Oxidation Kinetics of Iron Alloy Drops in Oxidizing Slags

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The kinetics of reactions between drops of Fe-C, Fe-C-P and Fe-C-S alloys and synthetic oxidizing slags at 1550°C have been studied. The reaction kinetics are obtained either from chemical analysis of quenched samples, or, for decarburization,* by continuous measurement of the flow rate of evolved gas. The marked effect, on the kinetics, of the metal emulsification during carbon removal is evidenced. A decrease in slag oxygen potential results in the slow-down of decarburization. Sulfur shows a tendency to limit interfacial reactions, but it enhances metal emulsification. Both mass transfer processes and interfacial reactions, as well as nucleation, are believed to play their part on the rate of decarburization.

SEVERAL recent studies[1-10] have shown that the high reaction rates observed in the top blowing refining processes are largely due to the formation of slag-metal-gas emulsions. Very large interfaces are thus created by the projection in the slag of metal drops which react and return to the bulk. The understanding of the factors affecting the rates of reactions between a single metal droplet and oxidizing slags should therefore be of help in the interpretation of the actual reactions taking place in a converter.

Laboratory studies[11-20] have concentrated on reactions between metal drops and oxidizing gases. Depending upon the experimental conditions, the kinetics of the process is reported to be controlled either by the transport of oxygen in the gas phase or, in some cases, by the interfacial reactions. The extrapolation of these results to the conditions of slag-metal emulsions is not straightforward. In particular, the oxygen supply to the reaction site, from a steelmaking slag, might be more efficient than that from a gaseous mixture, given the high values of oxygen diffusivities (in the range 10^{-4} to $5 \cdot 10^{-4}$ cm^2 s^{-1}) measured in such slags.[21] On the other hand, studies conducted from sampling in a converter give no unequivocal information as to the factors controlling the reactions at the level of an individual metal droplet. In particular, they yield no clue regarding the evolution of the shape of the metal drops when reacting in the slag.

The intense agitation and fragmentation of the metal due to CO bubble evolution has recently been evidenced by an X-ray visualization of the behavior of iron alloy drops immersed in oxidizing slags.[22] However, the results of this study are chiefly qualitative in nature. The objective of the present investigation was to devise experimental techniques allowing the measurement of the kinetics of the fast reactions occurring between a metal drop and an oxidizing slag, with special emphasis on decarburization. These methods were used to study the reactions at 1550°C, between drops of Fe-C, Fe-C-P and Fe-C-S alloys of various compositions and synthetic oxidizing slags of constant basicity and varied degrees of oxidation.

EXPERIMENTAL PROCEDURE

Apparatus

The crucible assembly used in the study is shown in Fig. 1. The experiments were performed in a vertical resistance furnace with three molybdenum windings powered independently to improve the constant temperature zone. At 1550°C, 150 mm of the furnace tube were within ±5°C. An automatic temperature regulation based on the adjustment of the resistance of the heating elements was used. The thermocouple for temperature readings was set against the bottom of the alumina crucible containing the slag. The metal was initially contained in a small alumina crucible held just above the surface of the slag. The drop was dispensed by tilting the small crucible by the rupture, by Joule's effect, of a thin platinum wire holding it in the upright position, thus establishing time zero of the reaction. The experiments were performed under an atmosphere of purified nitrogen.

Measurement of Reaction Rates

Two methods were used to determine the reaction rates.

The first method consists in water quenching the crucible containing the metal and the slag after various times of contact, and in obtaining the advancement of the reactions from the chemical analysis of both phases. It was used to study the kinetics of oxidation of iron, phosphorus and, in some cases, carbon. However, the precision on the reaction time is relatively poor, especially for short times, and we did not succeed in quenching the crucible for contacts of less than 10 seconds.

The second method, used only to follow decarburization, consists in measuring continuously the flowrate of gas evolved: the instantaneous rate of decarburization is thus obtained at any time, including the first instants of reaction. A carbon balance

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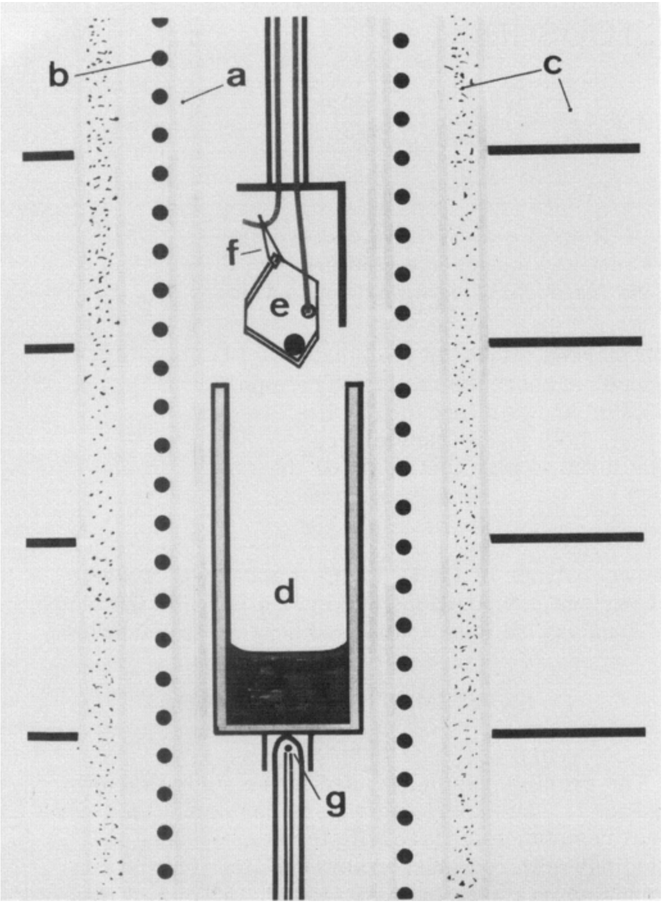

Fig. 1—Experimental set-up. (*a*) Laboratory tube, (*b*) heating element, (*c*) furnace insulation, (*d*) alumina crucible containing the slag, (*e*) alumina crucible containing the metal, (*f*) platinum fuse for dispensing the metal, and (*g*) thermocouple.

can then be applied to calculate the change, with reaction time, in the carbon content of the metal, the kinetics of iron oxidation having previously been determined by the first method. The flow-rate of gas evolved is obtained from the continuous recording, by means of a differential pressure sensor, of the pressure drop in a capillary tube through which the gases leaving the reaction tube are channeled. Calibration curves, determined for the appropriate gaseous mixtures (*i.e.* N_2, and CO and CO_2 formed by the reaction), allow the calculation of the instantaneous flow-rate. It has been verified that within the domain of flow-rates relevant to this study, variations of the relative proportions of N_2, CO and CO_2 do not significantly alter the calibration curves, so that the knowledge of the gas composition is not necessary to the exploitation of the results. The input flow-rate of nitrogen was also checked to be insensitive to the pressure drop created. This apparatus allows flow-rates as low as 0.05 cm^3/s to be detected, with the capillary tube used. The pressure drop was in the order of 10 mbars during the most intense stages of decarburization. The precision of the method is difficult to assess, and it depends essentially on the uncertainties on the calibration curves. However, the difference between the carbon content analyzed in the metal quenched at the end of the reaction, and the content calculated by mass balance from the flow-rate measured never exceeds 5 pct.

Operating Procedure

The furnace was constantly held at temperature. The crucible containing 20 g of slag was introduced at the bottom of the laboratory tube, and slowly raised to its position in the hot zone of the furnace. The small crucible containing 2 g of alloy was then lowered just above the surface of the slag, held in that position for a few minutes to allow proper melting of the metal, and then tilted. A possible oxidation of the metal by the gas, during its melting, was prevented by blowing a small quantity of CO, directly into the small crucible, before dispensing the drop. The molten slag dissolves alumina from the crucible, and its composition is changed significantly; it was therefore necessary, in order to ensure reproducible conditions, to follow a strict time-table for these operations. Blank runs were performed to determine the exact slag and metal compositions in the initial conditions.

The crucible containing the reacting slag and metal was recovered by opening the bottom of the furnace, and water quenched either after various times of reaction, or, in the runs with flow-rate measurement, after 3 min. The metal was then separated from the slag and weighed, and chemical analyses of both phases (that is $\underline{C}$, $\underline{P}$, $\underline{S}$, $\underline{O}$, . . . for the metal, Fe^{2+}, Fe^{3+}, CaO, SiO_2, P_2O_5 Al_2O_3 . . . for the slag) were performed. A macroscopic examination of the metal beads obtained gave an idea of the tendency for spontaneous emulsification.

Preparation and Composition of Alloys and Slags

Small ingots of the desired alloys were prepared by fusion, under a reducing atmosphere, of mixtures of pure iron and iron-carbon, iron-phosphorus and iron-sulfur master alloys. These ingots were then quenched and sectioned into 2 g beads. The following compositions were obtained:

- Fe-C alloys with carbon contents of 0.96 pct, 2.5 pct and 4.2 pct.
- Fe-P alloys with 1.5 pct P.
- Fe-C-P alloys with 2.5 pct C and 1.5 pct P.
- Fe-C-S alloys with 2.5 pct C and sulfur contents varying between 0.008 pct and 0.88 pct.

The slags were prepared by homogenizing mixtures of the carefully dried oxide powders. Iron oxides were added as hematite and wustite in appropriate proportions to yield various degrees of oxidation. The analyses of the slags recovered in the blank runs are as follows:

- for the experiments with Fe-C-S alloys: 44.2 pct CaO – 4.5 pct SiO_2 – 30 pct Al_2O_3 – 16 pct Fe_t with $N_O/N_{Fe} = 1.17$;

- for all the other experiments: 48 pct CaO – 5 pct SiO_2 – 24 pct Al_2O_3 – 17 pct Fe_t with N_O/N_{Fe} varying between 1.17 and 1.43. N_O/N_{Fe} represents the ratio of the number of oxygen g-atoms linked to iron to the number of iron g-atoms in the slag. This parameter has been used in the whole study to represent the oxidizing power of the slag, since the lack of thermodynamic data does not allow a precise estimation of the oxygen potential. The ratio $N_O/N_{Fe} = 1.17$ would be slightly above that corresponding to the equilibrium with metallic iron, and $N_O/N_{Fe} = 1.43$ would be close to that in equilibrium with air.

EXPERIMENTAL RESULTS

Reactions With a Slag of High Degree of Oxidation: Influence of Metal Composition

The first experimental method was used to study the reactions between a slag with degree of oxidation $N_O/N_{Fe} = 1.43$, and respectively, pure iron drops, an Fe-P alloy with 1.5 pct P and an Fe-C-P alloy with 2.5 pct C and 1.5 pct P.

The tendency for metal emulsification in the slag due to CO bubble evolution is evidenced by the aspect of the metal recovered after quenching:

- Fe and Fe-P beads were not divided and presented a shiny smooth surface;
- in contrast, the configuration of Fe-C-P samples varied depending on the advancement of decarburization (see Fig. 2). The metal separated from the slag after short reaction times was mainly composed of a single hollow bead with a rough surface; it was later divided into little fragments which coalesced into a single smooth bead at the end of decarburization.

The oxidation rates of the various elements were strongly influenced by the agitation and metal division created by the decarburization (see Fig. 3):

- iron oxidation rates in the first instants of reaction increased from a value of 0.007 g/s for Fe and Fe-P alloy samples, to a value of 0.035 g/s for Fe-C-P alloys;
- dephosphorization was very fast and strongly enhanced by decarburization: the phosphorus content of the metal dropped from 1.5 pct to 0.006 pct in a minute for Fe-P alloys, whereas only ten seconds were necessary to reach that value for Fe-C-P alloys;
- decarburization was also very efficient, the carbon content of the metal being lowered from 2.5 pct to 0.6 pct within thirty seconds of reaction, and reaching 0.02 pct after 2 min.

Iron consumed more oxygen than carbon, even during the instants of most intense decarburization (see Fig. 4). As for phosphorus, its very fast rate of removal and the lack of data for short reaction times allow no conclusion to be drawn on that point.

Oxidation of Iron Carbon Alloys: Influence of the Degree of Oxidation of the Slag

The second experimental method was used to study the decarburization of Fe-C alloy drops containing initially between 1 pct and 4.2 pct C by slags of initial degree of oxidation N_O/N_{Fe} varying between 1.43 and 1.17. Typical results for the flow-rates obtained, and for the decrease with time of the carbon content of the metal, as calculated by carbon balance, are shown in Fig. 5.

The flow-rate curves exhibit three distinct parts:

- an initial peak during the first 5 to 10 seconds of reaction. A similar peak, although broader, was also observed when immersing solid alloy in the slag;
- a zone with constant, or slightly decreasing decarburization rate, especially marked on Curve 1 of Fig. 5(*a*);
- when the carbon content of the metal reached a value as low as 0.3 to 0.5 pct a sudden decrease in the rate of decarburization.

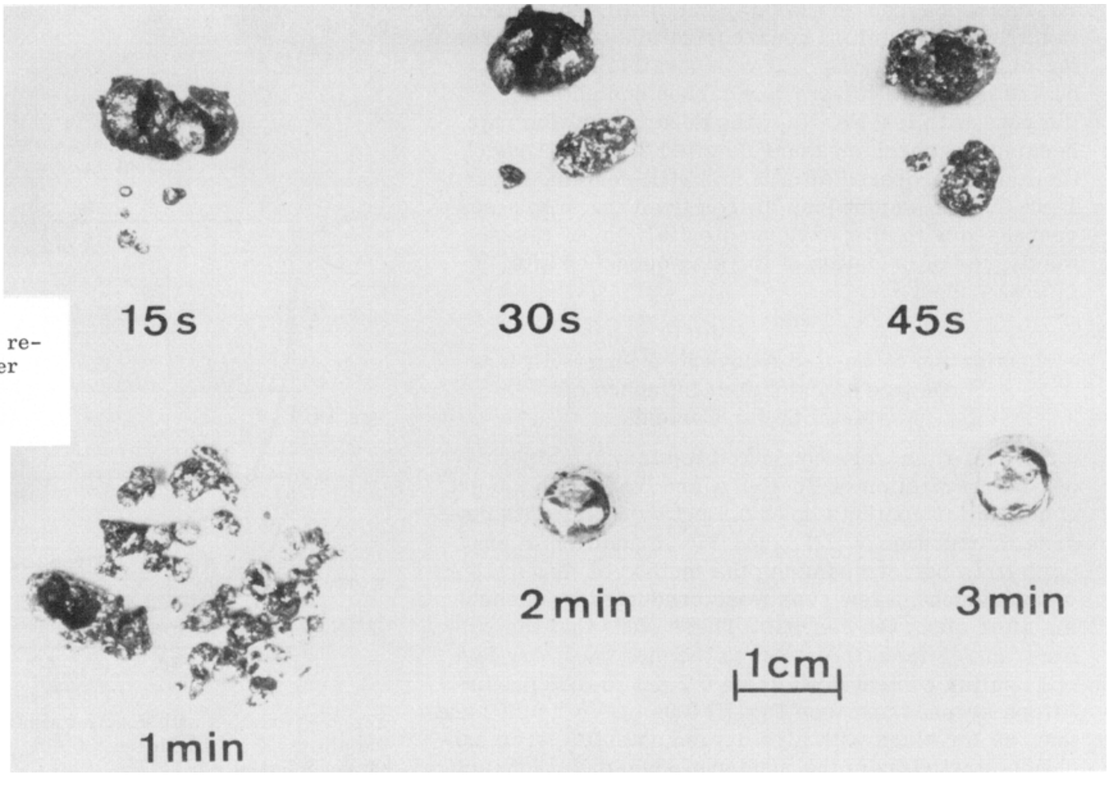

Fig. 2—Fe-C alloy beads recovered by quenching after various reaction times.

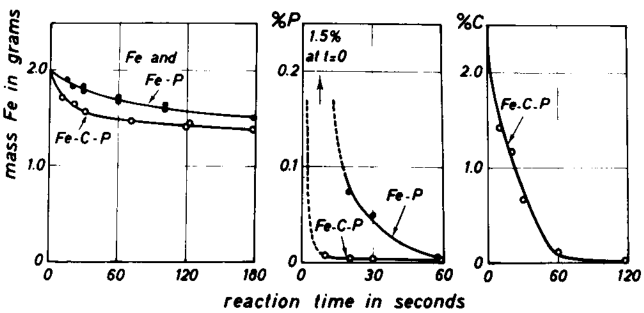

Fig. 3—Oxidation kinetics for iron base alloy drops. The three diagrams show the variation with reaction time of, respectively, the Fe weight, P and C contents of the metal droplet.

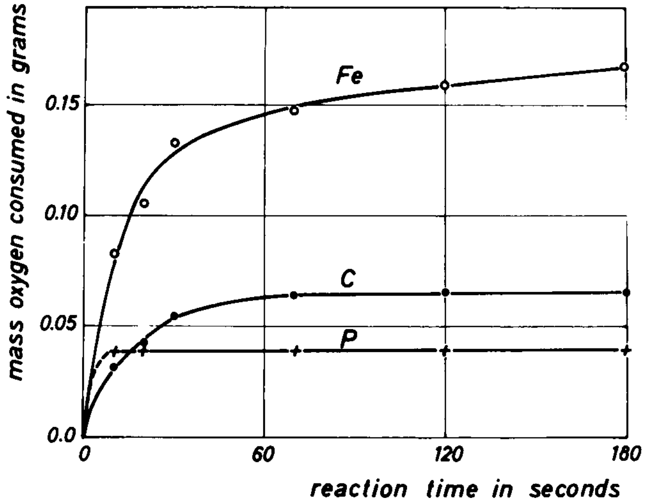

Fig. 4—Oxygen consumption by iron, carbon and phosphorus during the oxidation of Fe-C-P alloy drops.

The influence of the slag initial oxygen potential was more marked on the later stages of decarburization than on the initial decarburization rates: whereas for high initial N_O/N_{Fe}, it was possible to decarburize the metal to very low carbon contents, for the runs with low N_O/N_{Fe}, the decarburization rate became no longer measurable after 2 min although the metal recovered after 3 min still contained over 1 pct C. The weight loss of iron from the drop also decreased with slag oxygen potential. In all cases, the degree of oxidation of the slag quenched after 5 min was about 1.1.

Oxidation of Fe-C-S Alloys by a Slag With Low Degree of Oxidation: Influence of Metal Sulfur Content

Several runs were conducted to study the kinetics of decarburization of Fe-C-S alloy drops with 2.5 pct C and sulfur contents up to 0.9 pct by a slag with degree of oxidation $N_O/N_{Fe} = 1.17$. In addition to experiments performed using the method of flow-rate measurement, a few runs were conducted by quenching after about ten seconds. These show that the sulfur transfer from the metal to the slag was very fast (*e.g.* sulfur content down from 0.2 pct to 0.06 pct in fifteen seconds and (see Fig. 6) 0.04 pct in 2 min), and that, as for slags with high oxygen potential, iron oxidation started from the instant of slag-metal contact.

The presence of sulfur markedly affected both the configuration of the metal recovered (see Fig. 7), and the shape of the flow-rate curves (see Fig. 8). In particular, the fragmentation of the metal was most intense for the drops initially containing 0.064 pct S. The effect of sulfur on the flow-rate curves was principally marked in the region of the initial

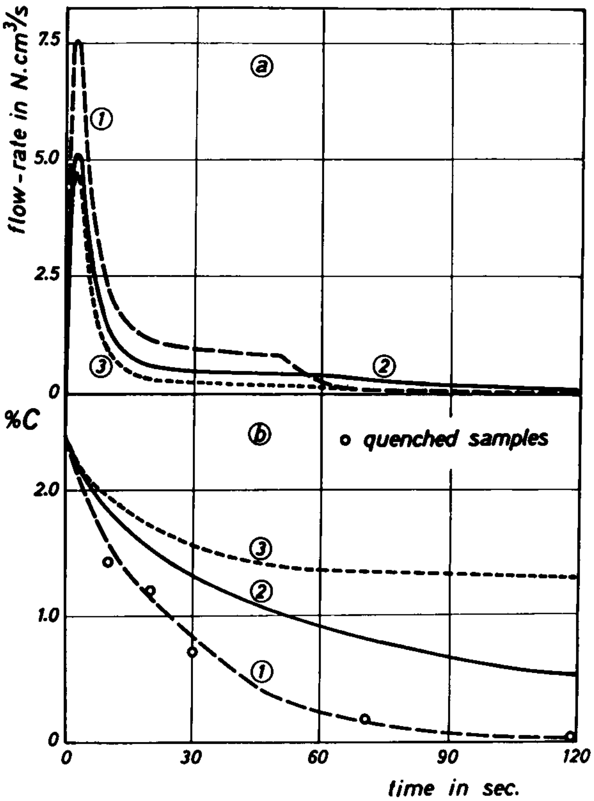

Fig. 5—Decarburization of Fe-C alloy drops: Gas (CO + CO_2) flow rate (*a*) and carbon content change (*b*), as a function of reaction time.

Metal		Slag
2.5 pct C	48 pct CaO	(1) $N_O/N_{Fe} = 1.43$
	5 pct SiO_2	(2) $N_O/N_{Fe} = 1.32$
	24 pct Al_2O_3	(3) $N_O/N_{Fe} = 1.17$
	17 pct Fe_t	

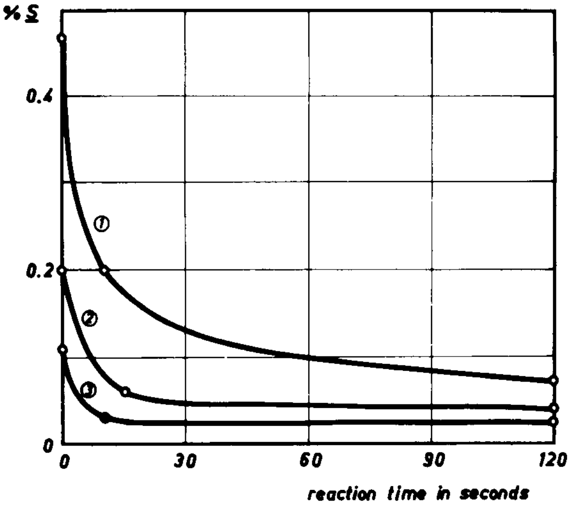

Fig. 6—Variation with reaction time of the sulfur content of the alloys. (1) pct S initial = 0.465; (2) pct S initial = 0.20; and (3) pct S initial = 0.11.

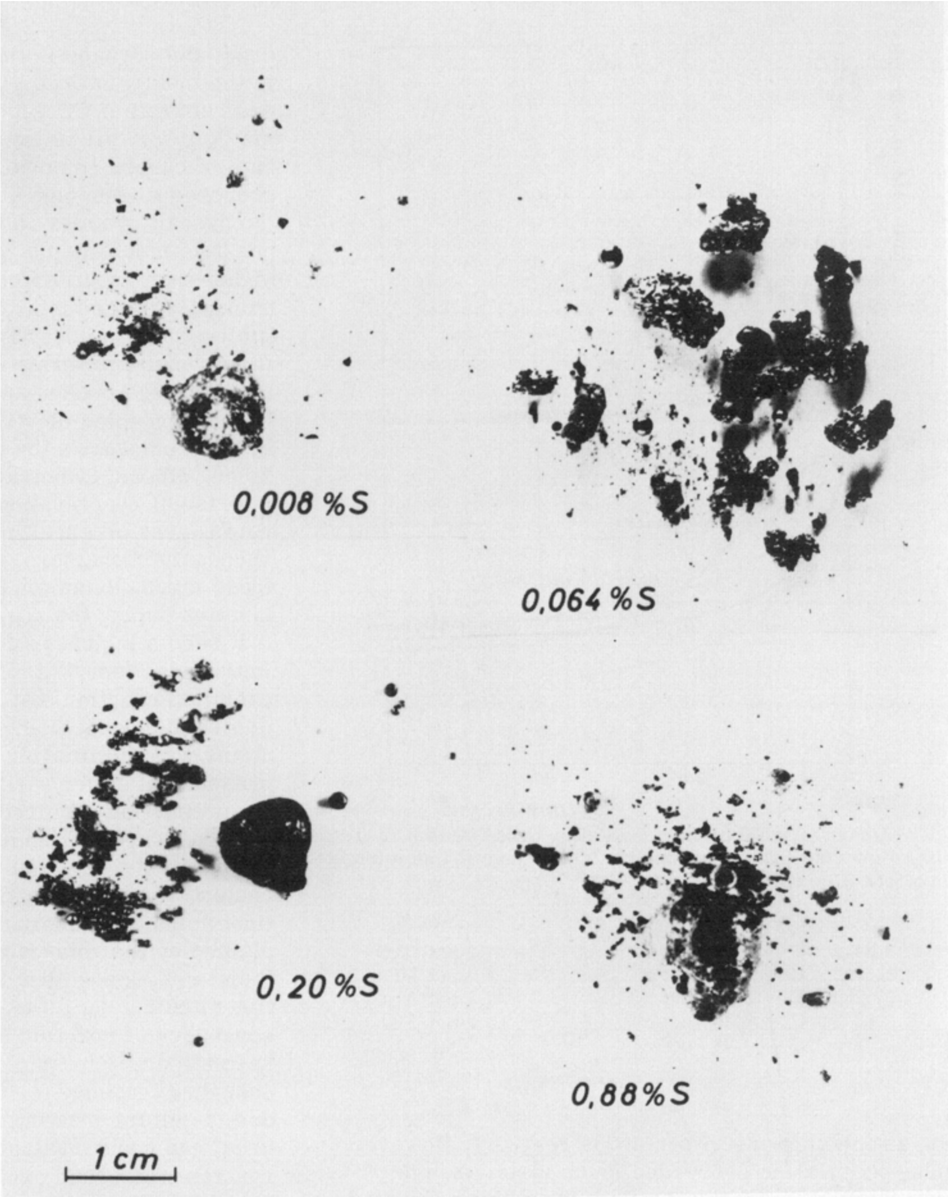

Fig. 7—Fe-C-S alloy having initially various sulfur contents recovered by quenching after three minutes of reaction.

peak: whereas a very sharp peak was observed for low sulfur contents, it became broader and its amplitude decreased as the sulfur content of the metal was increased. The carbon contents of the metal when decarburization tapered off were in all cases approximately 1 pct.

It was possible, in some experiments, to obtain separate chemical analyses for the large metal drops and the small ones recovered after quenching. The latter were in general more decarburized and presented slightly higher sulfur contents.

DISCUSSION OF RESULTS

The important variation of the slag-metal interfacial area during reaction, which has also been clearly evidenced by the experiments of Mulholland *et al*[22] should be emphasized. The determination of rate constants for the reactions, from this kind of experiment, should therefore be approached very cautiously.

The vigorous gas evolution taking place during decarburization of Fe-C drops is sufficient to create an important emulsification of the metal in the slag. The metal fragmentation is strongly enhanced by the presence of a tensio-active agent decreasing the slag-metal interfacial energy, such as sulfur with contents approximating those encountered in industrial converters. At larger sulfur contents, the decrease in decarburization rate may hinder the metal fragmentation (Fig. 7). A comparison of Fig. 2 and 5 shows that the instant of most intense emulsification does not coincide with that of largest decarburization rate. This result substantiates the idea of a change in the conditions of CO bubble nucleation, from heterogeneous nucleation at the metal-slag interface, to nucleation inside the metal droplet towards the end of decarburization, when the carbon supply is no longer sufficient to sustain the reaction at the interface.[22]

Our results show clearly that the oxidation of the various elements of the metal phase takes place simultaneously rather than sequentially. Indeed, the large increase in dephosphorization rates observed in runs with Fe-C-P alloys, as compared to runs with Fe-P drops, can only be explained if the intense agitation resulting from decarburization starts as

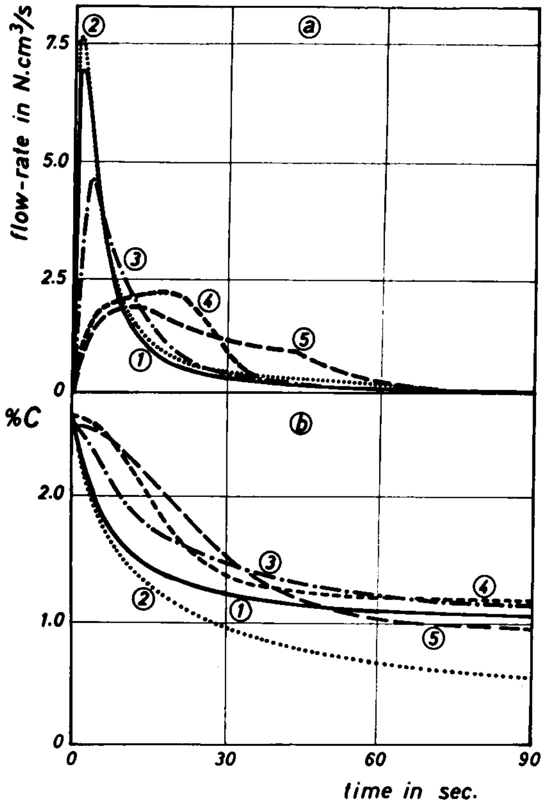

Fig. 8—Decarburization of Fe-C-S alloy drops : Gas (CO + CO_2) flow rate (*a*) and carbon content change (*b*) as a function of reaction time.

Metal	Slag
(1) 2.64 pct C — 0.008 pct S	44.2 pct CaO
(2) 2.62 pct C — 0.064 pct S	4.5 pct SiO_2
(3) 2.57 pct C — 0.11 pct S	30.0 pct Al_2O_3
(4) 2.61 pct C — 0.20 pct S	16.0 pct Fe_t
(5) 2.53 pct C — 0.88 pct S	$N_O/N_{Fe} = 1.17$

soon as the slag-metal contact is realized. However, dephosphorization proceeded much faster than decarburization, a conclusion also drawn from the study of samples taken in industrial converters.[5,23] Similarly, the capture of oxygen by carbon does not impede iron oxidation; on the contrary, the agitation created by decarburization enhances iron oxidation, which consumes more oxygen than carbon does. This result is in contradiction with the conclusion of Mulholland *et al*,[22] that iron oxidation occurs mainly at the end of decarburization. The few results gathered show that sulfur transfer in the emulsion is also very fast. Yet, the lack of data on sulfur capacities of the slag does not allow a conclusion on whether sulfur equilibrium has been reached: the larger sulfur contents analyzed in the smaller, more refined droplets– also observed on the industrial scale[5,23]– could be created by a slow-down in sulfur transfer from metal to slag due to the lowering of the sulfur activity coefficient of the alloy with decreasing carbon content, as well as by a sulfur reversion linked to an increase in oxygen potential of the droplet.

The interpretation of the curves of flow-rate of CO evolved in terms of mechanisms limiting decarburization is made difficult by the variation with time of the geometry of the system. Transport of oxygen in the slag or through the bubbles surrounding the metal drop, and perhaps in the metal, transfer of carbon in the metal, interface chemical reaction, nucleation and removal of CO bubbles from the reaction sites may *a priori* all be important in determining the rate of carbon removal. Several models have been proposed to describe quantitatively the kinetics of the overall process on the basis of only one of these possible mechanisms (at least for carbon contents higher than about 0.5 pct, under which level carbon transport in the metal is generally accepted as the limiting step). Thus, Tarby and Philbrook[24] interpret their results in terms of control by transport in the slag phase, Acheson and Hills[25] propose a model based on coupled electrochemical reactions with CO bubble removal as the ultimate limiting step, and, among others, Okhotskij[26] favors the hypothesis of interfacial reaction control. The shape of the flow-rate curves obtained in this study, displaying several successive behaviors, suggests that more than one of these mechanisms must play a role in limiting the kinetics during the course of decarburization.

It seems logical to consider that, in the region of the initial peak (see Fig. 5 and 8), it is an interfacial chemical reaction that controls the kinetics of the process. Indeed, if any one of the transport mechanisms was the limiting step, it is doubtful that the presence of sulfur would affect the transfer rate in the proportion required to alter the overall kinetics as significantly as shown in Fig. 8. On the other hand, the marked slow-down of the reaction as sulfur content is increased, also observed in gas-metal reactions[20] and in Mulholland's experiments,[22] can be explained by the retardating effect of sulfur on the interfacial reaction, either by a dynamic blocking of reaction sites during its transfer,[27] or through a static occupancy of reaction sites at the droplet surface. A result specific to slag-metal emulsions is that the enhanced tendency for emulsification of the metal due to sulfur, creating an increase in interfacial area, can counterbalance the decrease in specific reaction rate, thus explaining the very high initial decarburization rate observed with the alloy initially containing 0.064 pct S. If we assume a spherical droplet, the results obtained for Fe–2.5 pct C alloys lead to an initial carbon consumption of 10^{-4} to $1.5 \cdot 10^{-4}$ $g \cdot at. \cdot C \cdot cm^{-2} \cdot s^{-1}$. As a comparison, Okhotskij's model[26] would make use, for the same conditions, of a value for the reaction constant of about $1.5 \cdot 10^{-5}$ $g \cdot at. \cdot C \cdot cm^{-2} \cdot s^{-1}$.

A reasonable hypothesis to explain the nearly constant rates observed after the initial peak is that of control by oxygen transport, either in the slag locally depleted in oxygen during the early period of reaction, or through the gas halo surrounding the drop. Indeed, the carbon content of the metal varies in a large proportion during this stage of the reaction, and the effect of this variation on the global kinetics would be felt if either carbon transport or interfacial reaction were the limiting steps. Yet, Acheson and Hills' model[25] would also lead to a constant reaction rate, and it cannot be discarded.

The sudden decrease in decarburization rate when the carbon content of the metal reaches a value in the range 0.3 to 0.5 pct C can be attributed to a shift to carbon transfer control, a widely accepted interpretation.

Somewhat surprising is the observed tapering off of the decarburization with high residual carbon contents, in the case of reaction with slags of low oxygen potential (*e.g.* 2.4 pct for a droplet containing initially 4.2 pct C, immersed in a slag of initial degree of oxidation $N_O/N_{Fe} = 1.17$, which would correspond to a partial pressure of CO in equilibrium with the carbon and the oxygen dissolved in the metal of 450 at.). At that stage of the reaction, foaming of the slag has subsided, and the metal drop lies at the bottom of the crucible. An estimation of the possible rates of transfer of the reactants shows that these steps would allow reaction rates measurable with our experimental set-up: the reaction must then be hindered by the nucleation of CO bubbles. It is to be noted that when a drop of the same characteristics as the final metal is immersed in this final slag, decarburization starts again, which could be interpreted as an improvement in the conditions for heterogeneous nucleation.

CONCLUSIONS

An experimental method has been devised for the study of various factors which may influence the kinetics of refining reactions. The following conclusions can be drawn:

–the spontaneous emulsification of the metal, and the agitation created during CO bubble evolution increase drastically the oxidation rates of iron and phosphorus;

–the oxidation of the various elements from the metal take place simultaneously. Thus, iron oxidation starts as soon as slag-metal contact is realized, and iron can consume more oxygen than carbon, even during the moments of most intense decarburization;

–the rates of decarburization achieved decrease markedly as the oxygen potential of the slag is lowered. With slags having a low degree of oxidation, decarburization stops despite very large supersaturations: this seems to be linked to the problem of CO bubble nucleation;

–the presence of sulfur affects decarburization in several ways: on the one hand, it lowers the specific rate of interfacial reaction, and on the other hand, it can accelerate the global kinetics by enhancing metal emulsification. For typical industrial sulfur contents, it seems that the second effect can be the most important.

The method of continuous measurement of the flowrate of evolved gas allowed a precise evaluation of the instantaneous rates of decarburization. The variation of the interfacial area during the course of decarburization permits no unequivocal conclusion to be drawn regarding the reaction mechanisms. However, it seems that interfacial reaction limits the kinetics only during the first five to ten seconds of contact, transport steps then becoming the limiting ones.

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