

THERMODYNAMIC CONDITIONS FOR THE NUCLEATION OF BORON COMPOUNDS DURING THE COOLING OF STEEL

TERMODINAMIČNI POGOJI ZA NUKLEACIJO BOROVIH SPOJIN PRI OHLAJANJU JEKLA

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The higher the value of the product of boron and oxygen concentrations, or of boron and nitrogen concentrations, than the value corresponding to the balance for the given temperature, is the thermo-dynamic criterion for the nucleation of a new phase (B_2O_3 or BN). It follows from the calculations that the theoretical temperature of the beginning of B_2O_3 nucleation is higher than the temperature of the beginning of BN nitride nucleation. During the solidification and cooling down of steel the boron oxide will be formed preferentially before the boron nitride.

Keywords: boron steel, nucleation, non-metallic inclusions

Večji produkt vsebnosti bora in kisika ter bora in dušika kot ravnotežna vrednost pri izbrani temperaturi je termodinamični pogoj za nukleacijo nove faze (B_2O_3 oz. BN). Izračuni so pokazali, da je teoretično temperatura začetka nukleacije oksida B_2O_3 višja kot pri nitridu BN. Zato bo pri ohlajanju jekla borov oksid nastal pred nitridom.

Gljučne besede: bor, jeklo, nukleacija, nekovinski vključki

1 INTRODUCTION

This paper presents a thermodynamic analysis of the probability of the formation of boron oxide and nitride in boron- and nitrogen-microalloyed stainless steels. The steels are designated for forgings for the production of valves of nuclear power plants' primary circuits and their chemical composition is given in **Table 1**.

Table 1: Chemical composition of the steel (in mass fractions w%)

Tabela 1: Kemična sestava jekel (v masnih deležih w%)

Element. (w%)							
C	0.04	S	0.001	V	0.05	Nb	0.017
Mn	1.57	Cr	17.5	W	0.02	B	0.004
Si	0.6	Ni	10.5	Al	0.050	N	0.0126
P	0.020	Mo	0.07	Ti	0.40		

The objective of this work is to determine at which temperatures the B_2O_3 or BN is formed during the cooling and solidification of the steel. The formation of a new phase (inclusion) is related to the content of boron, nitrogen and oxygen in the steel.

2 THERMODYNAMIC BALANCE

The temperature dependencies of the Gibbs energy for the formation of B_2O_3 and BN were derived from table data^{1,2} with the use of the equations:



$$\Delta G_1^0 = -411\,990 + 143,585 T \quad (3)$$

$$\Delta G_2^0 = -227\,737 + 97,95 T \quad (4)$$

Due to the fact that the melting temperature of B_2O_3 is 450 °C, this oxide is at the temperatures of steel solidification in the liquid state².

It is possible to derive from equations (3) and (4) the following relations for the temperature dependencies of the equilibrium constants:

$$\lg K_1 = \frac{21517}{T} - 7,50 \quad (5)$$

$$\lg K_2 = \frac{11894}{T} - 5,116 \quad (6)$$

The following is valid for the equilibrium constants of the reactions (1) and (2):

$$K_1 = \frac{a_{B_2O_3}^{1/2}}{(a_{[B]} \cdot a_{[O]}^{3/2})_{\text{equilibrium}}} \quad (7)$$

$$K_2 = \frac{a_{BN}}{(a_{[B]} \cdot a_{[N]})_{\text{equilibrium}}} \quad (8)$$

Assuming that pure boron oxide and boron nitride are formed, it is possible to consider their activities to be equal to one. It is similarly possible to assume unequivocally that the solutions of boron, oxygen and nitrogen in steel are diluted and that the activities of these elements

are equal to a mass percentage. It is then possible to adjust the equations (7) and (8) to these forms:

$$([B] \cdot [O]^{3/2})_{\text{equilibrium}} = \frac{1}{K_1} \quad (9)$$

$$([B] \cdot [N])_{\text{equilibrium}} = \frac{1}{K_2} \quad (10)$$

Due to the fact that the equilibrium constants K_1 and K_2 are a function of temperature only in accordance with equations (5) and (6), the equilibrium products of the concentrations of boron and oxygen, as well as boron and nitrogen, depend only on the temperature (see equations (11) and (12)) and can be calculated from the temperature dependencies.

$$\lg([B] \cdot [O]^{3/2})_{\text{equilibrium}} = -\frac{21517}{T} + 7,50 \quad (11)$$

$$\lg([B] \cdot [N])_{\text{equilibrium}} = -\frac{11894}{T} + 5,116 \quad (12)$$

It is subsequently possible to affirm logically that the formation of boron trioxide or boron oxide at the temperature T is conditioned by a higher value of the real product of boron and oxygen, or a boron and nitrogen concentration that would correspond to the equilibrium.

$$([B] \cdot [O]^{3/2})_{\text{real}} \geq ([B] \cdot [O]^{3/2})_{\text{equilibrium}} \quad (13)$$

$$([B] \cdot [N])_{\text{real}} \geq ([B] \cdot [N])_{\text{equilibrium}} \quad (14)$$

It follows from equations (11) and (12) that with decreasing temperature the value of equilibrium products (13) and (14) also decreases, and therefore the probability of the formation of the inclusions B_2O_3 and BN increases, since the real products (13) and (14) remain constant.

3 DISCUSSION OF THE RESULTS

The derived relationships were applied to the steel microalloyed with boron and nitrogen of required chemical composition – see **Table 1**.

The theoretical dependencies of the temperatures of the beginning of formation of the B_2O_3 or BN on the content of oxygen and nitrogen are given in **Figures 1 and 2**.

These dependencies were calculated from equations (5) and (6), adjusted for mass fractions 0.001 %, 0.006 %, 0.03 % and 0.05 % of boron.

It follows from **Figure 2** that, for example, the theoretical temperature of the beginning of nucleation of BN nitride is for the nitrogen content of 100 $\mu\text{g/g}$ (ppm) in the interval 903 °C, 1001 °C, 1104 °C and 1040 °C, or for 200 $\mu\text{g/g}$ of nitrogen in the interval 939 °C, 10043 °C, 1154 °C and 1193 °C. The theoretical temperature for the start of nucleation of the oxide B_2O_3 is for the achieved oxygen contents (10 $\mu\text{g/g}$) higher, i.e., 1161 °C,

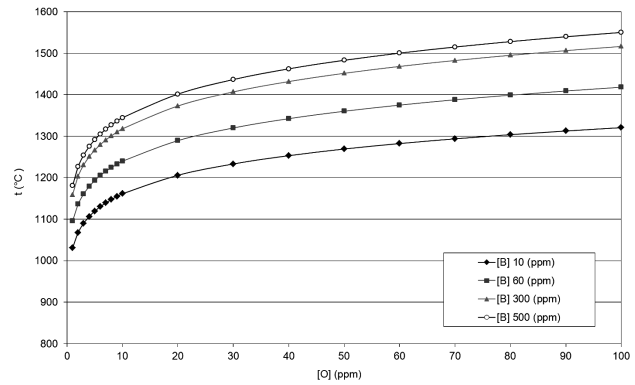


Figure 1: Dependence of the beginning temperature of formation of B_2O_3 and the content of oxygen in steel

Slika 1: Začetna temperatura tvorbe B_2O_3 v odvisnosti od vsebnosti kisika v jeklu

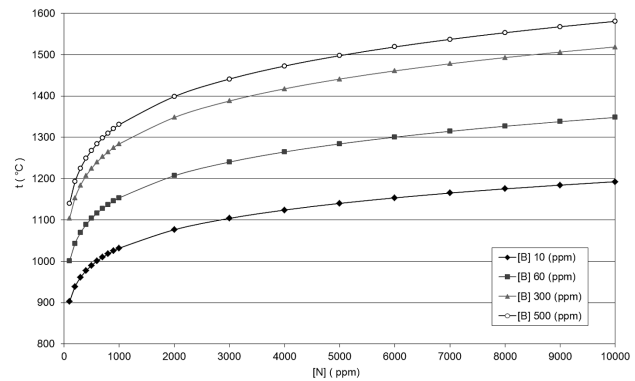


Figure 2: Dependence of the starting temperature on the formation of BN and the content of nitrogen in steel

Slika 2: Začetna temperatura tvorbe B_2O_3 v odvisnosti od vsebnost dušika v jeklu

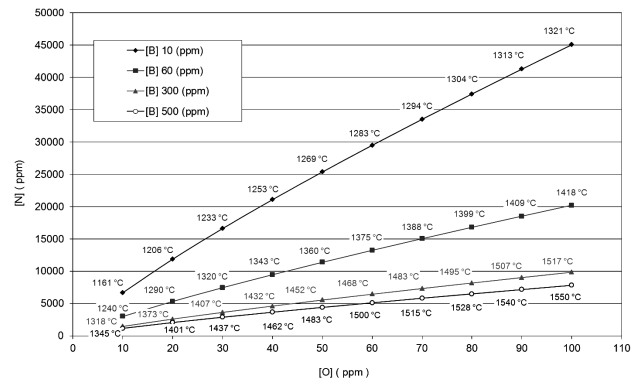


Figure 3: Equilibrium temperatures and equilibrium contents of nitrogen corresponding to the oxygen content in steel of 10–100 $\mu\text{g/g}$

Slika 3: Ravnotežne temperature in ravnotežne vsebnosti dušika pri vsebnosti 10–100 $\mu\text{g/g}$ kisika v jeklu

1240 °C, 1318 °C and 1345 °C, and for 20 $\mu\text{g/g}$ of oxygen it is 1206 °C, 1290 °C, 1373 °C and 1402 °C. It follows, therefore, that boron oxide will be formed preferentially before boron nitride during the cooling of the steel.

For the steels with the above-mentioned boron contents the equilibrium temperatures and equilibrium

nitrogen contents corresponding to 10–100 µg/g of oxygen in steel are shown in **Figure 3**. It is evident from the figure that B₂O₃ oxides can be formed only at higher contents of oxygen than would correspond to an equilibrium (right to the curve). Similarly, boron nitrides can be formed only at higher nitrogen contents than would correspond to an equilibrium (above the curve), since inequalities (13) and (14) are fulfilled.

4 CONCLUSIONS

The thermodynamic balance of probability for the formation of oxide B₂O₃ and nitride BN in boron-microalloyed steels was calculated. The balance proved that the oxide is more stable than the boron nitride and,

therefore, during the cooling of steels it is formed preferentially.

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