

## MANUFACTURE OF FERROUS AND NONFERROUS METALS

# Deoxidizer Activity and the Composition of the Oxide Phase in Chromium Steel

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**Abstract**—Nonmetallic inclusions in various chromium steels are studied. The contents of silicon and aluminum oxides in the nonmetallic phase are shown to correlate with the activities of these elements in the metal. Relations are obtained to calculate the fraction of the oxide of a deoxidizing element in the nonmetallic inclusions from its activity.

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One of the main metallurgical factors that exert a substantial effect on the properties of steel is its contamination with nonmetallic inclusions. To provide high quality of the metallic product, one should, first, minimize the total quantity of nonmetallic inclusions in the metal and, second, provide their optimum composition. The reproducibility of the achievement of these conditions can be enhanced by using information on the current composition of the oxide phase in steel at the stage of liquid steel production. In this work, we study the possibility of determining the composition of inclusions (the content of the deoxidizing element oxide) from the chemical composition of the steel.

We investigated two model alloys of a chromium steel with 3 and 9% Cr (hereafter, Kh3 and Kh9) and chromium steels 1Kh13M2BF (EP142), 01Kh14N5MF, Kh17N14M3, 01Kh18M2B (EP882), 01Kh18Yu (EP994), and 15Kh2NMFA. The procedure of melting and analyzing the samples and inclusions in the Kh3 and Kh9 steels was described in [1]. The other steels were melted at the Energomashspetsstal' plant (Kramatorsk, Ukraine) in a VIP-30 industrial vacuum induction furnace in a 30-t crucible (the 01Kh14N5MF steel was produced in a 7-t crucible). The metal was produced by bottom casting in vacuum. Nonmetallic inclusions were sampled for analysis from an ingot. The 15Kh2NMFA reactor steel was melted at OOO OMZ–Spetsstal' in an arc furnace from a charge of 50 t, subjected to two-stage degassing in an ASEA-SKF setup, and poured into a mold in a vacuum chamber. Samples were taken from a ladle before casting and from

the top, middle, and bottom of the central extruded part of the ingot.

The total amount and chemical composition of the inclusions in all the steels, except for the Kh3 and Kh9 steels, were determined by analyzing the precipitate formed upon the electrolytic dissolution of the samples. The methods used for the precipitation of inclusions, separation of oxide phases from carbide phases, and the determination of the oxide content in the precipitate were described in detail in [2].

The activities of silicon and aluminum were determined by calculation from analytical data on the steel chemical composition using available published data on first-order interaction parameters (Table 1).

The results obtained were generalized and compared with the published data on the following chromium steels: 15Kh1M1F [8–10], Kh15N25M3V6 [11], 1Kh18N12 [12–14], and Kh20N45B [12–14].

The results of the studies of the nonmetallic inclusions in the Kh3 and Kh9 steels were presented in [1]. They demonstrate that the composition, shape, and size of the nonmetallic inclusions can change depending on the deoxidizer content in the metal. The systematization and generalization of the earlier data and the results of this work made it possible to distinguish certain activity ranges of the strongest deoxidizer (silicon or aluminum) at which a certain type of oxide inclusions dominates (Tables 2, 3); i.e., the threshold values of the deoxidizer activity at which the main type of nonmetallic inclusions in steel is replaced were determined.

**Table 1.** First-order interaction parameters [3]

$e_i^j$	C	Si	Mn	S	P	Cr	Ni	V	Al
$e_{Si}^j$	0.180	0.11	0.002	0.056	0.11	-0.0003	-0.0088 [4]	0.025	0.058
$e_{Al}^j$	0.091	0.0056	-0.0129 [4]	0.030	0.033 [5]	0.012 [6]	0.0128 [7]	–	0.045

It is noteworthy that the data on the metal deoxidized by only silicon were obtained when studying the Kh3 and Kh9 steel sampled in quartz cans, i.e., cooled at a relatively high rate. Taking into account that SiO<sub>2</sub> inclusions at these silicon concentrations and at the corresponding activity of oxygen precipitate during crystallization (hence, their amount depends on the cooling rate), it should be expected that, for a slowly cooled metal deoxidized by silicon, the curve of the fraction of SiO<sub>2</sub> in the nonmetallic inclusions versus  $a_{Si}$  is somewhat shifted to the left, i.e., toward a higher SiO<sub>2</sub> content.

The data on the composition of the inclusions in a steel deoxidized by aluminum (and by both aluminum and silicon) were obtained for both a rapidly cooled metal (Kh3, Kh9 steels) and a metal cooled at a substantially lower rate (1Kh13M2BF, 01Kh14N5MF, Kh17N14M3, 01Kh18M2B, 01Kh18Yu, 15Kh2NMFA steels).

A quantitative analysis of the compositions of the inclusions at different activities of silicon in the Kh3 and Kh9 steels (Fig. 1) shows the following change in the inclusion composition. For a silicon activity lower than 0.1%, i.e., when a chromium–manganese spinel and heterogeneous manganese silicates are the main type of nonmetallic inclusions (Table 2), the SiO<sub>2</sub> content in the oxide phase is low and does not exceed 10%. At higher values of  $a_{Si}$ , the fraction of SiO<sub>2</sub> increases and reaches 80% at  $a_{Si} \approx 1.0\%$ . On the whole, the dependence of the silicon oxide content in the nonmetallic phase on the silicon activity in the metal at  $a_{Si}$  higher than 0.12% is satisfactorily described by the equation

$$(\text{SiO}_2) = 91.5 - 10.1/a_{Si} \quad (r = 0.94). \quad (1)$$

A comparison of the compositions of the nonmetallic inclusions in a chromium steel with different contents of aluminum shows the following change in the oxide phase composition. The content of Al<sub>2</sub>O<sub>3</sub> in the oxide phase increases sharply (from 10 to 80%) in a relatively narrow range of aluminum activities (from 0.006 to  $\approx 0.020\%$ ). For  $a_{Al} > 0.02\%$ , the character of the dependence of the content of (Al<sub>2</sub>O<sub>3</sub>) on  $a_{Al}$  changes substantially, and the content of (Al<sub>2</sub>O<sub>3</sub>) in the nonmetallic inclusions asymptotically approaches 100% (Fig. 2). On the whole, for  $a_{Al} > 0.005\%$ , the Al<sub>2</sub>O<sub>3</sub> versus  $a_{Al}$  dependence is satisfactorily described by the equation

$$(\text{Al}_2\text{O}_3) = 96.8 - 0.41/a_{Al} \quad (r = 0.861). \quad (2)$$

The threshold values of the aluminum activity corresponding to the replacement of the predominant type of inclusions are marked in Fig. 2. When the oxide phase is represented by inclusions corresponding to regions II and III (Table 2), the scatter of the fraction of aluminum oxide is the largest, and it is unlikely to determine the nonmetallic-phase composition at such values of the aluminum activity. For these aluminum concentrations, the rate of metal cooling can exert a substantial effect on the composition of inclusions.

**Table 2.** Dependence of the type of oxide inclusions on the silicon activity in Kh3 and Kh9 steels

Region	$a_{Si}$ , %	Main type of inclusions in steel
I	<0.08	Chromium–manganese spinel
II	0.08–0.20	Manganese silicates with spinel inclusions
III	0.20–0.40	Homogeneous manganese silicates
IV	0.40–0.80	Manganese silicates with a quartz component inside (as numerous inclusions) or on the surface (as a continuous and incomplete shell)
V	>0.80	Silica

**Table 3.** Dependence of the type of oxide inclusions on the activity of aluminum and silicon in various chromium steels

Region	$a_{Al}$ , %	$a_{Si}$ , %	Main type of inclusions in steel
I	<0.006	<0.10	Chromium–manganese spinel
		0.35	Silica and heterogeneous Mn silicates
II	0.006–0.010	<0.10	Aluminum–manganese spinel
		0.35	Heterogeneous inclusions containing Al, Si, and Mn
III	0.010–0.020	<0.10	Chromium aluminates
		0.35	Aluminosilicates
IV	>0.020	<0.10	Corundum
		0.35	Corundum

Since segregation processes during crystallization begin to develop more slowly at high rates and, correspondingly, complex inclusions containing SiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub> difficultly form, the fraction of Al<sub>2</sub>O<sub>3</sub> increases. At high activities of aluminum, almost all the oxygen is already bound before the beginning of crystallization; hence, the influence of the cooling rate is much less substantial in this case.

These statements are confirmed by the fact that the arrangement of points referring to the Kh3 and Kh9 steels does not completely correspond to the general tendency (Fig. 2): their position is somewhat overestimated and the difference decreases with an increase in the activity of aluminum in the metal. It should be mentioned that this behavior can also be related to the application of different analytical methods: not all the nonmetallic particles but the most prevalent ones were studied by electron-probe microanalysis; therefore, the averaged Al<sub>2</sub>O<sub>3</sub> content somewhat exceeds the corresponding values obtained by an analysis of the precipitate of inclusions formed upon the electrolytic dissolution of the metal samples.