METABK 58(3-4) 199-202 (2019)
UDC – UDK 669.15.781-621.822:536.7.517:66.049.669/781.786/71.786/71.786/295.786:539.26=111

THERMODYNAMIC ANALYSIS OF BN, AlN AND TiN PRECIPITATION IN BORON-BEARING STEEL

Received – Primljeno: 2018-10-25
Accepted – Prihvaćeno: 2019-02-19
Original Scientific Paper – Izvorni znanstveni rad

In this paper, the precipitation behavior of BN, AlN and TiN particles in boron-bearing steel was studied based on thermodynamic calculation. During solidification process, precipitation amount of BN has a positive relationship with boron content, while has negative relationship with temperature. The binding capacity of boron and nitrogen is greater than that of aluminum and nitrogen, BN is preferentially precipitated as boron added to steel. BN particle reduces the free nitrogen content in steel and then prevents the formation of AlN particle. Combination of titanium and nitrogen element is more precedence than of boron and nitrogen element. Formation of TiN particle precedes BN particle, and the precipitation amount of BN is significantly reduced by adding titanium element to boron-bearing.

Key words: B-bearing steel; Thermodynamic; BN, AlN, TiN precipitates; SEM, TEM, SIMS; cracks

INTRODUCTION

Boron element can significantly improve the hardenability and hot ductility of steel. This beneficial effect is attributed to the grain boundary segregation of boron, and solute boron atoms around grain boundaries can occupy vacancy and thus retards the transformation of austenite to ferrite by reducing the grain boundary energy [1-4]. The formation and propagation of microcracking at grain boundaries can be prevented. However, defects on surface of continuous casting billet appear in the production process of boron-bearing steel, such as surface cracks, internal half way cracks, folds, pockets and ridges [5, 6]. In recent years, much research has been done on surface cracks of boron-bearing steel, and large amount of BN particles were detected at austenite grain boundaries. Thermal stress concentration at grain boundaries is hard to eliminate, leading to a decrease of thermoplastic of boron-bearing steel [7-9]. Moreover, AlN and BN particles at austenite grain boundaries were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), when temperature of the slab corner was lower. Tiny cracks start to extend under the influence of thermal stress in continuous straightening process [10]. As a result, surface cracks finally appear in continuous casting process.

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An example given in the upper part of Figure 1 is the photo of a surface crack from a slab of boron-bearing steel. The lower part of Figure 1 is the distribution of boron element near the crack detected by secondary ion mass spectroscopy (SIMS). It is clear that the distribution of boron element around crack is uneven, mainly gathered at the grain boundaries.

In this paper, the precipitation behavior of BN, AlN and TiN particles in boron-bearing steel was studied based on thermodynamic calculation, and the correlation of BN, AlN and TiN was clarified. This study provides a reference for the control of surface cracks during continuous casting of boron-bearing steel.

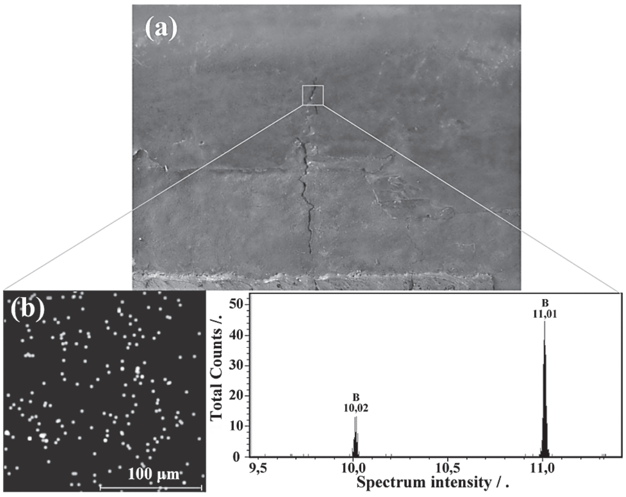

Figure 1 Surface crack and boron distribution of boron-bearing steel slab

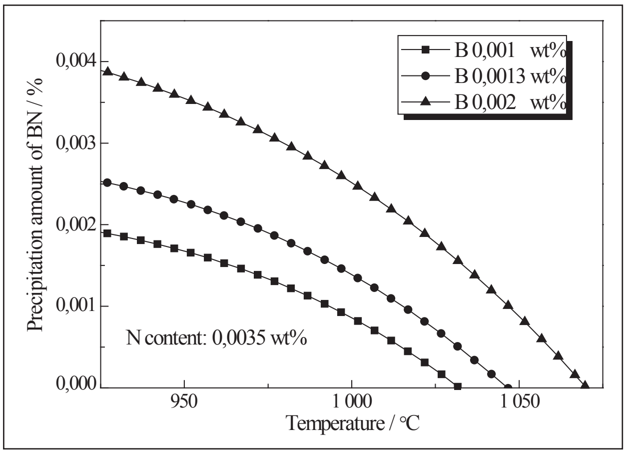

Figure 2 Precipitation amount of BN vs temperature with different boron content

THERMODYNAMIC ANALYSIS AND DISCUSSION

Thermal stability of precipitates

The relationship between temperature and solid solubility product of BN, AlN and TiN in austenite phase has the following expression.

$$\lg K_{BN} = \lg[B][N] = -\frac{13\,970}{T} + 5,24$$

$$\lg K_{AlN} = \lg[Al][N] = -\frac{7\,184}{T} + 1,79$$

$$\lg K_{TiN} = \lg[Ti][N] = -\frac{15\,490}{T} + 5,40$$

The precipitation amount of BN particle is represented in the following Equation.

$$\lg[w(B) - \frac{11}{25}w(BN)][w(N) - \frac{14}{25}w(BN)] = -\frac{13\,970}{T} + 5,24$$

Where T is austenite temperature, and K is solid solubility product in austenite.

Nitrogen content in boron-bearing steel is fixed to 0,0035 wt%, and boron content is 0,001 wt%, 0,0013 wt% and 0,002 wt% respectively, the relationship between precipitation amount of BN and temperature is shown in Figure 2. The result show that precipitation amount has positive relationship with boron content, while has negative relationship with temperature. The starting precipitation temperature is 1 033 °C, 1 047 °C and 1 070 °C, respectively. The maximum precipitation amount reaches to 0,0039 % with boron content of 0,002 wt% during solidification.

In general, boron-bearing steel contains nitrogen, aluminum, and boron element, and titanium element could be attached to molten steel in alloying process. Therefore, the second phase particles precipitated during solidification may include AlN, BN and TiN.

The starting precipitation temperature of AlN and BN particle is shown in Figure 3(a). During solidification process, it can be seen that BN is preferentially precipitated as the temperature decreases. When the boron content is 0,001 wt%, and aluminum content is 0,05 wt%, the two precipitation line cross at the nitrogen content of 0,0043 wt%. The precipitation temperature of BN is higher with the nitrogen content below 0,0043 wt%, which leads to a preferential precipitation of BN particle. Conversely, AlN particle will be preferentially precipitated during solidification, when the nitrogen content is higher than 0,0043 wt%.

Figure 3(b) shows the starting precipitation temperature of TiN and BN particle. It can be seen that TiN is more easily precipitated during solidification. For boron-bearing steel containing titanium and boron element, precipitation of TiN is earlier than BN in cooling process. Moreover, precipitation of TiN consumes nitrogen element at solidification front. As a result, precipitation of BN is restrained.

Competitive precipitation of AlN and BN

The relationship between precipitation amount of AlN and aluminum content is shown in Figure 4. Boron content has significant influence on AlN precipitation. At 950 °C, the three boron level (0 wt%, 0,001 wt% and 0,002 wt%) correspond to the precipitation amount of 0,002%, 0,005% and 0,009%. Meanwhile, the starting

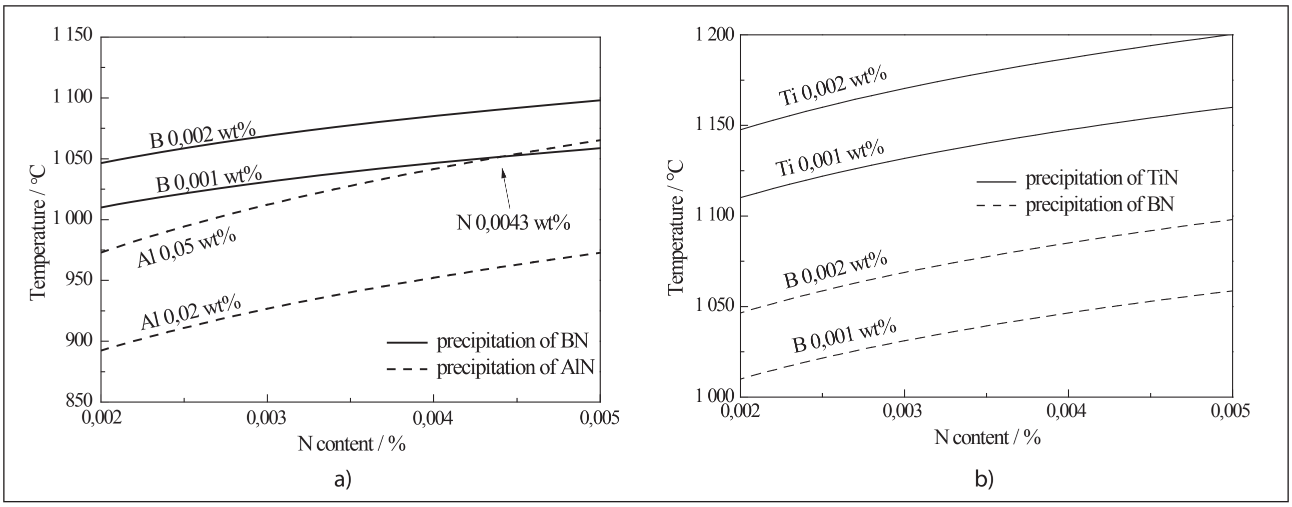

Figure 3 The effect of nitrogen content on starting precipitation temperature at different B, Al, and Ti content, a), b)

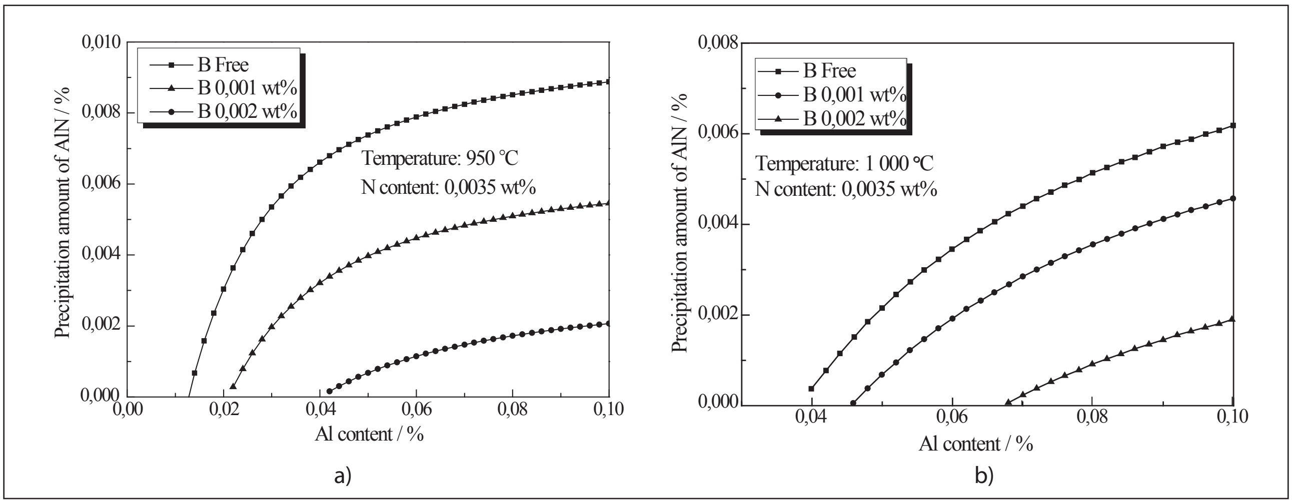

Figure 4 The effects of aluminum and boron content on AlN precipitation at 950 °C and 1 000 °C, a), b)

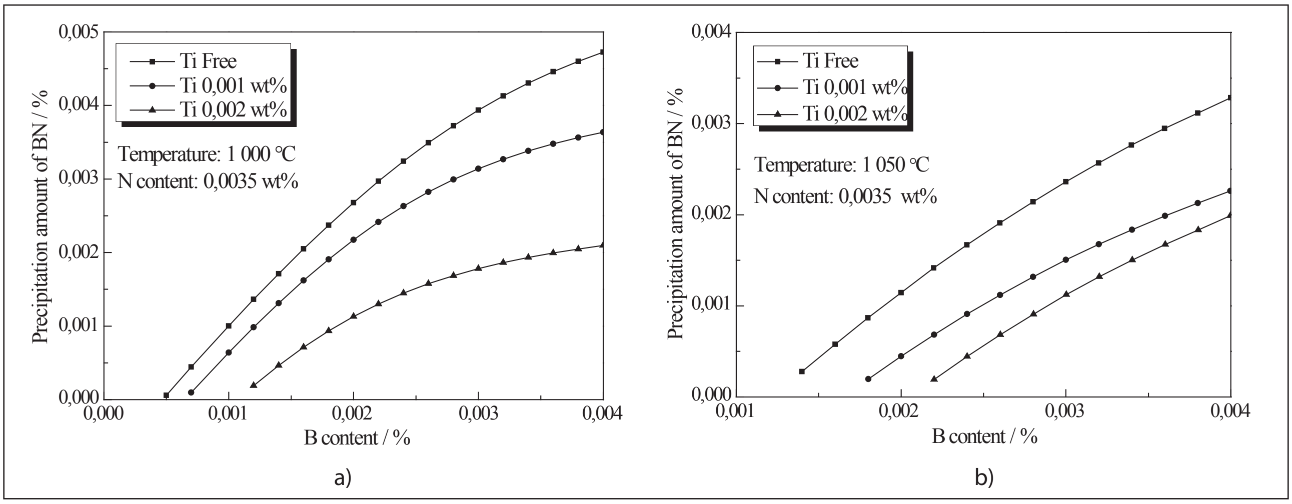

Figure 5 The effects of boron and titanium content on BN precipitation at 1 000 °C and 1 050 °C, a), b)

precipitation of AlN consumes different aluminum element with the three boron level. It is clear that higher boron content leads to fewer AlN precipitation, boron element has inhibitory effect on AlN precipitation.

The result shows a negative relationship between temperature and precipitation amount of AlN, due to the different solidification fraction. It is worth noting that the same precipitation amount of AlN consumes more aluminum element at 1 000 °C relative to 950 °C. The binding capacity of boron and nitrogen is greater than that of aluminum and nitrogen, BN is preferentially precipitated as boron added to steel. BN particle reduces the free nitrogen content in steel and then prevents the formation of AlN particle.

Competitive precipitation of TiN and BN

The relationship between competitive precipitation of TiN and BN is shown in Figure 5. At 1 000 °C, the starting precipitation of BN is 0,0005 wt% B, 0,0007 wt% B, and 0,0012 wt% B with different titanium addition amount. As the temperature rising to 1 050 °C, the corresponding consumption of boron element is at the range from 0,0013 to 0,0022 %. Addition titanium element to boron-bearing steel could obviously reduce the precipitation amount of BN particles during solidification, and there is negative relationship between temperature and precipitation amount.

Combination of titanium and nitrogen element is more precedence than of boron and nitrogen element. Formation of TiN particle precedes BN particle, as a result, the precipitation amount of BN is significantly reduced by adding titanium element to boron-bearing. The precipitation of the second phase particle of BN is the main cause of surface cracks for boron-bearing steel. Addition of titanium can eliminate defects of boron-bearing steel during production process.

CONCLUSION

Based on thermodynamic calculation, the precipitation behavior of BN, AlN and TiN particles in boron-bearing steel are analyzed, the following conclusions are drawn.

(1) Precipitation amount of BN has positive relationship with boron content, while has negative relationship with temperature.

(2) Higher boron content leads to fewer AlN precipitation amounts, BN particle reduces the free nitro-

gen content in steel and then prevents the formation of AlN particle.

(3) Addition titanium element to boron-bearing steel could obviously reduce the precipitation amount of BN particles during solidification, and there is negative relationship between temperature and precipitation amount.

Acknowledgments

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 51604198 and 51704105).

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