SECTION 3. METALLURGY

ON THE MECHANISM OF OXIDES REDUCTION
BY CARBIDES AND CATALYTIC ADDITIVES ACTIVITY
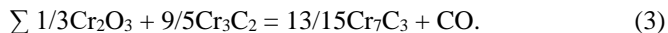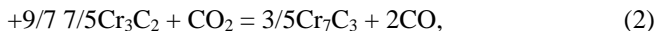
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Metal reduction from ore material is the most important stage of pyrometallurgical technology. The carbon-containing reductant used in this case provides the reduction (independently or together with the gas phase) of almost any metal. The thermodynamic parameters of such a process are the temperature of the onset of reduction and the equilibrium composition of the gas phase. Algorithm for the calculation of parameters, applied to the carbon-thermal reduction of chromium oxide by its higher carbide, Cr_3C_2. presented by [1]. The transition to complex reduction with the participation of carbide does not change the calculation methodology. The given algorithm is also applicable for the variant of reducing a mixture of oxides, which is important for the production of multicomponent spongy addition alloys.

Chromium oxid reduction with a higher carbide of the latter develops according to a two-stage mechanism and can be described by the reactions:

$$+1\ 1/3Cr_2O_3 + 11/7CO = 2/21Cr_7C_3 + 9/7CO_2, \tag{1}$$

$$+9/7\ 7/5Cr_3C_2 + CO_2 = 3/5Cr_7C_3 + 2CO, \tag{2}$$

$$\sum 1/3Cr_2O_3 + 9/5Cr_3C_2 = 13/15Cr_7C_3 + CO. \tag{3}$$

The aim of this work was a practical confirmation of this mechanism based on the performed thermodynamic and kinetic studies, as well as further analysis of the mechanism of action of catalytic additives on the process.

Measurement of the rate of the process under isothermal conditions showed that the process develops much more slowly than when using free carbon in the charge. So, at 1400^0C the degree of reduction of Cr_2O_3 with carbide Cr_3C_2 for 25 min was 93,6%, while in experiments with graphite, the $Cr_2O_3 \rightarrow Cr_3C_2$ transformation is completed for ~15 min. The rise in temperature to 1400^0C provided a slightly higher level of recovery ~ up to 70%. In order to further increase the rate of Cr_2O_3, small additions to the charge of alkali metal salts, namely potassium and sodium in the amount of 1% by weight were used. K_2CO_3, KCl, Na_2CO_3 и NaCl were used as catalysts. Experimental data indicate the most significant acceleration of the process in the presence of K_2CO_3: the degree of reduction within 25 min. increased from 68 to 79.5%. The introduction of sodium carbonate into the charge led to an increase in ω of more than 77%. The catalytic action of the tested additives was preserved at 1400^0C. The research results [2] made it possible to conclude that solid-phase reduction of chromium (III) oxide by Cr_3C_2 carbide develops mainly through the gas phase. Confirmations were obtained for these ideas about the mechanism of the process [2]: the introduction of a loosening additive Al_2O_3 into the charge mixture practically does not affect the rate of the process (Figure 1).
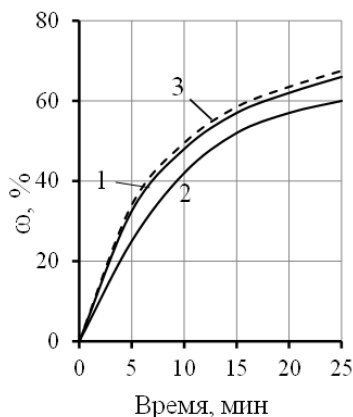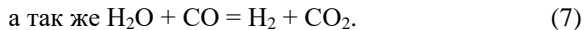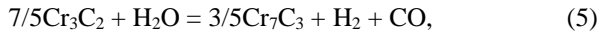

Figure 1. Reduction kinetics Cr_2O_3 with carbide Cr_3C_2 at 1350^0C: 1,2 - without additive; 3 - with Al_2O_3; 1,3 - sample weight 740 mg; 2 - Sample weight 370 mg.

Consequently, the direct contact interaction of the carbide and oxide phases does not play a decisive role. At the same time, an increase in the mass (and volume) of the charge mixture significantly accelerates the process. It is likely associated with the development of reactions (2) and (1). Their robust relationship leads to the following cycles of transformation:

$$CO \xrightarrow{Cr_2O_3} CO_2 \xrightarrow{Cr_3C_2} CO \xrightarrow{Cr_2O_3} CO_2 \xrightarrow{Cr_3C_2} CO \rightarrow \ldots \quad (4)$$
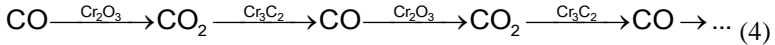
Due to the chain of transformations, gas molecules during their residence in the volume of the charge can repeatedly participate in reactions (2) and (1). The duration of the cycles increases with an increase in the volume of the charge mixture, which should lead to an acceleration of the reduction of Cr_2O_3, which has been established experimentally.

With complex reduction in the vapor-gas phase, hydrogen and water vapor appear, which leads to the development of the reaction:

$$7/5Cr_3C_2 + H_2O = 3/5Cr_7C_3 + H_2 + CO, \quad (5)$$

$$1/3Cr_2O_3 + H_2 + 4/7CO = 2/21Cr_7C_3 + H_2O + 2/7CO_2, \quad (6)$$

$$\text{а так же } H_2O + CO = H_2 + CO_2. \quad (7)$$

Along with cycles (4), the following cycles of transformation:

$$H_2 \xrightarrow{Cr_2O_3} H_2O \xrightarrow{Cr_3C_2} H_2 \xrightarrow{Cr_2O_3} H_2O \xrightarrow{Cr_3C_2} H_2 \rightarrow \ldots. \quad (8)$$
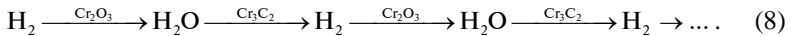
The course of reactions (1) and (6) seems to be the most probable through the preliminary formation of oxycarbide fluctuations, from which oxygen is gradually removed with the help of CO and H_2. As a result, an independent phase Cr_7C_3 appears. The authors of [3] pointed out the possibility of the formation of chromium oxycarbides during the reduction of Cr_2O_3 with carbon.

The intensification of the process during the transition to complex reduction is associated primarily with the replacement of argon with hydrogen, which leads to an increase in the concentration of reducing gases in the reaction zone. Their repeated regeneration is possible by reactions (2) and (5). Moreover, the latter, apparently, has rate advantages over (22). This is confirmed by the results of the study of carbon gasification with CO_2 and H_2O. (for example [4]).

By analogy with the processes of reduction of iron oxides [5], it can be assumed that hydrogen has adsorption-chemical advantages over CO in

42

interaction with Cr_2O_3, which explains the higher rates of reaction (6) compared to (1). The diffusion advantages of $H_2 - H_2O$ over $CO - CO_2$ are manifested with any mechanism of gas transfer.

The mechanism of intensification of the Cr_2O_3 gas reduction link (with carbon monoxide and hydrogen) by catalytic additions of alkali metal salts was investigated in detail by us and is associated with the replacement of Cr^{3+} cations by monovalent potassium and sodium ions, which leads to the enrichment of the oxide surface with electron holes. This, in turn, favors the chemo-sorption of reducing gas molecules and the desorption of CO_2 and H_2O gaseous products. At the same time, these substitution processes are accompanied by the appearance of new vacancies in the crystal lattice of the oxide. The concentration of unsaturated valences is growing. The weakening of the $Cr - O$ chemical bonds facilitates the removal of oxygen from the oxide phase.

The interdependence of individual links of recovery and the development of transformation cycles (4), (8) leads to the fact that the intensification of one link favors the development of another one. Therefore, the acceleration of gas reduction reactions of Cr_2O_3 by catalytic additives should, to a certain extent, accelerate the gasification of chromium carbide with carbon dioxide and water vapor. The direct effect of the catalyst on the gasification process requires special studies. We can only tentatively express the following considerations. Chromium carbide is characterized by mixed electron-hole conductivity [6]. The fraction of hole-type increases in the sequence $Cr_3C_2 - Cr_7C_3 - Cr_{23}C_6$. Oxidative gasification of carbides should be accompanied by acceptor chemisorption of CO_2 and H_2O molecules. Its development will be facilitated by the enrichment of the surface of carbide crystals with electrons.

In work [6] it is shown that at the temperatures of the experiment, the tested additives dissociate with the transition of alkali metals into the gas phase. Being adsorbed on the carbide surface, potassium and sodium atoms can donate their valence electrons to the solid reducing agent. The chemisorption of CO_2 and H_2O molecules will increase, accelerating the links in the gasification of carbides and the reduction of Cr_2O_3 in general.

Taking into account the possibility of implementing the above mechanism, it should be noted that the catalytic effect of the addition of alkali metal salts manifested itself more strongly when using free carbon in the charge.

References:

1.   V.K. Simonov, O.M. Hryshyn Thermodynamic analysis and features of the kinetics of Cr_2O_3 reduction by carbon independently and in a CO flow. H_2. *Electrometallurgy*. 2015.

2.   V.V. Zolotareva, V.K. Simonov, V.N. Vlasenko. Kinetics and mechanism of chromium reduction from oxide phases in the absence of melts. *Metallurgical and mining industry.* 1999. No 4. pages 43-45.

3.   A.G. Vodopianov, G.N. Kozhevnikov. Kinetics and mechanism of interaction of refractory metal oxides with carbon. *Physical chemistry of metal oxides* M.: Science, 1981. pages 30-34. 30-34.

4.   Investigation of velocity regularities of gasification of carbonaceous materials/V.K. Simonov, L.N. Rudenko, O.M. Hryshyn and others *Izvestiya vuzov. Ferrous metallurgy.* 1994, No 11. pages 6-8.

5.   S.G. Rostovtsev, V.K. Simonov, L.N. Rudenko. Kinetics of gas reduction of iron oxides and some possibilities of intensifying the process. *Physical chemistry of metal oxides.* M.: Science, 1981. pages 42-47.

6.   T.Ya. Kosolapova, Carbides.– M.: Metallurgy, 1968. 300 p.