

Rate of Growth of Boride Layers on Highly Alloyed Steels

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Experimental results of thermochemical boriding of low-alloyed steel (CSN 11302) and high-alloyed chromium and nickel steels are presented. A semiquantitative model describing the rate of growth of boride layers as a function of composition of borided steel, composition of boriding medium, time and temperature of boriding is proposed. Parameters of the model are calculated. The model enables one to estimate the experimental conditions for boriding of alloyed steels.

The distribution of chromium and nickel in the boride coatings and in the matrix has been determined metallographically and by electron probe microanalysis. It was found that the formation of the boride layer is accompanied by a redistribution of the alloying elements: the highest concentration of chromium was determined in the Fe₂B underlayer whilst in the phase FeB it was lower than in the matrix. An opposite behaviour was observed for nickel which concentrated preferentially in the outer FeB phase, this resulting in a Ni depletion in the Fe₂B underlayer.

Boriding of metallic bases, namely steels has been found to be one of the most effective methods for the formation of hard-surface layers with an increased corrosion resistivity at elevated temperatures [1]. According to the literature data reviewed in monographs [1, 2], the following methods of boriding are mostly used:

– electrochemical boriding in molten salt mixtures based on Na₂B₄O₇ or KBF₄ at the temperatures of 800–950 °C,

– thermochemical boriding in molten, powder or gaseous mixtures at the temperatures of 850–1000 °C.

Rate of formation of the boride layer depends on the activity of boron in the boriding medium, temperature, time of boriding, and composition of the borided base. It is generally accepted that the rate of growth of the boride layer slows down and the relative content of the boron-rich FeB phase increases with the increasing content of specific alloying elements. The influence of carbon, nickel, and chromium additives has been discussed recently by several authors [1, 3–13]. The situation seems to be quite clear in the case of carbon [1, 4, 7, 8]: carbon is practically insoluble in iron borides and therefore it diffuses ahead of the boride layer into the matrix, which results in its increased concentration of carbon under the boride layer. It should be noted that a similar behaviour has been observed for silicon [3, 4, 8]. The situation, however, is different in the case of chromium and nickel. Their distribution is rather controversial.

In this paper we will discuss the influence of alloying elements in highly alloyed steels on the

rate of growth of boride layers. We will also present a mathematical model describing dependence of the rate of growth of boride layers on the nature of boriding bath and the used method (electrolytic or electroless boriding).

EXPERIMENTAL

Thermochemical boriding has been carried out in boriding mixtures (suspensions) of two compositions:

1. 60 mass % Na₂B₄O₇ + 40 mass % B₄C,
2. 60 mass % Na₂B₄O₇ + 40 mass % SiC.

Temperature was changed in the interval 850–1000 °C, time of boriding changed from 1 to 6 h. The following bases were used (composition in mass %):

Steel CSN 11302 (0.06 % C, 0.17 % Si, 0.3 % Mn);

Steel CSN 19312 (0.79 % C, 0.40 % Si, 2.00 % Mn, 0.17 % Cr);

Steel CSN 19436 (1.85 % C, 0.50 % Si, 0.26 % Mn, 11.25 % Cr);

Steel CSN 19824 (0.75 % C, 0.50 % Si, 0.50 % Mn, 4.34 % Cr, 1.30 % V, 17.2 % W);

Cr–Ni steel 1 (0.15 % C, 0.90 % Mn, 0.49 % Si, 16.4 % Cr, 4 % Ni);

Cr–Ni steel 2 (0.09 % C, 1.07 % Mn, 24.8 % Cr, 2.15 % Mo, 21.8 % Ni).

The thickness of boride layers was determined by means of the metallographic microscope Epipty 2 (Zeiss, Jena) and the scanning microscope JSM-840 (Jeol) which made it possible to determine

also the thickness of the layers formed by individual boride phases. The phase and chemical composition of the boride layers have been determined by the X-ray phase analysis and the X-ray micro-analyzer Superprobe 733 (Jeol).

Mathematical Model Describing the Influence of Alloying Elements and of Activity of Boron in the Boriding Mixture on the Rate of Growth of Boride Layer

For description of the influence of alloying elements and of the activity of boron on the kinetics of growth of boride layer the following model is proposed.

1. Let us assume that the amount of boron which diffuses into steel can be described by the relationship

$$\frac{I dm}{A d\tau} = \frac{D \Delta c}{\Delta x} \quad (1)$$

where m is the mass of diffusing boron, τ the time of boriding, A area of the borided surface, D the diffusion coefficient, Δc the difference in boron concentration in the boriding mixture and in steel, and Δx the effective (apparent) thickness of the borided layer. Thus it is assumed that the ratio $\Delta c/\Delta x$ is the driving force of the boriding process. (In fact, it is the change in the Gibbs energy which is the driving force of the process and the model assumes that this is proportional to the ratio $\Delta c/\Delta x$.)

2. The effective thickness of boride layer Δx in eqn (1) is not identical with the real thickness of the boride layer. Its meaning follows from the following consideration. Boron diffuses through a boride layer of thickness l (real thickness of boride layer). When steel contains alloying elements, these can form a diffusion barrier. The influence of this barrier on the rate of boriding process can be formally described as an increase of the thickness of the boride layer.

We may assume that the thickness of this barrier b is proportional to the real thickness of boride layer. When we denote the proportionality constant as ϑ it holds

$$\Delta x = l + b = l + \vartheta l = l(1 + \vartheta) = l\omega \quad (2)$$

When steel does not contain alloying elements, $\omega = 1$ and the real thickness l and the effective thickness Δx are identical. The constant ω characterizes the influence of alloying elements on the retardation of growth of boride layer. The higher is its value, the slower is the growth of boride layer. We will show that the value of the constant ω

depends on the nature of alloying element and that it is proportional to their concentration.

3. Parameter Δc (driving force of boriding process) reaches its maximum value Δc_{\max} when the surface of the borided sample is covered with pure boron. This can be achieved at electrolytic boriding when the cathodic current density is sufficiently high (about 50 mA cm^{-2}). In all other cases (e.g. at thermochemical boriding) the activity of boron on the surface is lower and it holds

$$\Delta c = \Delta c_{\max} \xi \quad (3)$$

Constant ξ characterizes the activity of boron in boriding mixture.

4. In the first approximation we can assume that the thickness of boride layer is related to the amount of diffusing boron by the relationship

$$m = I A \rho \quad (4)$$

where ρ is the density of boride layer. It is assumed that the density is the same for both phases Fe_2B and FeB . This is an acceptable approximation because of the definition of thickness of boride layer to the end of "teeth" [2]. (The real values of densities of boride phases are different: $\rho(\text{FeB}) = 6.47\text{--}6.80 \text{ g cm}^{-3}$; $\rho(\text{Fe}_2\text{B}) = 6.93\text{--}7.30 \text{ g cm}^{-3}$ [1].)

After introducing relationships (2–4) into eqn (1) we obtain

$$\frac{dl}{d\tau} = D \frac{\Delta c_{\max} \xi}{\rho l \omega} \quad (5)$$

By integration of this equation we obtain the "parabolic law" for the growth of boride layer

$$l^2 = (D^* \xi \tau) / \omega \quad (6)$$

where $D^* = (2D\Delta c_{\max})/\rho$.

Values of the constants D^* , ξ , ω can be determined from experimental data in the following way:

i) D^* characterizes diffusion of boron into pure iron ($\omega = 1$) under the condition that $\xi = 1$. The latter condition can be achieved at electrolytic boriding at $j_c = 50 \text{ mA cm}^{-2}$. This current density is sufficient for production of elemental boron with unit activity on the surface of borided sample. The experimental data for calculation of D^* at different temperatures were taken from [2].

ii) Values of parameter ξ can be determined from the investigation of boriding of pure iron base in different boriding mixtures (see later).

iii) The parameter ω can be calculated from the data on electrolytic boriding ($\xi = 1$) of alloyed steels [2].

RESULTS AND DISCUSSION

$$l = k\sqrt{t} \quad (7)$$

The literature data [1, 2] on the influence of composition of boriding mixture on phase composition of boride layers at the thermochemical boriding of low-alloyed steels were confirmed. When the mixture of molten $\text{Na}_2\text{B}_4\text{O}_7$ with B_4C was used the boride layer consisted of two phases, viz. FeB and Fe_2B . Amounts of these phases depend on temperature. At the temperatures lower than 850°C mainly the phase Fe_2B is formed. When as a reducing agent SiC instead of B_4C was used only formation of the phase Fe_2B was observed. In this case also formation of the phase Fe_3B has been reported [13]. Lower activity of boron in the mixtures containing SiC results also in slower growth of boride layer in comparison with the mixture $\text{Na}_2\text{B}_4\text{O}_7\text{--B}_4\text{C}$.

Experimental data on the dependence of thickness of boride layers vs. time are plotted for different temperatures in Fig. 1. It follows that the boride layers grow linearly with square root of time. This is in agreement with eqn (6) which can be written as

Square of the proportionality constant k^2 has the dimension of diffusion coefficient ($\text{m}^2 \text{s}^{-1}$). Similarly as in the case of diffusion coefficient we can describe temperature dependence of this coefficient by the Arrhenius equation

$$k^2 = k_0^2 \exp(-Q_d/RT) \quad (8)$$

where Q_d is close to the value of activation energy of diffusion. (These values are identical only under validity of the simplifications used at derivation of the parabolic law.) For low-alloyed steel (CSN 11302) it was found that using the mixture $\text{Na}_2\text{B}_4\text{O}_7\text{--B}_4\text{C}$ it holds

$$Q_d = 190 \text{ kJ mol}^{-1} \quad k_0^2 = 3.19 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

and for the mixture $\text{Na}_2\text{B}_4\text{O}_7\text{--SiC}$

$$Q_d = 320 \text{ kJ mol}^{-1} \quad k_0^2 = 19.5 \text{ m}^2 \text{ s}^{-1}$$

High values of activation energy suggest that the diffusion is combined with a chemical reaction. The value of activation energy obtained at thermochemical boriding in the mixture containing B_4C is close to the value of activation energy obtained at electrolytic boriding of low-alloyed steels ($Q_d = 175 \text{ kJ mol}^{-1}$ [2]). The value of activation energy for the mixtures containing SiC is substantially higher.

In the boriding of the high-alloyed steels, chromium appears to be one of the alloying elements which affects both the rate of growth and the phase composition of the boride layer, apparently due to slowing down the diffusion of boron into the substrate. This may be explained by the influence of chromium on the region of formation of ferrite which lowers dissolution of elements in steel. This is documented in Fig. 2 showing the dependence of the thickness of boride layers vs. square root of time for all steels investigated. The samples were borided at 950°C in the $\text{Na}_2\text{B}_4\text{O}_7\text{--B}_4\text{C}$ mixture. It can be seen that the rate of growth of boride layers decreases remarkably with increasing concentration of chromium in the substrate.

Fig. 3 shows the concentration profiles of iron, chromium, and boron in the borided steel CSN 19436. It can be seen that the average concentration of chromium in the boride phase essentially is the same as in the substrate, though a marked tendency of chromium to concentrate at the $\text{FeB}/\text{Fe}_2\text{B}$ and $\text{Fe}_2\text{B}/\text{FeB}$ phase boundaries is observed. Similar conclusion on the Cr distribution has been drawn by *Shibuya* and *Kimura* [11]. The differences in the distribution of chromium, however, become more apparent at higher Cr contents in the substrate. This is evidenced by Fig. 5 showing the concentration profiles of Fe, Cr, and Ni in Cr-Ni

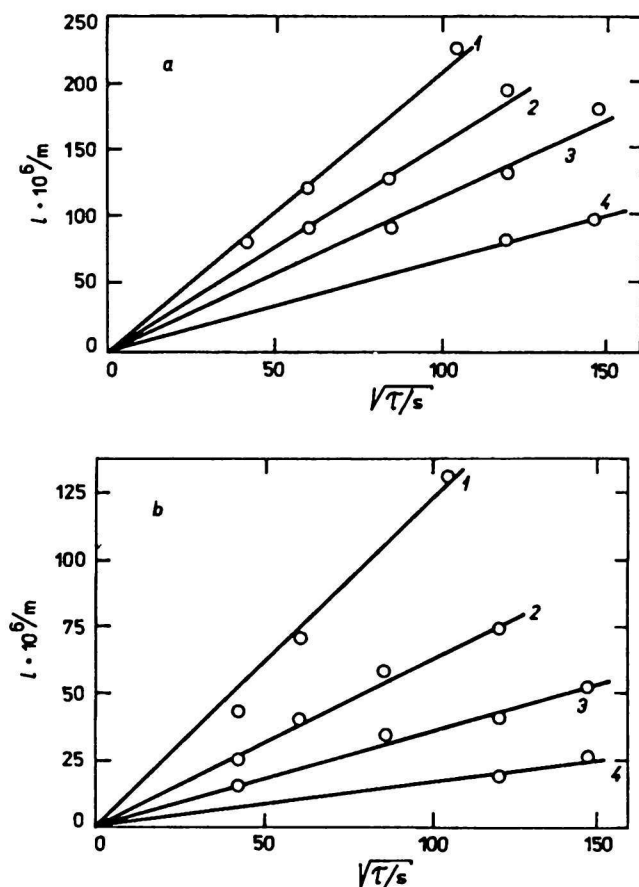


Fig. 1. Dependence of the thickness of boride layer as a function of square root of time of boriding in the $\text{Na}_2\text{B}_4\text{O}_7\text{--B}_4\text{C}$ (a) and $\text{Na}_2\text{B}_4\text{O}_7\text{--SiC}$ (b) mixtures for low-alloyed steel CSN 11302. 1. 1000°C ; 2. 950°C ; 3. 900°C ; 4. 850°C .

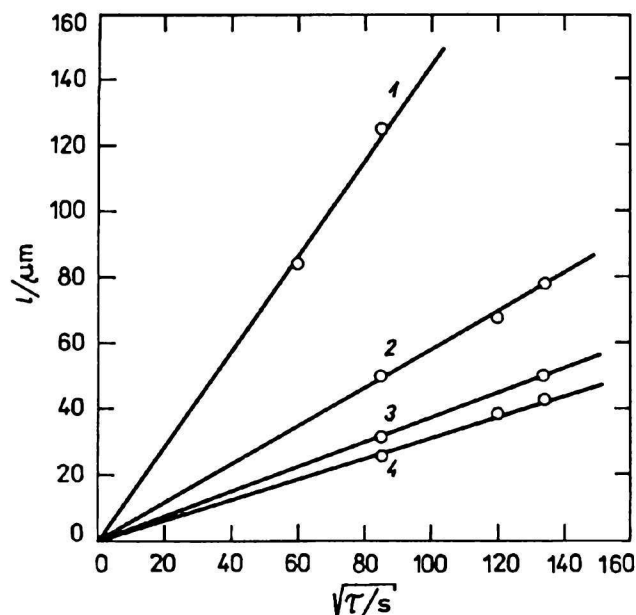


Fig. 2. Dependence of the thickness of boride layer as a function of square root of time of boriding in the $\text{Na}_2\text{B}_4\text{O}_7\text{-B}_4\text{C}$ mixture at 950°C . 1. Steel CSN 11302; 2. steel CSN 19436; 3. Cr-Ni steel 1; 4. Cr-Ni steel 2.

steel 2 borided in the $\text{Na}_2\text{B}_4\text{O}_7\text{-B}_4\text{C}$ mixture for 4 h at 950°C . In this case, the concentration of chromium in the Fe_2B phase is distinctly higher and in the FeB phase lower than in the substrate. This phenomenon can be explained by the isomorphism of the couple Fe_2B and Cr_2B so that a substitution of the Fe and Cr atoms under formation of a ternary boride may be assumed (it may be mentioned that the ternary compound $\text{Fe}_{1.1}\text{Cr}_{0.9}\text{B}_{0.9}$ has been identified by *Brown and Beerntsen* [14]). Conversely the borides FeB and CrB are not isomorphous and this may explain the depleted chromium content in the FeB phase and its displacement into the Fe_2B layer.

The tendency of Cr to concentrate in the Fe_2B phase is illustrated by Fig. 6 showing the concentration profiles of Fe, Cr, and Ni in boride layer grown on the same steel in the $\text{Na}_2\text{B}_4\text{O}_7\text{-SiC}$ boriding mixture in which a single-phase Fe_2B layer is formed. This indicates that the chromium content in the Fe_2B phase is enriched also by its diffusion from the substrate and not only from the FeB phase. A decrease in the concentration of chromium in the substrate in the proximity of the boride layer/steel phase boundary was observed also by *Voroshin and Lyakhovich* [1]. The formation of a Cr-rich zone under the boride layer claimed by *Rus et al.* [12] has not been confirmed.

Distribution of nickel in the boride layer of Cr-Ni steel is shown in Figs. 4 and 5. The behaviour of nickel is opposite to that of chromium. This may be explained by the fact that nickel influences

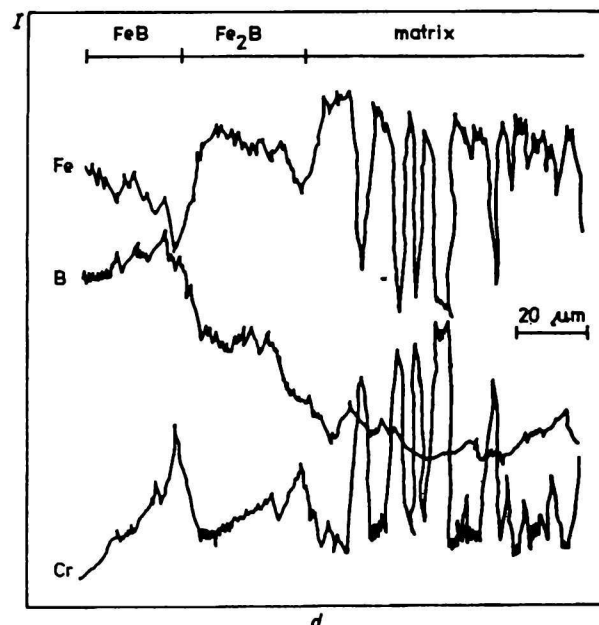


Fig. 3. Concentration profiles (X-ray intensities) of boron, iron, and chromium in the boride layer and in steel CSN 19436. Boriding mixture $\text{Na}_2\text{B}_4\text{O}_7\text{-B}_4\text{C}$, temperature 950°C , time 5 h. d denotes the distance from the surface of sample.

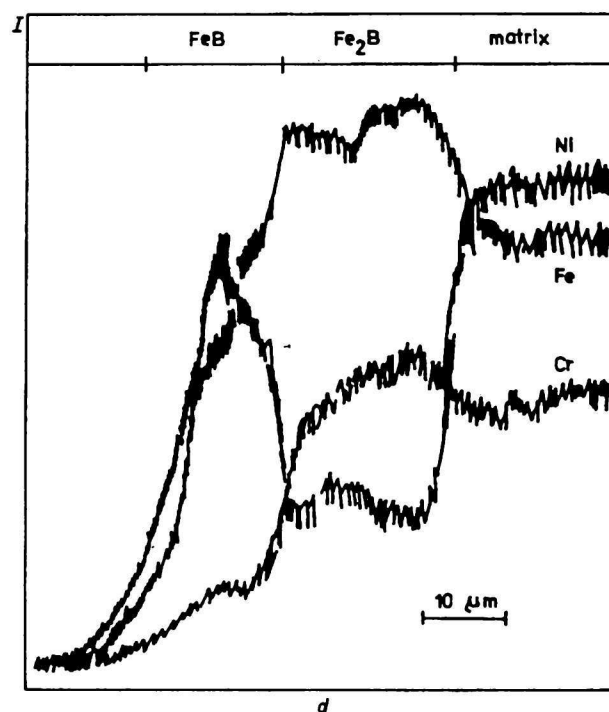


Fig. 4. Concentration profiles of iron, chromium, and nickel in the boride layer and in Cr-Ni steel 2. Boriding mixture $\text{Na}_2\text{B}_4\text{O}_7\text{-B}_4\text{C}$, temperature 950°C , time 4 h.

positively the region of formation of austenite which has the ability to dissolve other elements. When the boride layer consists of two phases, nickel concentrates in the phase FeB and its concentration in the phase Fe_2B is lower than in the substrate. Compound Ni_3B was identified by the X-ray phase

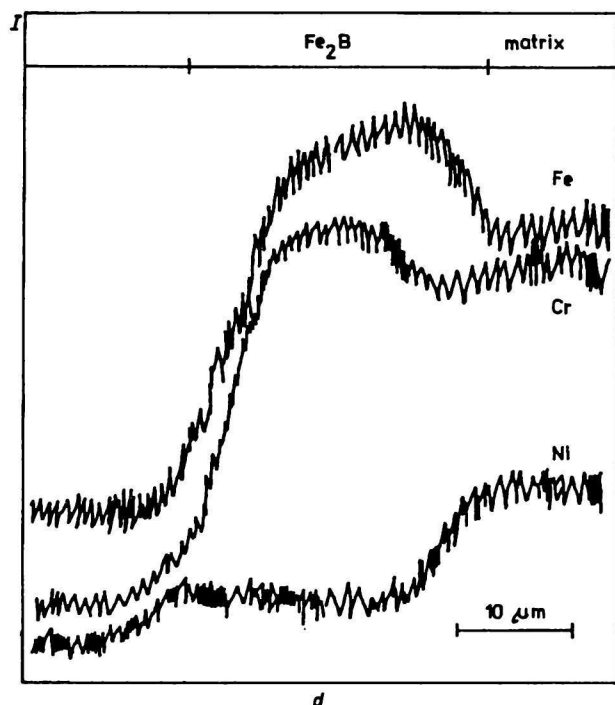


Fig. 5. Concentration profiles of iron, chromium, and nickel in the boride layer and in Cr–Ni steel 2. Boriding mixture $\text{Na}_2\text{B}_4\text{O}_7$ –SiC, temperature 950 °C, time 5 h.

analysis in the boron-rich phase. Analogous distribution characteristics of nickel were reported by Goeuriot *et al.* [7] for a borided steel substrate containing 14 mass % Ni. On the other hand, the data on the Ni distribution in borided steel substrates with a nickel content up to about 10 mass % [1–6] are rather controversial. Although Voroshin and Lyakhovich [1] and Pokhmurskii *et al.* [3] claim for nickel the same redistribution as for chromium, most authors [6, 8–10, 12] have observed only slight, if any differences in the Ni content across the borided steel. These differences obviously become apparent only at high concentrations of nickel in the steel substrate.

Calculation of Numerical Values of Parameters in Eqn (6)

The constant D^* was determined from experimental data on electrochemical boriding of low-alloyed steel CSN 11302 [2]. It was found

$$D_{900\text{ }^\circ\text{C}}^* = 5625 \text{ m h}^{-1} \quad D_{950\text{ }^\circ\text{C}}^* = 11\,000 \text{ m h}^{-1}$$

Values of the parameter ξ were determined from experimental data on thermochemical boriding presented in this work. They are summarized in Table 1.

Values of the parameter ω were determined from experimental data on electrochemical boriding of

Table 1. Values of the Parameter ξ Calculated from the Data Obtained at the Thermochemical Boriding of Steel CSN 11302

Boriding mixture	$\xi(900\text{ }^\circ\text{C})$	$\xi(950\text{ }^\circ\text{C})$
$\text{Na}_2\text{B}_4\text{O}_7$ – B_4C	0.820	0.782
$\text{Na}_2\text{B}_4\text{O}_7$ –SiC	0.100	0.150

Table 2. Values of the Parameter ω Obtained from the Data on Electrolytic Boriding of Alloyed Steels

Steel	$\omega(900\text{ }^\circ\text{C})$	$\omega(950\text{ }^\circ\text{C})$
CSN 19312	1.291	1.169
CSN 19436	7.716	8.487
CSN 19824	14.063	14.030

Table 3. Comparison of the Experimental and Calculated Thickness of Boride Layers Formed at Thermochemical Boriding at 950 °C for 4 h

Steel	$\text{Na}_2\text{B}_4\text{O}_7$ – B_4C		$\text{Na}_2\text{B}_4\text{O}_7$ –SiC	
	l_{exp}	l_{calc}	l_{exp}	l_{calc}
CSN 19312	166	162	75	75
CSN 19436	70	64	45	28
CSN 19824	40	49	28	22
Cr–Ni (1)	51	51	30	23
Cr–Ni (2)	37	34	25	15

alloyed steels [2]. The results are presented in Table 2. It was found that parameter ω depends

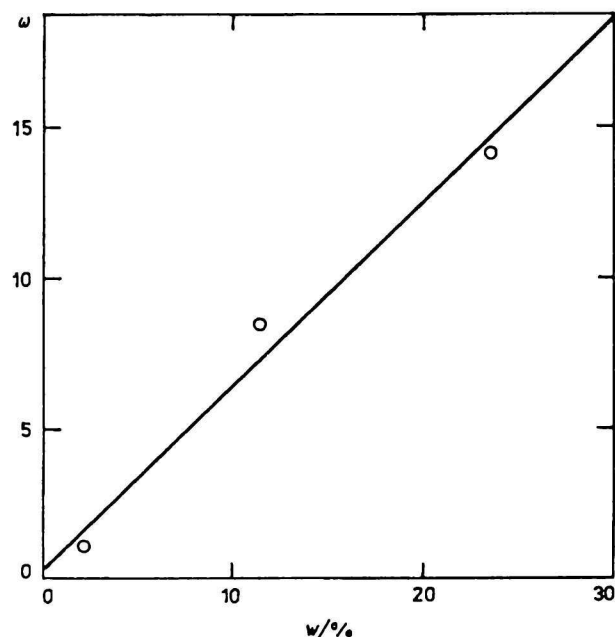


Fig. 6. Dependence of the parameter ω on the total mass content of metal alloying elements, *i.e.* Cr, Ni, Mn, W, V, and Mo at 950 °C.

linearly on the concentration of alloying elements (Fig. 6). It holds

$$\omega = 0.3235 + 0.607 c_{\text{total}} \quad (9)$$

where c_{total} denotes the total mass content of metal alloying elements, i.e. Cr, Ni, Mn, W, V, and Mo.

Comparison of the experimental thickness of boride layers obtained under different conditions with the values calculated according to the presented model (eqn (6)) is given in Table 3. It can be seen that the agreement is reasonably good. This enables one to predict optimum conditions for boriding of alloyed steels.

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