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OXYGEN-BLOWING REMELTS OF LOW-ALLOYED Cr-Mn-Ni-Mo STEELS WITH THE VARIABLE OXIDATION RATE OF CARBON, CHROMIUM AND PHOSPHORUS

1. INTRODUCTION

Systematic growth of steel production in the world results in the growth number of steel castings, especially alloyed steel: chromium – nickel and high manganese grades. They are popular because of high functionality in such areas as power industry, ore and mineral processing industry and petrochemistry.

Technology of melting the above mentioned grade of steels is based on using the scrap in the charge (risers, ingate systems and defected castings). Electric arc furnace with basic lining and crucible induction furnace are used to melt of the low-alloyed steel. Induction furnace gives only the possibility of remelting the alloyed steel scrap with good quality charge. Electric arc furnace, on the other hand, enables to get cast steel characterized by wide range of chemical content both with high and low quality charges. Additionally implementation of arc furnace results in getting well deoxidized steel with low content of carbon, phosphorus and sulfur which are particularly important in case of high alloyed chromium, chromium – nickel and manganese steel grades, characterized by higher solubility of nitrogen and oxygen.

Introduction of oxygen-blowing re-melting process makes it possible to recovery the alloyed elements and brings about economic profits by reducing the costs.

In the foundries, which have constructed pure oxygen installations it is possible to implement this method of melting, based on Hilty's process and its modern modifications for steel foundries:

- DETEM [1],
- LF [2] which enables oxidation of carbon before oxidation of chromium and manganese.

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Such technologies has been used for the production of castings from Hadfield steel [3, 4, 6, 8] and wear resistant Cr-Ni-Mo steels [8–10].

2. EXPERIMENTAL

Industrial melts were carried out in the 8 Mg electric arc furnace with basic lining, by the oxidation method using 100% Cr-Mn-Ni-Mo scrap grade L70H2GNM and 70–100 kg of lime. After melting period steel was heated to 1560–1600°C and then oxidized by iron ore (melts 1–4) or pure oxygen (melts 5–8). Depending on the oxidizer used and concentration of carbon, phosphorus and chromium in the charge, different rate of oxidation of the elements was observed. There were 4 melts oxidized by iron ore and 4 by pure oxygen chosen for the analysis. The measurements were realised during the characteristic period of melting: prior to blowing oxygen into the bath, and after the end of oxygen blowing. Consumption of pure oxygen was an average 0.47 Nm³/min for one Mg of liquid steel. The average consumption of ore changed between 0.9–1.1 kg/0.01% C for one Mg of steel. A lance introduced oxygen, was ¾ inch in diameter. When oxygen blowing was over, the slag was taken off, the steel was deoxidised by FeSi75 and reduction process started.

Table 1. The content of charge and chemical content analysis after melting process for the heats with 100% of returned scrap

| Melt | Charge weight, Mg | Time | Chemical composition, % | | | | | | |
|------|-------------------|---------|-------------------------|------|------|------|-------|-------|--------|
| | | | C | Si | Mn | Cr | P | S | Period |
| 1 | 8.50 | 0:00 | 1.00 | 0.32 | 0.31 | 1.25 | 0.124 | 0.040 | (1) |
| | | 1:35 | 0.41 | 0.00 | 0.09 | 0.24 | 0.003 | 0.029 | (2) |
| | | 2:15 | 0.64 | 0.56 | 0.96 | 1.81 | 0.030 | 0.018 | (3) |
| 2 | 8.50 | 0:00 | 1.35 | 0.28 | 0.66 | 1.54 | 0.108 | 0.025 | (1) |
| | | 3:10 | 0.58 | 0.01 | 0.17 | 0.40 | 0.024 | 0.031 | (2) |
| | | 4:00 | 0.61 | 0.32 | 0.88 | 1.67 | 0.037 | 0.024 | (3) |
| 3 | 8.50 | 0:00 | 1.16 | 0.16 | 0.44 | 1.08 | 0.105 | 0.032 | (1) |
| | | 2:45 | 0.89 | 0.01 | 0.11 | 0.31 | 0.030 | 0.046 | (2) |
| | | 3:15 | 0.79 | 0.30 | 0.91 | 1.80 | 0.050 | 0.030 | (3) |
| 4 | 8.40 | 0:00 | 1.12 | 0.10 | 0.30 | 0.99 | 0.120 | 0.060 | (1) |
| | | 2:00 | 0.53 | 0.01 | 0.14 | 0.37 | 0.024 | 0.047 | (2) |
| | | 3:00 | 0.65 | 0.46 | 0.90 | 1.77 | 0.038 | 0.035 | (3) |
| 5 | 8.00 | 0:00:00 | 0.68 | 0.08 | 0.38 | 0.90 | 0.041 | 0.029 | (1) |
| | | 0:05:00 | 0.58 | 0.03 | 0.30 | 0.72 | 0.031 | 0.028 | (2) |
| | | 1:20:00 | 0.66 | 0.58 | 1.05 | 1.88 | 0.035 | 0.022 | (3) |
| 6 | 8.20 | 0:00:00 | 0.60 | 0.03 | 0.18 | 0.81 | 0.024 | 0.024 | (1) |
| | | 0:05:30 | 0.41 | 0.01 | 0.13 | 0.70 | 0.014 | 0.018 | (2) |
| | | 1:20:00 | 0.68 | 0.47 | 1.08 | 1.97 | 0.025 | 0.010 | (3) |
| 7 | 8.50 | 0:00:00 | 0.93 | 0.25 | 0.41 | 0.87 | 0.047 | 0.036 | (1) |
| | | 0:03:45 | 0.80 | 0.14 | 0.36 | 0.85 | 0.044 | 0.023 | (2) |
| | | 1:20:00 | 0.68 | 0.43 | 0.99 | 1.97 | 0.040 | 0.019 | (3) |
| 8 | 7.80 | 0:00:00 | 0.81 | 0.10 | 0.31 | 1.61 | 0.030 | 0.041 | (1) |
| | | 0:07:00 | 0.69 | 0.04 | 0.23 | 1.39 | 0.030 | 0.040 | (2) |
| | | 1:10:00 | 0.74 | 0.45 | 1.09 | 1.79 | 0.033 | 0.019 | (3) |

(1) – start of oxidation period; (2) – end of oxidation period; (3) end of melt

Each melt was done with white slag and the steel was deoxidised in a ladle by aluminium at 1 kg/1 Mg of steel. The melting period changed from 1 h 45 min to 3 h 45 min. For the melts with the oxidation by iron ore, the oxidation period changed from 1 h 35 min–3 h 10 minutes and total heat time – 4 h 15 min to 7 h. For the melts with pure oxygen injection, the oxidation period changed from 3 min 45 s – 7 min and total melt time was 3 h 40 min to 4 h 15 min. The chemical composition changes during each heat are shown in Table 1.

3. RESULTS AND DISCUSSION

Data presented in Table 1 show that the melting of 100% returned scrap provide to different chemical composition at the end of melting period. After melting the charge, the content of chromium fluctuated between 0.81–1.61% and the carbon content 0.60–1.35%. The chemical composition of the bath before oxygen blowing depends on the percentage of high-alloy chromium steel scrap used in the charge, the time of melting and chemical content of slag.

In the oxidation period, when the concentration of oxygen in the bath is over 150 ppm there can be observed strong oxidation of carbon and other elements characterised by their high affinity to oxygen, i.e. silicon, manganese and chromium. In remelting process of Cr-steels by means of oxygen blowing, there is a possibility of decreasing of alloyed elements losses by precise choice of thermo-physical conditions. Such processes can be controlled by the temperature of the liquid steel, the pressure of gaseous reaction products above the bath, the concentration of oxides in the slag and by slag basicity.

Table 2 presents calculated results of the rate of carbon, phosphorus and chromium oxidation at the different temperatures of the bath. In the heats oxidized by oxygen, it was observed a much higher, in comparison to the melts oxidized by ore, the rate of phosphorus oxidation despite the higher temperature of the process. In two melt of this group, marked as 7 and 8, an oxidation rate of phosphorus is lower than the average. It should be emphasised that in one of this melts (7) there was obtained 0.25% Si, which means that this element diminished the slag basicity. In the both melts (7, 8) the temperature was over 1625°C and it is possible to reduce P_2O_5 from slag to metal. Low basicity of slag results in lowering the rate of dephosphorisation. In the melts oxidised by the iron ore there is not observed any significant lowering of the rate of dephosphorisation despite the silicon level up to 0.32% after melting because of the constant adding of lime and ore in portions during the oxidation period. During these additions the SiO_2 content in the slag doesn't have decisive role in rate of dephosphorisation. Much important role is played by the presence of chromium oxides in slag, which increase its viscosity and diminish the metal – slag interfacial surface.

In practical condition, the loss of chromium is important at the constant chemical content of the other elements. In our investigations the metallurgical processes were controlled in order to reduce melting losses of chromium at intensive oxidation of carbon. The most important parameter in own provided melts was the regulation of the bath temperature before the oxygen injection. Because of the high content of carbon in the bath 0.60–1.35%, an oxidation of this element is highly facilitated in the presence of 1.0% Cr in liquid steel. On the basis of Table 2 it is obvious that at such concentration of chromium, the temperature above 1620°C enables considerably reduce melting loss of chromium, while intensive oxidation of carbon.

Table 2. The results of oxidation rate with the use of iron ore and pure oxygen for the heats with 100% of returned scrap

| Melt | Oxidizer | Oxidizing time, min | Oxidation rate | | | Temperature °C |
|----------------|----------|---------------------|----------------|--------|-------|----------------|
| | | | % C/h | % Cr/h | % P/h | |
| 1 | Iron ore | 95:00 | 0.37 | 0.64 | 0.076 | – |
| 2 | | 190:00 | 0.24 | 0.36 | 0.027 | – |
| 3 | | 165:00 | 0.10 | 0.28 | 0.027 | – |
| 4 | | 120:00 | 0.30 | 0.31 | 0.048 | – |
| Average | | 142:30 | 0.25 | 0.40 | 0.045 | – |
| Std. deviation | | 42:55 | 0.12 | 0.17 | 0.023 | – |
| 5 | Oxygen | 5:00 | 1.20 | 2.16 | 0.120 | 1580 |
| 6 | | 5:30 | 2.07 | 1.20 | 0.110 | 1625 |
| 7 | | 3:45 | 2.08 | 0.32 | 0.048 | 1625 |
| 8 | | 7:00 | 1.03 | 1.88 | 0.000 | 1635 |
| Average | | 5:19 | 1.60 | 1.39 | 0.070 | – |
| Std. deviation | | 1:21 | 0.56 | 0.82 | 0.056 | – |

The reduction of chromium oxides by carbon is characterised in Hilty's process by the following equation [12]:



$$\lg K' = -13\,800/T + 8.76 \quad (2)$$

According to the research by W.E. Dennis and F.D. Richardson [11], the influence of temperature is essential. At 1600°C the carbon content can be lowered to 0.10% and at the temperature 1650 – to 0.07% as shown at Figure 1. These data are important for partial CO pressure = 1 at.

Steelmaking shops in foundries use smaller electric arc furnaces with capacities 8–15 Mg. In comparison to the oxidation remelting processes of Cr and Cr-Ni steels in metallurgical plants based on AOD, BOF, VAD [10, 16] and the innovative steel production unit, Conarc process [13] or Vacuum Induction Degassing and Pouring VIDP [14], steel foundries are equipped with ladle-furnace LF, DETEM units [1, 2] but generally EAF [9] or EAF-VD, EAF-VOD technologies are used [15, 16]. Their main purposes are connected on the oxygen blowing conditions, i.e.: carbon and chromium concentrations and bath temperature before blowing.

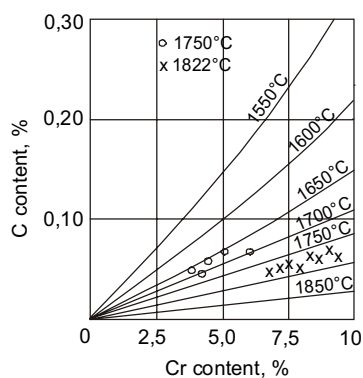


Fig. 1. Influence of temperature and chromium concentration on carbon content in the alloys Fe-Cr-C [12]

Figure 2 presents the results of Cr melting losses in comparison to final carbon content in the bath, in re-melting process. It was shown that increasing the carbon content of the end of oxidation process allows for significant decrease of chromium loss.

Application of pure oxygen decreases the rate of chromium oxidation and increases the rate of carbon oxidation, Table 2. At the temperature 1580°C the rate of carbon oxidation was low (1.20% C/h) and at 1620°C – was over 2% C/h. These results allow for the introduction of re-melting process by means of oxygen blowing of chromium steel bath. Simultaneously, this process is lowering annual costs of such operation, through shorter oxidizing periods and consequently – decreasing of energy consumption.

Comparison of the rate of carbon, silicon, and phosphorus oxidation favours oxygen-blowing technology. Particular rate of carbon oxidation in re-melting method is presented in Figure 3. We can observe that carbon oxidation rate changes between 0.10–0.37% C/h in oxidizing by iron ore technology. In oxygen blowing technology, the rate of carbon oxidation was 1.03–2.08% C/h.

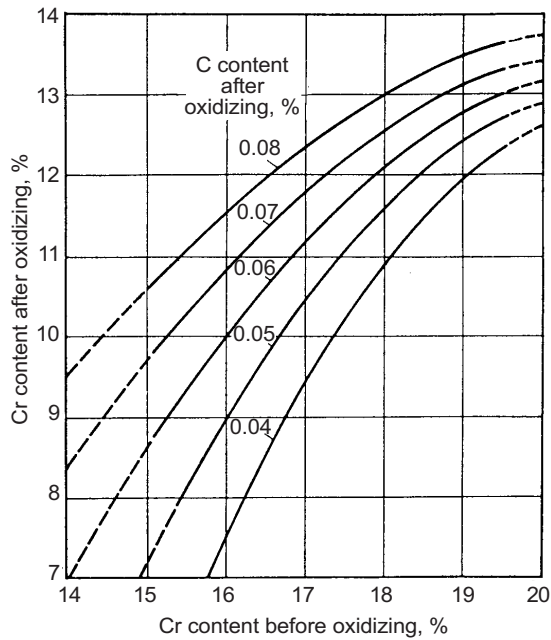


Fig. 2. Comparison of Cr content before and after oxidizing in relationship with final C content [17]

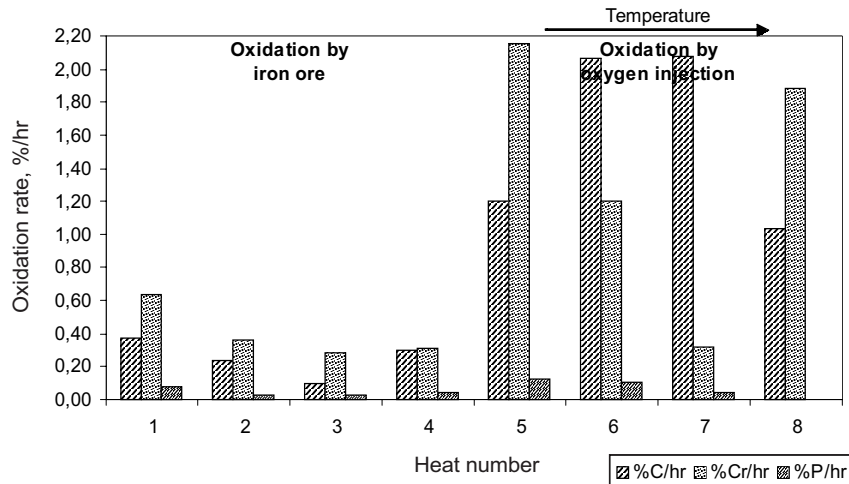


Fig. 3. The rate of carbon, silicon, and phosphorus oxidation in re-melting process

As can be observed average rate of carbon oxidation is 1.60% C/h in oxygen blowing melts, and only 0.25% C/h in melts oxidized by iron ore. Similar to carbon, also the phosphorus oxidation rate, rises when pure oxygen is used during bath oxidation and constitutes 0.070% P/h instead of 0.045% P/h. It has been observed that in the melts oxidized by oxygen, the higher temperatures make the lower Cr losses (in accordance with theory – see equation (1)–(2).

The most economical effect of oxygen blowing technology is connected with lower time of melts oxidized by oxygen than the melt oxidized by iron ore.

4. CONCLUSIONS

- The carbon and chromium oxidation rates in oxygen-blowing remelted chromium low-alloyed steels are respect three and two times higher than in the melts oxidized by iron ore.
- The chromium oxidation rate can be limited by increasing the bath temperature above 1620°C (Tab. 2).
- At temperatures exceeding 1630°C we observed lowering of the dephosphorisation rate.
- In remelting processes at the use of iron ore the rates of carbon and phosphorus oxidation are lower than in re-melting processes by means of oxygen blowing.
- The dephosphorisation in the heats oxidized by oxygen injection are two times higher than in the heats oxidized by iron ore.

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