Dephosphorization of Manganese Ferroalloys with CaO & MnO Based Slag-Forming Mixtures

V.Ya.Dashevskii*, V.I.Kashin*, N.P.Lyakishev*, B.F.Velichko** and A.V.Koval**

*A.A.Bailov Institute of Metallurgy, Russian Academy of Science, Moscow, Russia
**Nikopol Ferroalloys Works, Nikopol, Ukraine

Manganese ferroalloys, used to deoxidize and alloy many steel grades, are one of the main phosphorus contaminant. Increased phosphorus content in manganese ferroalloys produced by CIS-works is attributed to low manganese content (20-28%) and comparatively high one of phosphorus (0.2-0.3%) in manganese ores [1].

Therefore, it is necessary both to develop effective methods to dephosphorize manganese ores and solve the problem of high enrichment and dephosphorization of manganese ores.

Analysis of published data on phosphate capacity of slags and thermodynamics of phosphorus solutions in Mn-based melts showed that dephosphorization of high-carbon ferromanganese and silicomanganese with CaO- and BaO-based slags is possible at slightly oxidizing conditions ($\lg p_{O_2} \leq 10^{-16} \div 10^{-17}$)[2-4]. In so doing a phosphorus metal-slag transfer is limited by oxidation of manganese and silicon.

Dephosphorization of high-carbon ferromanganese can be made with BaO-based slags. The BaO-BaF_2-MnO system [2] could be chosen as a refining mixture. Inasmuch there are rather deep eutectics for BaO-MnO and BaO-BaF_2 systems [3,5], BaO-BaF_2-MnO slags are fluid at the ferroalloys production temperatures. Dephosphorization of high-carbon ferromanganese can also proceed because of the $BaCO_3$-flux treatment [2].

Dephosphorization of fines (formed through fractionating highcarbon ferromanganese and silicomanganese) with CaO-and BaO-slagforming mixtures in their combined melting in high-frequency induction furnace has been studied in this work.

The high-carbon ferromanganese (76.5% Mn; 0.6-0.7% P; 7.25% C; 0.1% Si) was treated with slag forming mixtures which contained (%): (30 ÷ 40)CaO-(50 ÷ 60)CaF_2-(0 ÷ 20)$CaCl_2$; (26 ÷ 34)BaO-(39 ÷ 51)BaF_2-(15 ÷ 35)MnO; 100 $BaCO_3$ Heats were made in argon atmosphere at 1400 °C and 0.1-slag ratio. Fractionated metal was mixed with slag forming mixture before melting. The dephosphorization degree (ε_P) approached to 20-25% just on metal melting and decreased while melt holding in contact with the slag. As for CaO-CaF_2 mixture, phosphorus slag-metal distribution coefficient achieves 2-2.5. It is two orders by large as compared with slags which are characteristic for high-carbon ferromanganese production. Replacing CaF_2 for $CaCl_2$ slightly changes to the worse characteristics of dephosphorization.

Dephosphorization is significantly more progressive as a result of the treatment of high-carbon ferromanganese with BaO-BaF_2 slag mixtures (Fig.1): dephosphorization degree was 30-40% on melting and distribution coefficient L_P = 2.5 ÷ 6.5. Rephosphorization markedly proceeded through the melt holding in contact with the slag. Figure 2 shows dependencies of L_P and ε_P on CaO and BaO contents in slag. Characteristics of dephosphorization in the case of BaO-based mixtures were better by factor of 2-3 as compared with CaO-based ones. Therefore, the treatment of high-carbon ferromanganese with CaO- and BaO-based slags allows us to decrease substantially phosphorus content in metal at comparatively low slag ratio.

Dephosphorization of silicomanganese with CaO-SiO_2-MnO slags has been studied Silicomanganese (74.4% Mn; 0.37% P; 17.1% Si; 1.7% C) was treated with slag forming mixtures which contained (%): (30 ÷ 40)CaO-(30 ÷ 45)SiO_2 -(10 ÷ 20)MnO-(6 ÷ 8)CaF_2 Heats were made at 1300 °C in argon atmosphere and 0.1-slag ratio. Fractionated metal was mixed with slag forming mixture consisted of pure oxides before melting.

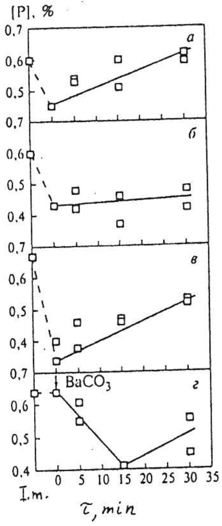

Fig. 1. Dependence of Phosphorus Content in High-Carbon Ferromanganese on Time of Its Contact with Refining Mixture (I.m. - initial metal; τ - time after total melting). Composition of Initial Refining Mixture, %: a - 26 BaO-39 BaF_2-35 MnO; b - 30 BaO-45 BaF_2-25 MnO; c - 34 BaO-51 BaF_2-15 MnO; d - 100 $BaCO_3$

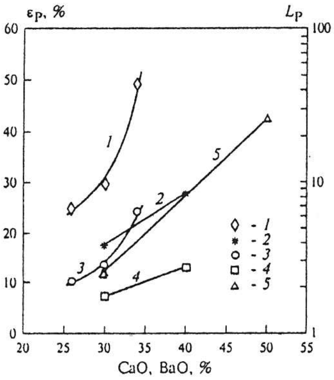

Fig. 2. Dependence of Dephosphorization Degree (1, 2) of High-Carbon Ferromanganese and Phosphorus Slag-Metal Distribution Coefficient (3-5) on Content of BaO (1, 3, 5) and CaO (2, 4) in Slag: 1-4 - experimental data; 5 - data of [5]

Dephosphorization degree was 30-40% and $L_P = 5 \div 6$ (Fig.3). Additions of 5-10% Al_2O_3 and MgO into slag don't markedly influence dephosphorization characteristics. The partial substitution of CaO for BaO results in an increase of dephosphorization degree. The partial substitution of SiO_2 for B_2O_3 doesn't practically influence dephosphorization degree.

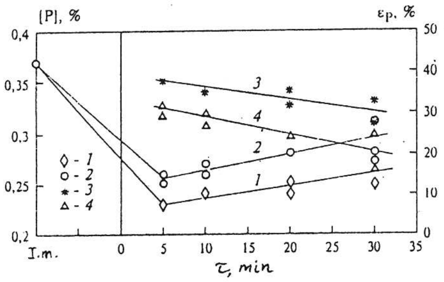

Fig. 3 Dependence of Phosphorus Content in Silicomanganese (1, 2) and Dephosphorization Degree (3, 4) on Time of Its Contact with Refining Mixture. Composition of Initial Refining Mixture, %: 1, 3 - 30 CaO-45 SiO_2 -19 MnO-6 CaF_2 ; 2, 4 - 33 of lime, 30 of quartzite, 30 of low phosphate slag, 7 of fluorite concentrate

Lime, quartzite, low phosphorus manganese slag and fluorite concentrate can serve as original materials to prepare refining mixtures with the above given composition [6] in industry. Basing on the above, dephosphorization of silicomanganese has been studied as a result of its melting with the mixture containing 33% of lime (86% CaO), 30% of quartzite (98% SiO_2), 30% of low phosphorus manganese slag (54.6% MnO; 28.5% SiO_2; 5.3% CaO; 0.012% P), and 7% of fluorite concentrate (95% CaF_2). Up to total melting the dephosphorization degree was 27-30% ($L_P = 3 \div 4$). It is slightly lower as compared with the mixture consisted of pure oxides (Fig.3). The low phosphorus manganese slag, being a commodity product, contributes the required portion of MnO into the refining mixture. It can be replaced to a large degree for waste slags of high-carbon ferromanganese (16-18% MnO) and silicomanganese (15-17% MnO) productions or their mixture [6]. In this case some changing to the worse in characteristics of dephosphorization can be compensated through increasing the slag ratio as high as 0.20-0.25 (Fig.4).

Efficiency of dephosphorization of manganese ferroalloys with slag forming mixtures depends on a reaction surface and intervals of softening and melting temperatures for burden components. Dephosphorization degree depends on a granulometry of materials used for a given composition of the refining mixture. Therefore, effect of the granulometry of metal and slag forming materials on dephosphorization degree of silicomanganese has been studied. Waste slag of high-carbon ferromanganese was used as a refining material. The best results, ε_P = 25-35%, (for argon atmosphere, 100g-samples and 0.2-slag ratio) were observed for (2-3)mm-size of metal and waste slag. When melting in air of 250g-samples with 0.2-slag ratio, the higher dephosphorization degree (ε_P = 35-50%) was achieved. It can be explained through the high oxidizing potential of gas phase.

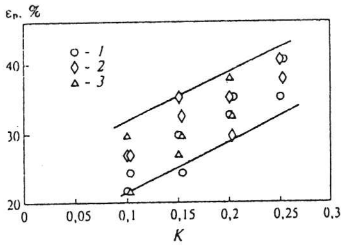

Fig. 4. Dependence of Dephosphorization Degree of Silico-manganese on Refining Slag Ratio (K) Containing Waste Slags of High-Carbon Ferromanganese (1), Silicomanganese (2) and Mixture of These Slags (3)

Thus, results obtained showed that the treatment of high-carbon ferromanganese and silicomanganese with CaO- and BaO-based slags, including materials and waste products of ferroalloys production, allows the significant decreasing phosphorus content in metal at comparatively low slag ratio. The use of this process in industry is feasible, e.g. to compact fines of high-carbon ferromanganese or silicomanganese formed as a result of fractionation of the alloys.

REFERENCES

1. Gasik M.I., Lyakishev N.P., Emlin B.I. Theory and Technology of Ferroalloys Production. Moscow.: Metallurgiya. 1988. 784 p

2. Lee Y.E. // Proceedings of Sixth Iron and Steel Congress. Nagoya : ISIJ. 1990. V. 1. Fundamentals. P. 327-333.

3. Fuitta M., Katayama H., Yamamoto A., Matsuo T. // J. Iron and Steel Institute Japan. 1988. V. 74, No 5. P. 816-822

4. Dashevskii V.Ya., Katsnelson A.M., Krylov A.S., et al.// Theory and Practice of Manganese Metallurgy Moscow.: Nauka. 1990 P. 9-18

5. Hara T., Tsukihashi F., Sano N. // J. Iron and Steel Institute Japan. 1990. V. 76, No 3. P. 46-53.

6. Patent of RF No.2049121. Mixture for Dephosphorization of Ferroman- ganese. Authors: Dashevskii V.Ya., Katsnelson A.M., Makarova N.N., et al. Izobreteniya 1995. No 33.