enhanced, which was observed during hardness testing as regards boron-free concentration [14]. ASTM has recommended that hardness value for 9%Cr steels should not exceed 28HRC (265VHN). The maximum permissible hardness as per ASTM was observed for investigated 100 ppm boron modified 9%Cr steel, which signified that samples having boron modification greater than 100 ppm was under recommended tempering condition. It means that tempering time should be increased, having more than 100 ppm boron modified 9%Cr steels (i.e., more than 3 h). Additionally, it was reported that boron modification increases hardness due to the boron hardness effect, which came from precipitation of TiN on adding a very small amount of Ti/Al/N [25]. TiN is thermodynamically more stable than BN. Hence, the addition of a small amount of Ti/Al maintained hardness effect by forming MX, which was also predicted here. It was also reported that AlN does not contribute to mechanical strength [30]. Hence, its concentration must be in a trace.

3.3.2. Properties of different boron modified 9%Cr steels

(a) Experimental properties

Tensile testing of five boron modified 9%Cr steels was done and is shown in figure 6(a). Figure 6(a) and table 2 show that boron addition increased yield strength (YS) and tensile strength (TS) by simultaneously decreasing linear elongation (%El) and strain hardening coefficient (n). It was noticed from table 2 that 10, 20, 50, and 100 ppm boron modifications increased YS and TS by 4.6, 6.0, 7.4, and 10.5% and 3.0, 4.9, 6.9, and 10.1% as regards boron-free 9%Cr steel, respectively. Whereas, %El and n decreased for 10, 20, 50, and 100 ppm boron modified 9%Cr steels by 4.6, 7.3, 11.4, and 12.1% and 1.21, 1.52, 2.23, and 5.27% as regards boron-free 9%Cr steel, respectively.

(b) Computed properties

Tensile properties were also computed for boron modified 9%Cr steels (figure 6(b)). It was observed that both YS and TS increased with the decrease in both %El and n (figures 7(a)–(b)). Results obtained from JMatPro computation were similar to the observation as found experimentally. The computation error range for YS, TS, %El, and n were 3%–5%, 6.9%–8.2%, 6.5%–10%, and 0.8%–2.1%, respectively. A careful observation at the error range for properties confirmed that computation values for further considerations can be accepted. It is also observed that YS and TS were increased for 5, 10, 20, 50, 80, 100, 150, 200, 300, 500, 800, 1000, 1500, and 2000 ppm boron modified 9%Cr steels by 1.02, 1.54, 2.43, 5.12, 7.93, 9.97, 13.43, 17, 21.10, 27.62, 34.27, 36.96, 36.96, and 35.55% and 2.47, 3.26, 4.75, 5.93, 8.01, 9.10, 13.65, 16.22, 19.38, 24.33, 29.38, 31.36, 31.36, and 30.37% as regards boron-free 9%Cr steel, respectively. The behavior for both YS and TS with boron

\[
(0 \leq \text{Boron[PPM]} \geq 2000)
\]
Table 2. Experimental and computational values of properties of different boron modified 9%Cr steels.

| Boron [PPM] | Hardness [HRC] (VHN) | YS [MPa] | TS [MPa] | Linear elongation, EL [%] | n |
|-------------|-----------------------|----------|----------|---------------------------|---|
|             | Experimental          | Predicted| Experimental| Predicted| Experimental| Predicted| Experimental| Predicted| Experimental| Predicted |
| 0           | 24.9 ± 1.0 (254.8 ± 10.3) | 26.7 ± 0.7 (261.0 ± 6.5) | 741 ± 30 | 782 ± 20 | 928 ± 36 | 1011 ± 25 | 20.34 ± 0.23 | 21.76 ± 0.22 | 0.0987 ± 0.0025 | 0.0978 ± 0.0020 |
| 5           | —                     | 27.0 ± 0.7 (262.3 ± 6.5) | — | 790 ± 20 | — | 1036 ± 26 | — | 21.37 ± 0.22 | — | 0.0969 ± 0.0019 |
| 10          | 26.3 ± 1.0 (259.4 ± 10.4) | 27.2 ± 0.7 (263.4 ± 6.7) | 763 ± 31 | 794 ± 19 | 971 ± 39 | 1044 ± 26 | 19.40 ± 0.22 | 20.87 ± 0.21 | 0.0975 ± 0.0024 | 0.0967 ± 0.0019 |
| 20          | 26.6 ± 1.1 (260.5 ± 10.3) | 27.4 ± 0.7 (265.7 ± 6.7) | 777 ± 32 | 801 ± 20 | 983 ± 40 | 1059 ± 27 | 18.85 ± 0.22 | 20.42 ± 0.21 | 0.0972 ± 0.0024 | 0.0961 ± 0.0019 |
| 50          | 27.1 ± 1.1 (262.9 ± 10.4) | 28.1 ± 0.8 (271.5 ± 6.9) | 792 ± 32 | 822 ± 21 | 997 ± 40 | 1071 ± 27 | 18.02 ± 0.21 | 20.03 ± 0.20 | 0.0965 ± 0.0024 | 0.0945 ± 0.0019 |
| 80          | —                     | 28.8 ± 0.8 (275.6 ± 6.9) | — | 844 ± 21 | — | 1092 ± 28 | — | 19.82 ± 0.20 | — | 0.0933 ± 0.0019 |
| 100         | 27.7 ± 1.2 (268.3 ± 10.5) | 29.2 ± 0.8 (278.9 ± 7.1) | 816 ± 33 | 860 ± 22 | 1025 ± 41 | 1103 ± 28 | 17.87 ± 0.21 | 19.64 ± 0.21 | 0.0935 ± 0.0023 | 0.0920 ± 0.0018 |
| 150         | —                     | 30.0 ± 0.9 (285.2 ± 7.1) | — | 887 ± 22 | — | 1149 ± 29 | — | 19.46 ± 0.21 | — | 0.0899 ± 0.0018 |
| 200         | —                     | 30.8 ± 0.9 (290.7 ± 7.3) | — | 915 ± 23 | — | 1175 ± 30 | — | 19.06 ± 0.20 | — | 0.0886 ± 0.0018 |
| 300         | —                     | 31.7 ± 0.9 (299.5 ± 7.5) | — | 947 ± 24 | — | 1207 ± 30 | — | 18.72 ± 0.20 | — | 0.0867 ± 0.0017 |
| 500         | —                     | 33.0 ± 1.0 (310.7 ± 7.9) | — | 998 ± 25 | — | 1257 ± 32 | — | 18.54 ± 0.19 | — | 0.0847 ± 0.0017 |
| 800         | —                     | 34.2 ± 1.0 (322.0 ± 8.2) | — | 1050 ± 26 | — | 1308 ± 33 | — | 18.36 ± 0.19 | — | 0.0812 ± 0.0016 |
| 1000        | —                     | 34.6 ± 1.0 (327.7 ± 8.3) | — | 1071 ± 26 | — | 1328 ± 33 | — | 18.16 ± 0.19 | — | 0.0802 ± 0.0016 |
| 1500        | —                     | 34.6 ± 1.0 (327.7 ± 8.7) | — | 1071 ± 26 | — | 1328 ± 34 | — | 17.96 ± 0.19 | — | 0.0803 ± 0.0016 |
| 2000        | —                     | 34.4 ± 1.0 (324.9 ± 8.8) | — | 1060 ± 27 | — | 1318 ± 33 | — | 17.75 ± 0.19 | — | 0.0806 ± 0.0016 |
modifications is expressed analytically (equations (24)/(25)). From these equations, it was observed that irrespective of similar stress amplitude, there was a marginal difference in decay constants and intercepts for both YS and TS. The negative sign of both decay constant and stress amplitude confirmed exponential growth behavior. Whereas, %El and n decreased for 5, 10, 20, 50, 80, 100, 150, 200, 300, 500, 800, 1000, 1500, and
2000 ppm boron modified 9%Cr steels by 1.79, 4.09, 6.16, 7.95, 8.92, 9.74, 10.57, 12.41, 13.97, 14.80, 15.62, 16.54, 17.46, and 18.42% and 0.92, 1.12, 1.74, 3.37, 4.60, 5.93, 8.07, 9.41, 11.35, 13.39, 16.97, 17.99, 17.89, and 17.59% as regards boron-free 9%Cr steel, respectively. The relationship between %El and boron is expressed analytically (equation (26)), which followed power-law type behavior having a negative exponent of 0.03. For n, the flow behavior between n and boron modifications was exponential decay and is represented by two different equations (equations (27)/(28)).

\[
\begin{align*}
YS &= 1073 - 290 \exp(-2.9 \times 10^{-3} \times \text{Boron}[\text{PPM}]) \quad (0 \leq \text{Boron}[\text{PPM}] \leq 2000) \\
TS &= 1330 - 290 \exp(-3.1 \times 10^{-3} \times \text{Boron}[\text{PPM}]) \quad (0 \leq \text{Boron}[\text{PPM}] \leq 2000) \\
%El &= 22.4 \times (\text{Boron}[\text{PPM}])^{-0.03} \quad (0 \leq \text{Boron}[\text{PPM}] \leq 2000) \\
R_{0.2-20} &= 0.096 + 0.002 \exp(-0.1 \times \text{Boron}[\text{PPM}]) \quad (0 \leq \text{Boron}[\text{PPM}] \geq 20) \\
R_{50-2000} &= 0.0804 + 0.018 \exp(-4 \times 10^{-3} \times \text{Boron}[\text{PPM}]) \quad (50 \leq \text{Boron}[\text{PPM}] \geq 2000)
\end{align*}
\]

A curve was obtained between YS/TS and two different hardness testing (figure 8). This curve confirmed that boron modification in 9%Cr steels exhibits a linear growth type relationship between both Rockwell and Vickers hardness values and YS/TS (equations (29)–(32)). From these equations, it was noticed that slope was in a similar range, but, the intercept for both the properties varied with both Rockwell and Vickers hardness values. However, the relation between %El and hardness (Rockwell/Vickers) was exponential, till 1500 ppm of boron (figure 8) and the elongation amplitude and hardness decay rate were 8600 and 0.234, respectively (equations (33)/(34)).

\[
\begin{align*}
YS &= 36.8 \times \text{HRC} - 210 \quad (\text{HRC} \geq 17) \\
TS &= 37 \times \text{HRC} + 35 \quad (\text{HRC} \geq 13.8) \\
YS &= 4.35 \times \text{VHN} - 353.5 \quad (\text{VHN} \geq 177) \\
TS &= 4.2 \times \text{VHN} - 51 \quad (\text{VHN} \geq 175) \\
%El &= 17.5 + 2385 \exp(-0.24 \times \text{HRC}) \quad (\text{HRC} \geq 9) \\
%El &= 18 + 57600 \exp(-0.039 \times \text{VHN}) \quad (\text{VHN} \geq 175)
\end{align*}
\]
It was reported that boron addition increases properties by hardened GBs/SGBs due to refinement in the size of M23C6 carbides [25]. However, the previous study was limited to 139 ppm boron modification [31]. It was speculated that boron modification retarded activation energy of carbon partition in the martensite phase [25], resulting in enhanced persistence of martensite, therefore, improved properties. ASTM stated maximum boron concentration should be 10 ppm and nitrogen concentration is recommended in between 0.035%–0.07% for 9%Cr steels, which will not produce an appreciable amount of BN as shown by the blue line in figure 9. A further increased concentration in both elements produces BN as shown by the yellow line in figure 9. Therefore, nitrogen concentration was reduced to 40 ppm in current work. A combination of 40 ppm nitrogen and 0–2000 ppm boron concentration did not produce any boron nitride (BN) as shown by the green line in figure 9. This prediction was in agreement with reported literature [13]. The detrimental effect of BN on properties of 9%Cr steels has been well reported [31]. Hence, we have reduced nitrogen contents from ASTM recommended value to increase boron. However, it was recommended that the mechanical strength of nitrogen-free 9%Cr steel was lower than 34 ppm nitrogen 9%Cr steel due to the absence of carbo-nitrides, hence, nitrogen cannot be avoided completely [9]. This was the reason that adopted boron modification and nitrogen did not affect properties as regards an increase in boron modification. However, its effect would vanish by adding high nitrogen contents (0.065%N) by forming undesirable phases (BN/AlN/Z-phase) [31]. But the figure 9 suggested that nitrogen content may further increase up to 100 ppm with boron revealing superior properties due to the formation of nitride type MX phase. This could enhance the boron memory effect. Subsequently, the boron is expected to provide more strength by altering phase transformation behavior by forming different types of MX, thus improved mechanical strength [9, 32].

3.4. Alloy design criteria for 9%Cr steels by boron modifications

The behavior of boron is quite mysterious and is progressive around the research community, which can be logically deduced by various mathematical laws that explain boron behavior in 9%Cr steels. In our previous research, we numerically deduced the behavior of boron in heat-affected zones from experimental observations [16]. Continuing further, the current study focussed to model the behavior of boron for phase/property. But the behavior of boron is not much simple to deduce it into an analytical model as the direct participation in such events is not feasible. Keeping in view, first, we did some experiments and validated closely them by the JMatPro...
the best combination of phases. These validated values were extrapolated to some extent and modeled by using simple mathematical laws. Boron value, at which phase temperature reached horizontal asymptote was considered as maximum boron limit (2000 ppm). In the narrow range, it often showed linear behavior (figures 1–4, 5, and 7), which was far from actual boron theory. That is the way, current investigations on the effect of boron modifications were proceeded by developing a theoretical model from the experimentation. The hallmark of a boron scientific theory is not, what it appears to describe, but rather, what was predicted from the experimental values. On behalf of obtained results, our theory is that the presence of free-boron atoms delayed the diffusion process and altered the GB characteristics making it prone to nucleation or dissolution of various phases leading to increased properties spontaneously. At the beginning level of this work, we don’t understand why this should be occurring; but from our current work, we have continued step by step, and so on, we initiated with simple boron theory, which has mostly been discussed above.

Phases/properties, which followed exponential decay/growth and other nonlinear type behavior have confirmed that boron in small amounts was more effective to alter phase/property. The exponential and power-law behavior, amount of phase/property changed fast at the initial stage, whereas, the change in phase/property reduced less during the second stage as regards the first stage, and so on. This phenomenon concluded that the periodic multiplication factor for nonlinear functions was not the same rather, it was decreasing in every level of boron modification. Thus, becoming less effective as concentration increased. This continuous change in phase/property led to horizontal asymptote, which is simply understood as limiting value as shown in figures 1(b)–(c), 2(a)–(c), 3(a), (e)–(f), and 4(a)–(b). Hence, for high concentration, its effect did not change much in the SBC. Whereas, phase/property that followed linear relationship had retained the altering behavior throughout the SBC as periodic multiplication factor was constant.

After all observations and discussion, it is time to fix the criteria for an upper limit of boron for optimizing the best combination of phases/properties. For the same, two alloy design parameters viz. mean (average) value (Mv) and half (median) value (Hv) of boron, VHN, and HRC were calculated (table 3). Mv is the sum of all values of boron up to an upper limit in the particular SBC, which is equal to the value at temperature/property (equal to minimum temperature/property in SBC + reciprocal of exponential × average temperature/property difference). For exponential functions, it is the reciprocal of CNT/CNT/decay constant/growth constant and considered as the origin of the curve. But it is excluded for boron design as it strongly depends on SBC and its realization is difficult. Hence, Hv was the most suitable parameter. The value required to exactly reduce it to one-half of the temperature/property difference between SBC, i.e., multiplication of Mv by the natural logarithmic value of two is called Hv. In the piecewise function, total Hv was the summation of individual Hv of the particular function. The phases, which did not obey any analytical model were excluded from the effect of boron modifications in alloy design. Hv of boron, VHN, and HRC for different phases/properties is shown in table 3 in descending order.

Concluding remarks in table 3 were not conclusive for properties, whereas, for phases it was, and its range was 346–468 ppm. Hence, to find the optimum combinations of YS, TS, and %El as regards boron, VHN, and HRC, gradients-based optimization of properties was further selected. These values were inserted in a $3 \times 3$ matrix and equated with ln2. As the mechanism behind the effects of boron modifications in alloy design was Hv. This incentive gave a non-singular solution and optimum solution in the SBC was described as below.

$$
\begin{bmatrix}
\frac{d(YS)}{d(Boron)} & \frac{d(YS)}{d(HRC)} & \frac{d(YS)}{d(VHN)} \\
\frac{d(TS)}{d(Boron)} & \frac{d(TS)}{d(HRC)} & \frac{d(TS)}{d(VHN)} \\
\frac{d(El)}{d(Boron)} & \frac{d(El)}{d(HRC)} & \frac{d(El)}{d(VHN)} \\
\end{bmatrix}
= \ln 2
$$

$$
\begin{align*}
0.841 \exp(-2.9 \times 10^{-7} \times \text{Boron[PPM]}) & = 36.8 \\
0.899 \exp(-3.1 \times 10^{-7} \times \text{Boron[PPM]}) & = 37 \\
-0.672(\text{Boron[PPM]})^{-1.03} & = -572.16 \exp(-0.24 \text{HRC}) \\
& = -2246.4 \exp(-0.09 \text{VHN})
\end{align*}
$$

By solving the above expression, boron modification was found 350 ppm, VHN was 195, and HRC was 31.76. The obtained value of VHN was lied out of SBC, whereas for HRC, it was in between and matching with 292 ppm boron. It is reported that hardness of 9%Cr steel weldment should not exceed 32HRC (303HV) after post-weld heat treatment [33], which is nothing but high-temperature tempering and the range for this treatment is 740 °C–780 °C. Such treatment is also given to 9%Cr steels; hence, this hardness range is applicable for them. By considering this hardness limit, the boron limit should be 300 ppm in 9%Cr steels. Also, Takahashi et al reported that properties of 12%Cr steel were improved by modification of 120–370 ppm boron at 650 °C [34]. However, the selected composition of 9%Cr steel other than boron provided an optimum combination of
Table 3. Half value of phase/property as regards boron/HRC/VHN and its implicit nature.

| Phase            | Boron Hv [PPM] | Boron Nature             | Remarks                                                                 |
|------------------|----------------|--------------------------|-------------------------------------------------------------------------|
| NiO              | 281 + 626 = 907 | NMNM + minimizing        | Excluded due to high Hv, which would bring more δ in case of welding,   |
|                  | 724            | NMNM                     | Excluded as it is related to melting/solidification practice and the    |
|                  |                |                          | decrease in L0 would reduce energy required to cast it.                |
| Laves phase      | 183 + 418 = 601 | Minimizing               | Excluded due as high Hv would increase risk of retained austenite,     |
|                  |                |                          | which would transform into brittle martensite during tempering.         |
| M23C6            | 468            | Minimizing               | Cannot be excluded as the major fraction of strengthening came from   |
|                  |                |                          | it, which further elevated by increasing boron modification.           |
| Laves phase      | 385            | Minimizing               | Cannot be excluded as their drops would destroy boundary hardening    |
|                  |                |                          | effect by grain-coarsening.                                           |
| Ti(N,C)          | 289            | Minimizing               | Excluded as (i) Ti(N,C) is not in high fraction, (ii) thermodynamically |
|                  |                |                          | stable till solidification, (iii) never make solid solution in α-Fe,   |
|                  |                |                          | and (iv) solution temperature is much higher than normalizing         |
|                  |                |                          | temperature up to upper limit of SBC.                                 |
| Laves phase      | 32             | Minimizing               | Excluded as (i) Ti(N,C) is not in high fraction, (ii) thermodynamically |
|                  |                |                          | stable till solidification, (iii) never make solid solution in α-Fe,   |
|                  |                |                          | and (iv) solution temperature is much higher than normalizing         |
|                  |                |                          | temperature up to upper limit of SBC.                                 |
| M2B              | 7 + 18 = 25    | Minimizing               | Excluded as (i) Ti(N,C) is not in high fraction, (ii) thermodynamically |
|                  |                |                          | stable till solidification, (iii) never make solid solution in α-Fe,   |
|                  |                |                          | and (iv) solution temperature is much higher than normalizing         |
|                  |                |                          | temperature up to upper limit of SBC.                                 |
| M2B              | 10             | Maximizing               | Excluded as in our previous works, beneficial effect of high boron     |
|                  |                |                          | studied as regards low boron in 9%Cr steel [16, 18]. Also, the effect  |
|                  |                |                          | of L0 in terms of GB dissolution was already studied previously which   |
|                  |                |                          | only changed location of cracking [11].                                |
| M2B              | 5              | Maximizing               | Excluded as in our previous works, beneficial effect of high boron     |
|                  |                |                          | studied as regards low boron in 9%Cr steel [16, 18]. Also, the effect  |
|                  |                |                          | of L0 in terms of GB dissolution was already studied previously which   |
|                  |                |                          | only changed location of cracking [11].                                |

Properties  | Boron Hv [PPM] | Boron Nature | Remarks
---          | ----------------|--------------|---------------------------------------------------------------
VHN          | 239             | Maximizing   | Cannot be excluded as high strength at room temperature is often  |
|             |                 |              | required. Also, above figures showed exponential nature, which   |
|             |                 |              | would find encouraging properties up to 500ppm appreciably.      |
|             |                 |              | Hence, limit should increase.                                    |
YS           | 239             | Maximizing   | Cannot be excluded as high strength at room temperature is often  |
|             |                 |              | required. Also, above figures showed exponential nature, which   |
|             |                 |              | would find encouraging properties up to 500ppm appreciably.      |
|             |                 |              | Hence, limit should increase.                                    |
TS           | 223             | Maximizing   | Cannot be excluded as high strength at room temperature is often  |
|             |                 |              | required. Also, above figures showed exponential nature, which   |
|             |                 |              | would find encouraging properties up to 500ppm appreciably.      |
|             |                 |              | Hence, limit should increase.                                    |
HRC          | 204             | Maximizing   | Cannot be excluded as high strength at room temperature is often  |
|             |                 |              | required. Also, above figures showed exponential nature, which   |
|             |                 |              | would find encouraging properties up to 500ppm appreciably.      |
|             |                 |              | Hence, limit should increase.                                    |
S             | 7 + 173 = 180   | Minimizing   | Excluded as it can be enhanced by optimising time and temperature  |
|             |                 |              | of normalizing and tempering treatments.                          |
%El           | 46              | Minimizing   |                                                                 |
|             |                 |              |                                                                 |
phase and properties for the maximum 350 ppm boron, which is also applicable for 9%–12%Cr steels. Hence, 0–350 ppm boron modification is called design boundary condition (DBC), which would also enable ease in the manufacturing of such high boron steel with good formability and weldability.

4. Conclusions

The effect of boron modifications in the 9%Cr steels was analytically modeled and briefly discussed with the help of phase/property. In this respect, nucleation and dissolution temperatures of phases were computed. In similar manner, properties evaluated by experimental were validated with computation values. After validation, values were extrapolated till horizontal asymptote, i.e., limiting value. The following conclusions were succinctly rationalized to boron modifications.

1. Boron modification decreased $\alpha'_0$, $\gamma_0$, and $L_0$ by following linear decay, exponential decay, and (linear decay, exponential decay, and linear decay), respectively, whereas, mixed behavior was observed for $\delta_0$.

2. Boron modification decreased $\alpha_{0.0}$, $\gamma_{0.0}$, $\delta_{0.0}$, $L_{100}$, $M_{23}C_6$, $Z_{0.0}$, $T_i_{0.0}$, lave phase, and sigma phase by following parabolic law, (exponential decay and power-law), (linear decay and exponential decay), linear decay, exponential decay, linear decay, exponential decay, (linear decay and exponential decay), and linear decay, respectively. Whereas, it increased the temperature by following exponential growth for $M_{2}B$ and $M_{3}B_2$.

3. Saddle point(s) for $\alpha'_0$, $\gamma_0$, $\delta_0$, $L_0$, $\alpha_{0.0}$, $\gamma_{0.0}$, $\delta_{0.0}$, $L_{100}$, $M_{23}C_6$, $Z_{0.0}$, $T_i_{0.0}$, lave phase, $M_{2}B$, $M_{3}B_2$, and sigma phase was/were 50 ppm, 20 ppm, (80, 200, and 500 ppm), (20, 300 ppm), 20 ppm, 100 ppm, 80 ppm, 20 ppm, absent, 10 ppm, 20 ppm, 500 ppm, 10 ppm, absent, and absent, respectively.

4. ZOS for $\alpha'_0$, $\gamma_0$, $\delta_0$, $L_0$, $\alpha_{0.0}$, $\gamma_{0.0}$, $\delta_{0.0}$, $L_{100}$, $M_{23}C_6$, $Z_{0.0}$, $T_i_{0.0}$, lave phase, $M_{2}B$, $M_{3}B_2$, MB and sigma phase was/were 0–50 ppm, 0–20 ppm, (0–10 and 20–80 ppm), absent, 0–20 ppm, (0–10 and 20–100 ppm), 0–10 ppm, absent, 1500–2000 ppm, 5–10 ppm, 100–2000 ppm, 5–10 ppm, and absent, respectively.

5. No definite relationship found for $V_{0.0}$, $N_{0.0}$, and $M_{2}B$ as regards boron, but, their values changed in the indefinite cycle. For $\delta_0$, $L_0$, $\gamma_{0.0}$, $\delta_{0.0}$, lave phase and n, piecewise behavior was observed.

6. Boron modification increased hardness and YS/TS by 1%–29% and 1%–35% with exponential growth relationship. Whereas, it decreased %El/n by 1%–18% with power law relationship and exponential decay.

---

**Table 3. (Continued.)**

| Phase | Boron Hc [PPM] | Boron Nature | Remarks |
|-------|----------------|--------------|---------|
| Properties | Hc | Hc Nature | |
| %El | 24.08 | Hc Properties | Excluded as it can be enhanced by optimising time and temperature of normalizing and tempering treatments. |
| YS | 203 | NMNM | Properties were found encouraging with Hc. But the decrease in %El may be compensated as stated above. |
| TS | 21.43 | NMNM | Properties were found encouraging with Hc. But the decrease in %El may be compensated as stated above. |
| Properties | Vh | Vh Nature | |
| %El | 221 | Vh Minimizing | The effects were in aggregate as explained in properties for boron Hv and Hc Hv sections. Also, for phase consideration, optimum boron fraction is 346–468 ppm. Hence, boron limit must be increased. |
| YS | 203 | NMNM | The effects were in aggregate as explained in properties for boron Hv and Hc Hv sections. Also, for phase consideration, optimum boron fraction is 346–468 ppm. Hence, boron limit must be increased. |
| TS | 203 | NMNM | The effects were in aggregate as explained in properties for boron Hv and Hc Hv sections. Also, for phase consideration, optimum boron fraction is 346–468 ppm. Hence, boron limit must be increased. |
respectively. Linear growth relationship observed between hardness and YS/TS, but, exponential decay relationship observed between hardness and %E.

7. ASTM recommended boron and nitrogen fraction would not produce any BN. But for robust alloy design of 9%Cr steels, it forced to reduce nitrogen content to increase boron by simultaneously avoiding BN. However, nitrogen value as recommended by ASTM with SBC for boron would produce BN.

8. Effectiveness of boron came from the nature of decay/growth like in linear decay periodic multiplication factor was constant, whereas, in exponential, parabolic, and power law, periodic multiplication factor continuously decreased, which controlled phase/property in 9%Cr steels and reaching to a horizontal asymptote.

9. For alloy design, Hv as design parameter selected, from phase consideration, it was between 346–468 ppm and for properties, it was 204–239 ppm. Due to the scope of improving properties, the gradient-based optimization approach was adopted, which gave the upper design limit of boron as 350 ppm.

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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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