Oxide Inclusions in Ferromanganese and Its Influence on the Quality of Clean Steels

Pei-wei HAN[1], Shao-jun CHU[1], Ping MEI[2], Yi-fei LIN[2]

(1. School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China; 2. Jiangsu Jiangnan Ferroalloy Co., Ltd., Changzhou 213119, Jiangsu, China)

Abstract: Low and medium carbon ferromanganese produced by oxygen decarburization process and electric silicothermic process was briefly introduced, and the quality of products by these two processes was analyzed. Results showed that the total oxygen content in medium carbon ferromanganese by electric silicothermic process in China, which ranged from 0.039% to 0.171%, was between those of the common and refined products by oxygen decarburization process outside of China. The increments of total oxygen content in liquid steel were estimated when ferromanganese was added for the purpose of Mn element adjustment at the end of smelting. Refined low and medium carbon ferromanganese, which had low total oxygen content, was recommended for composition adjustment of clean steels during final stage of a heat. It is possible that the inclusions in the ferromanganese alloy greatly influenced the quality of clean steel indirectly by affecting the amount, size and composition of inclusions in steel.

Key words: low carbon ferromanganese; medium carbon ferromanganese; oxide inclusions; clean steels

Inclusion control has attracted more attention recently, as more rigorous requirements on steel cleanliness are continually emphasized with the modern industry development and technology progress. Recently, researches on inclusions in steel have mainly concentrated on the following two aspects[1]. One is inclusion removal and inclusion modification during steel refining process. The other is the influence of factors such as lining refractory material, mold flux and reoxidation.

Ferroalloy addition is one of the important steps during secondary refining to deoxidize the steel or alloy. Limited by the purity of the ferroalloy, it is unavoidable to introduce some impurities such as inclusions into the steel, affecting the quality of the steel. However, there is very little information available concerning inclusions in ferroalloy and its influence on steel cleanliness during secondary steelmaking. Although many works have been done on the ferrosilicon[2, 3], ferrochromium[4, 5], ferromanganese[6-9] and some other ferroalloys[10], these work was not enough to figure out the effect of inclusion in ferroalloys. Especially, the inclusion strongly depended on the metallurgical process, but the information about the inclusions in the ferroalloys products produced in China was rarely reported. For example, the total oxygen content, an important composition for the steel production, is not even involved in existing ferroalloy national standards in China. The aim of present investigation is to introduce domestic product quality of medium carbon ferromanganese, and the possible problems incurred by ferroalloy addition are discussed when they are applied for clean steel production.

1 Detection Method for Inclusions in Ferromanganese

The morphology of inclusions in ferroalloys such as size, shape, and composition was usually determined by metallographic method combined with scanning electron microscopy (SEM)[5, 6]. Although convenient, the information about quantity and three-dimensional morphology were still difficult to obtain with metallographic method.

Bulk sample electrolysis was employed to study the morphology of inclusions in ferroalloy in this work, which was commonly used to detect macro inclusions in steel. The electrolyte for ferromanganese sample electrolysis contained 0.8%–1.0% potassium bromide, 1.2%–1.5% ascorbic acid, 0.2 g/L sodium sulfite, 0.3% glycerol, 3%–4% sodium citrate and 100 g/L ammonium sulfate. In the meanwhile, the morphology and composition of inclusions in ferroalloy were analyzed by SEM and X-ray diffraction (XRD) analysis.

The present investigation focused on detection of oxide inclusions in ferroalloy. The amount of oxide inclusions in ferroalloy could be determined indirectly

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Biography: Pei-wei HAN, Doctor Candidate; **E-mail:** hanpeiwei1988@163.com;
Corresponding Author: Shao-jun CHU, Doctor, Professor; **E-mail:** chushaojun@metall.ustb.edu.cn

by T.O. (the total oxygen content). Rod samples were preferred for oxygen analysis instead of powder samples, because the ferroalloy components were susceptible to oxidation.

2 Quality Analysis of Ferromanganese Produced by Different Metallurgical Process

Oxygen decarburization process and shaking ladle-electric silicothermic process were the main production methods of LC FeMn (low carbon ferromanganese) and MC FeMn (medium carbon ferromanganese). In the oxygen decarburization process, molten high carbon ferromanganese produced in submerged arc furnace or blast furnace as raw materials was added into oxygen basic converter. Oxygen was blown into the molten ferromanganese through oxygen lance, and carbon was oxidized into carbon monoxoide. The desirable concentration according to the requirement of LC and MC, could be achieved by controlling the amount of blowing oxygen. The reaction principle was described as,

$$2[C]+O_2=2CO \quad (1)$$

where, [C] is carbon dissolved in the molten ferromanganese.

In the shaking ladle-electric silicothermic process, silicomanganese ferroalloy with low carbon content as intermediate ferroalloy was firstly produced in submerged arc furnace. The silicon in the ferroalloy acted as the reducing agent, which reduced the manganese oxide in the manganese ore, and the manganese content in the ferroalloy increased. When the silicon content decreased and met the standard requirement, MC and LC FeMn was obtained. The reaction could be expressed as,

$$[Si]+2(MnO)+2(CaO)=(2CaO\bullet SiO_2)+2Mn \quad (2)$$

where, [Si] is dissolved silicon in the silicomanganese ferroalloy, (MnO) was manganese oxide in the manganese ore.

Due to the difference of process, T.O. in LC and MC FeMn was fairly different, as shown in Table 1. T.O. in LC FeMn by oxygen decarburization process was as high as 1.11% in common product, or as low as 0.04% in refined products. And they were 0.89% and 0.02% in MC FeMn, respectively. While, T.O. in MC FeMn by electric silicothermic process in China ranged from 0.039 wt.% to 0.17 1wt.%, which was between the common and refined products by oxygen decarburization process outside of China. There were no actual products of refined LC FeMn and MC FeMn in China, and T.O. in laboratory products varied between 0.011% and 0.015%. Oxygen decarburization process was chosen to produce LC and MC FeMn in ferroalloy plants outside of China. In order to meet the requirement of steel plant, their products were divided into the common and the refined, depending upon the differences between oxygen content in the ferroalloy.

Currently, LC and MC FeMn provided to domestic steel plant were produced with the electric silicothermic process, T.O. in which was between the common and refined products by oxygen decarburization process outside of China. As shown in Table 1, fluctuations of T.O. between different heats were fairly large, indicating that different process resulted in the difference in amount and distribution of oxide inclusions in MC FeMn. The SEM photo of oxide inclusions in MC FeMn was given in Fig. 1, in which corresponding composition of point A is 48 at.% O, 12 at.% Si, 40 at.% Mn, and corresponding composition of point B was 64 at.% O, 31 at.% Ca, 5 at.% Mn. The amount and size grading of inclusions

Table 1 Chemical composition of low and medium carbon ferromanganese

Ferromanganese process	Product		Chemical composition/%							Note
			Mn	Si	C	P	S	N	O	
Oxygen decarburization process	Common	MC	81.10	0.12	0.77	0.17	0.004	0.07	0.89	Ref. [6]
		LC	79.60	0.01	0.34	0.17	0.004	0.14	1.11	
	Refined	MC	81.00	0.39	1.38	0.16	0.003	0.07	0.02	
		LC	81.40	0.32	0.48	0.16	0.003	0.04	0.04	
Electric silicothermic process	Common	MC	78.39	0.99	1.40	0.18	0.010	—	0.039 — 0.171	Product of a certain ferroalloy plant in China
	Refined	MC	82.25	0.20	1.43	0.18	0.010	—	0.011 — 0.015	Laboratory product