

Hydrogen Reduction of Wustite Single Crystals Doped with Mg, Mn, Ca, Al, and Si

M. MOUKASSI, M. GOUGEON, P. STEINMETZ, B. DUPRE, and C. GLEITZER

In order to investigate the reduction mechanism of wustite in the presence of impurities usually met in the ironmaking industry, single crystals have been prepared with Mg, Mn, Ca, Al, and Si as dopants. The amounts of dopant in the lattice is around 4, 4, 2.5, 0.5, and 0.01 mol pct, respectively, at 800 °C. For reduction with pure hydrogen, from 600 to 950 °C, Ca is the most efficient for accelerating the process at high degrees of reduction (75 pct) Mg and Mn are also active in this respect. Al has only a slowing down effect. Si also slows down the reaction at temperatures between $600 < T < 850$ °C, but it becomes accelerating at $T > 850$ °C. In the presence of 20 torrs of water vapor in the gas, Mg and Mn are less efficient and unable to prevent the same slowing down of reaction observed with pure wustite at around 850 °C and classically called the "rate minimum". Our interpretation of these results is mainly based upon the observations of microstructures of partly reduced crystals which show a change in the texture of the iron produced which can be correlated with the reduction rate. These observations lead to a possible explanation in terms of the role of inclusions of impurity oxides on the sintering process of the metal, correlated with their ability to dissolve into the wustite lattice. However, this suggestion cannot apply in the case of Si at low temperatures, and this element is therefore supposed to play a role in the stages of reaction associated with the surface of the crystals.

I. INTRODUCTION

In a preceding publication¹ we dealt with the reduction of wustite single crystals and attributed the slowing down of reaction which is frequently observed in the range of temperature 700 to 900 °C, at high degrees of reduction, to the diffusion barrier produced by the metal, the sintering of which produces in the same range of temperature a dense and impermeable layer.

In these studies single crystals of wustite had been prepared, reduced, and then observed optically and by SEM, so that the metal texture and the reaction zone could be clearly defined, allowing a clear picture of inner and outer parts of the particles to be obtained.

This technique also showed that the reaction zone was very irregular, particularly at low temperatures (650 to 850 °C) and far from the classical topochemical case. Moreover, inner reduction sometimes took place ahead of the reaction zone in some localized regions producing pores surrounded by a layer of iron. This behavior seems to be related to the existence of a dense layer of iron which covers the surface but which contains some weak places at which the metal formation is faster because iron is porous and allows an easy diffusion of gases. Alternatively, inner limited reduction may result from the oversaturation which must exist before nucleation.

A striking feature that we reported was the tremendous influence of some 20 torrs of water vapor added to pure hydrogen: the slowing down of the reduction was greatly increased, and we attributed this effect to the hindering of nucleation by adsorbed water.

Since then, El Moujahid has clarified the important role of iron nucleation on the reduction process.² He has shown that two types of nuclei may be obtained according to the experimental conditions: "hard reduction", with pure hydrogen, produces porous iron, whereas "soft reduction", with H₂-H₂O, leads to the formation of "whisker type" nuclei and, in a further step, to a dense and protective iron layer. This, of course, slows down the diffusion of gases and hence the rate of reduction. The recent results of St. John and Hayes³ are in agreement with El Moujahid's findings, although these authors have not investigated the mechanism of iron formation in as much detail.

Given this state of knowledge it seemed of interest to investigate the reduction of wustite doped with elements frequently found in iron ores, in order, first, to obtain a deeper insight on the above reduction mechanisms, and, second, to take into account the real situation in the iron-making industry when iron-rich ores are processed. We have therefore prepared wustite single crystals containing small quantities of Mg, Ca, Mn, Al, and Si, and studied their behavior in the course of reduction. The results have been compared with those for pure wustite as a reference.

II. LITERATURE SURVEY

A. General Comments on the Role of Additives in the Reduction of Oxides

Additives may be divided into two groups: those which are appreciably miscible with the matrix oxide, that is, up to some one tenth of a percent, and those which are not. It must be remembered, however, that some additives, although nonmiscible, may have an influence due to their affinity for the oxide surface which may produce a bidimensional compound or some other important surface effects.

Delmon has reviewed the different mechanisms by which additives may influence the kinetics of the reduction of oxides.⁴ For our study the relevant points are:

M. MOUKASSI is Etudiant, Ecole des Mines de Nancy. M. GOUGEON, Etudiant, P. STEINMETZ, Maître-Assistant, B. DUPRE, Attaché de Recherches, and C. GLEITZER, Directeur de Recherches, are all with the Université de Nancy I, B. P. 239, 54506 Vandoeuvre Les Nancy Cedex, France.

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- (i) formation of a barrier for the diffusion of reactive species, due to accumulation of the additive in a given position;
- (ii) modification of the adsorption of reactive species;
- (iii) catalysis of the nucleation of products or intermediates, including "spill over" effects; and
- (iv) modification of the texture of the product of the reaction.

B. Previous Results

Numerous publications have dealt with the influence of impurities or additives on the reduction of iron oxides and ores; however, most of them were devoted to pure hematite or ores and rather few to wustite.

Khalafalla and Weston have reported that a strong acceleration of the wustite reduction occurs in the presence of alkaline or alkaline-earth elements.⁵ Their interpretation of this result is based upon the supposition that the wustite lattice is modified by the cations substituted for iron. These would facilitate solid state diffusion thanks to local lattice distortions which, moreover, are favorable sites for nucleation. In the presence of these additives, the nucleation tends to produce whisker nuclei, which, it can be remarked, promote undesirable swelling in the industrial shaft furnaces.⁶⁻¹⁰

Piepenbrock *et al.* have reduced wustite samples doped with Mg, Ca, Ba, and Si¹¹ and observed that only Si did not produce a favorable result. According to Kasabgy and Lu, Mg and Ca increase the wustite rate of reduction and Ca favors the formation of whiskers.¹² Iguchi *et al.* have shown that with Ca the reduction proceeds in a mixed regime controlled by a chemical reaction step and by the diffusion of the reactive species, whereas with Al and Mg a dense iron layer is formed so that the overall reaction is limited by oxygen diffusion through the metal.¹³ The same situation has also been reported by Strangway *et al.* for addition of Mg, Al, Ti, or Si oxides to hematite,¹⁴ while Subat and Engell consider the higher reduction rate with CaO added to hematite pellets as due to a more favorable porosity.¹⁵

On the whole, these previous results, although not completely consistent, tend to focus attention on the texture of the reduced phase, with the exception of Khalafalla and Weston, who took into account the wustite lattice. Hence, it was considered worthwhile to investigate the reduction of wustite single crystals, properly doped, in order to allow a direct observation of the morphology of both the parent and resulting phases and especially of the reaction zone, at a resolution of a few hundreds of angströms as it is possible now with the technique of SEM.

III. EXPERIMENTAL

Preparation of Doped Wustite Crystals

Powder wustite was first obtained through reduction of hematite (Merck p.a.) with H₂-H₂O at 800 °C yielding a composition Fe_{0.94}O. Then Mg, Ca, Mn, Al, and Si were added as carbonates for Mg, Ca, and Mn, and as oxides for Al and Si, up to and including a molar percentage of 5. These mixtures were annealed at 800 °C in the same H₂-H₂O mixture as above, in order to obtain the desired interaction with wustite, namely, the formation of solid solutions whenever it is possible. It is well known that MgO and MnO are

completely miscible with Fe_{1-x}O, whereas the solubility of CaO is limited to a few percents at 800 °C, and that of Al₂O₃ and SiO₂ is very small (less than 1 pct for Al and far less for Si).¹⁶ The powdered materials so obtained were then annealed at 800 °C for two weeks in the presence of a tiny amount of FeCl₂ to recrystallize. The size range produced ranged from around 50 to 500 μm and as for pure wustite, they have grown as clusters of round-shaped crystals (see Figure 1). As for pure wustite, too, doped wustite crystals show no porosity.

The reduction experiments were carried out in a thermobalance under a flow of 100 l/H S.T.P. of hydrogen, either pure or with 20 torrs of H₂O, at 600 °C < T < 940 °C. Each sample was limited to 50 mg and was spread over a flat gold crucible, in order to avoid any transport problem across the layer of doped wustite itself.

After reduction, the surface was examined with an SEM and then the particles were embedded in a resin and polished to reveal the inner parts of the crystals. These were observed either optically or in an SEM, and, when needed, analyzed with an electron microprobe.

IV. RESULTS

A. Mg and Mn-Doped Wustite

The Mg and Mn content in the crystals, as determined with the electron microprobe, was around 4 mol pct.

As expected, Mg and Mn have the same influence on the reduction and hence they can be grouped together in the same section. It is sufficient to show, in Figure 2, the reduction isotherms obtained with Mg, which display a continuous decrease of the reaction rate (limited here to α = 0.75) and an induction period at low temperature. However, Figure 3 shows, more strikingly, that the reduction is faster than with pure wustite and that the "rate minimum" has been avoided although it must be emphasized that the given data refer to average reduction rates between α = 0 and α = 0.75. However, when "wet hydrogen" (20 torrs H₂O in H₂) is used, such a "rate minimum" is again observed, as in pure wustite (Figure 4), at around 730 °C for



Fig. 1—Clusters of single crystals.

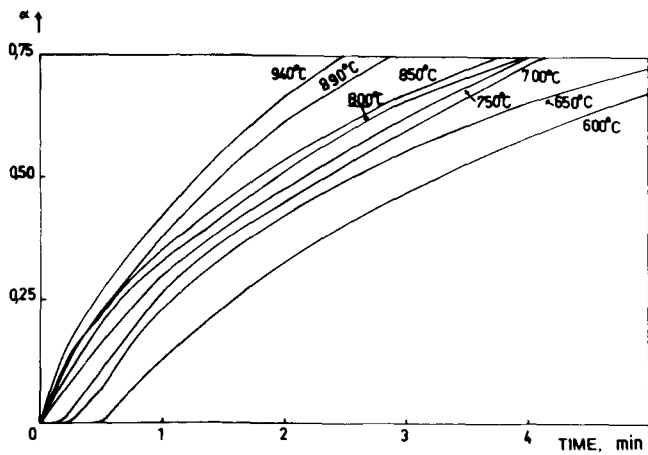


Fig. 2—Reduction in dry hydrogen of Mg-doped particles (α = oxygen weight loss at time t /oxygen weight contained in wustite prior reduction).

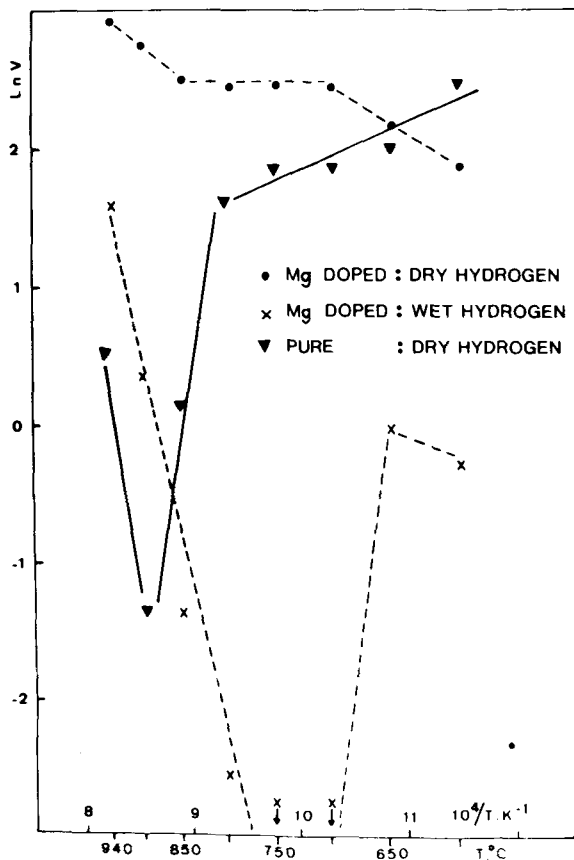


Fig. 3—Reduction of Mg-doped particles: Arrhenius diagram (V in h^{-1} means average reduction rate between $\alpha = 0.05$ and $\alpha = 0.75$; $V = 0.75 - 0.05/t(\alpha = 0.75) - t(\alpha = 0.05)$ with t expressed in hours). The arrows mean that the reduction has not reached the expected rate of progress when the experiment is stopped.

Mg and around 670 °C for Mn with which the rate is somewhat lower.

The micrographs (Figure 5) show that the reaction interface is far from topochemical. As in pure wustite, the progression into the crystal is very irregular, in dry and in wet hydrogen. In addition, the correlation between the average rate of reduction and the iron mean pore size found in pure wustite¹ and shown in Figure 6 clearly stresses the role

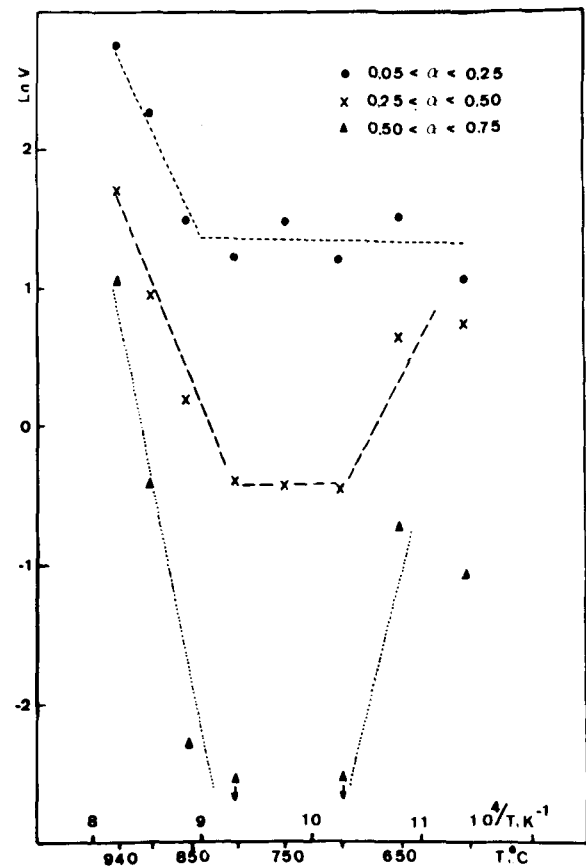


Fig. 4—Reduction in wet hydrogen of Mg-doped particles: Arrhenius diagram (V means average reduction rate in the given range). The arrows mean that the reduction has not reached the expected rate of progress when the experiment is stopped.

of the metal texture, suggesting that it acts as a diffusion barrier. Unfortunately, such a porous texture impeded any analytical investigation with the electron microprobe, but the data obtained in the nonreduced parts of the crystal prove conclusively that no segregation of Mg (or Mn) has occurred during the reaction time, showing that the involved temperatures are too low to allow diffusion of Mg^{2+} or Mn^{2+} from the reaction zone toward the nonreduced parts of the crystals. Hence, the metal produced must have small amounts of MgO (or MnO) incorporated as inclusions.

B. Ca-Doped Wustite

1. Crystallization with 5 mol pct CaO

The crystals obtained were somewhat smaller than with pure wustite, and were not homogeneous. They consisted of intergrowth of two phases, 2.5 pct CaO wustite and $CaFe_3O_7$. This result was proved by X-ray diffraction with optical observation showing coherence between the two phases. Such a coherence is not surprising as we have shown, in this laboratory, that $CaFe_3O_7$ has a structure where blocks of FeO alternate with $CaFe_2O_4$ blocks.¹⁷

Figures 7 and 8 show that the reduction rate is much faster than with pure or Mg and Mn-doped wustite, with nearly linear isotherms suggesting that the reaction is controlled by the chemical step without any slowing down by transport phenomena, so that no "rate minimum" can exist. However, the most striking difference with the Mg and Mn case is the

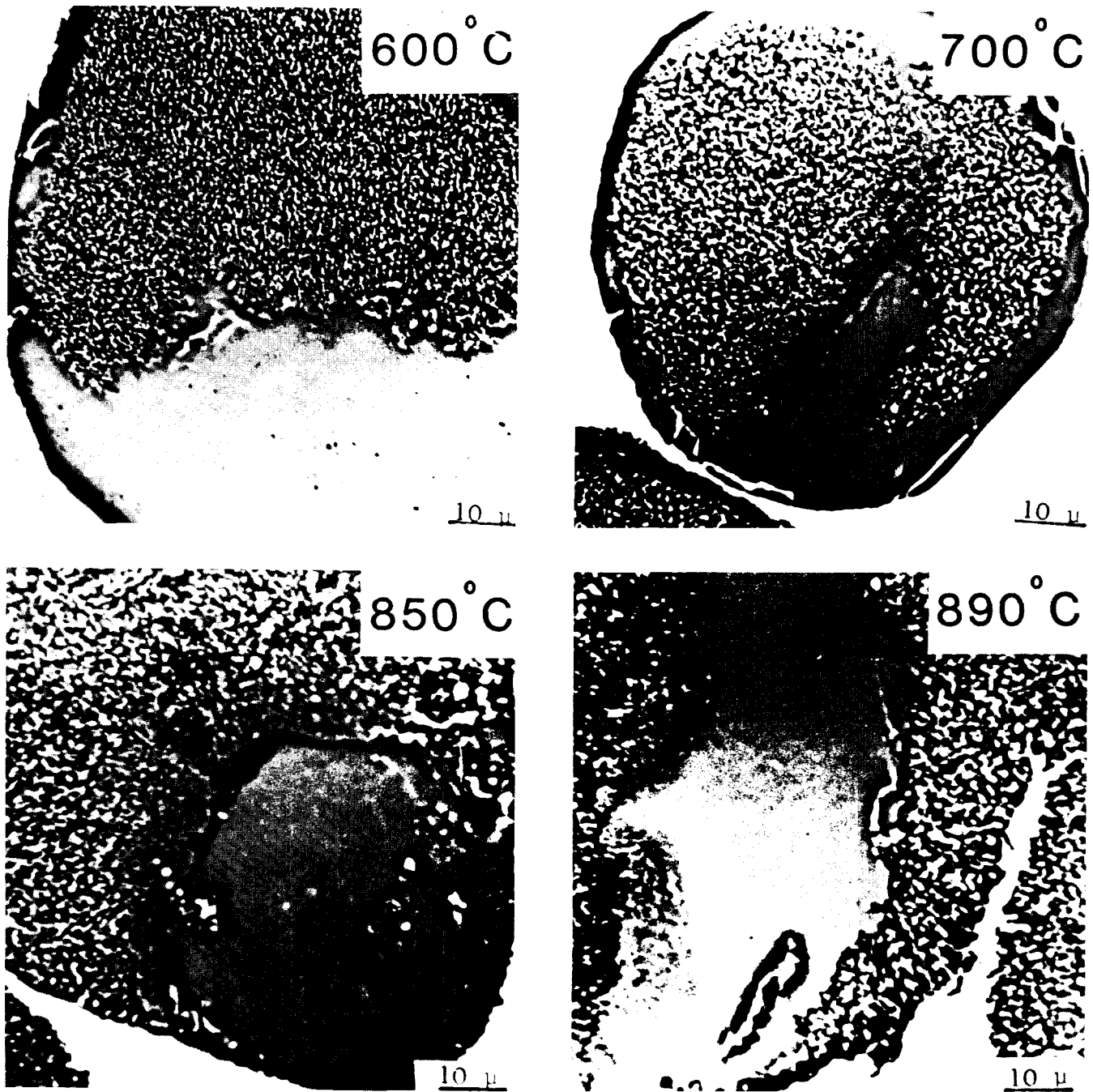


Fig. 5—Micrographs of Mn-doped particles after reduction in dry hydrogen. Reduction time: 600 °C: 10 min; 700 °C: 6 min; 850 °C: 4 min; 890 °C: 4 min.

fact that now the reduction is still fast even in presence of water vapor.

On the micrographs (Figure 9) it is apparent that the reduction of CaFe_2O_7 is slow and topochemical while the solid solution is already completely transformed into iron with CaO as inclusions.

2. Crystallization with only 1 mol pct CaO

The crystals obtained are a pure solid solution, without any intergrown CaFe_2O_7 . However, as shown in Figure 8, the reduction kinetics are not significantly different from above, at least as regards the average rate (from $\alpha = 0.05$ to $\alpha = 0.75$). This is not surprising as CaFe_2O_7 was the

minority phase in the first sample, and proves that there is no important difference between the 2.5 and 1 pct solid solutions as regards the kinetic features of reduction. In other words, a small quantity of Ca in wustite is sufficient for the "rate minimum" to be suppressed. Moreover, as shown in Figure 10, the iron texture changes very little in the range of temperature from 650 to 940 °C: the pores remain small and their distribution is fairly homogeneous compared with the reduction of pure wustite.

C. Al-Doped Wustite

As expected, the crystallization of wustite in the presence of 5 mol pct of Al_2O_3 yields a diphasic product consisting

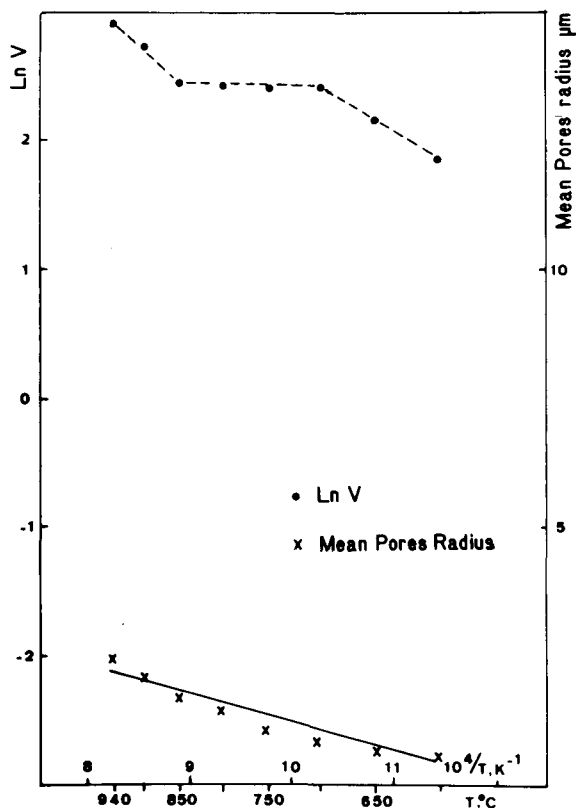


Fig. 6—Correlation between reduction rate and porosity of the metal; reduction in dry hydrogen of Mg-doped particles.

of 0.5 pct Al-doped wustite and particles of a spinel phase, the composition of which as determined through electron-microprobe technique is $Al_{1.77}Fe_{1.33}O_4$.

The kinetic measurements evidence a negative influence of Al on the reduction rate: the "rate minimum" is even more pronounced than with pure wustite, and somewhat displaced toward low temperatures. It may be said that Al slows down the reduction rate at any temperature between 650 and 940 °C.

According to the micrographs, above 600 °C, the iron obtained is quite dense, with a few big pores, so that, in the absence of any cracking of this layer, it certainly constitutes a diffusion barrier for the gas.

D. Si-Doped Wustite

1. Crystallization with 5 mol pct SiO_2

Fayalite (Fe_2SiO_4) is formed, as expected, and appears as small crystals of around 1 μm diameter which stick to the surface of the wustite crystals. No detectable Si content has been found within the wustite crystals with the electron microprobe technique, so that its content is certainly less than 100 ppm.

As shown in Figure 11, the wustite reduction rate is strongly influenced by the silica, being slower at low temperatures and much higher above 850 °C; at 890 and 940 °C, the reduction rate is nearly as high as with calcium. The main difference, observed on the micrographs, with the reduction of pure wustite, is the iron texture in the "rate minimum" region: the pores are significantly larger and the metal is less dense, while the interface seems to be approxi-

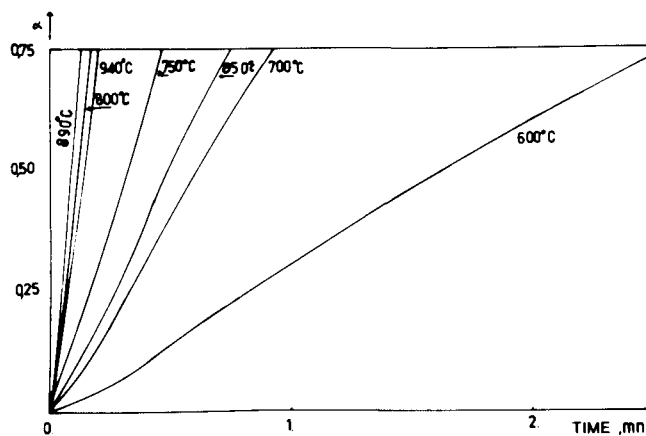


Fig. 7—Reduction in hydrogen of Ca-doped particles (5 pct molar CaO).

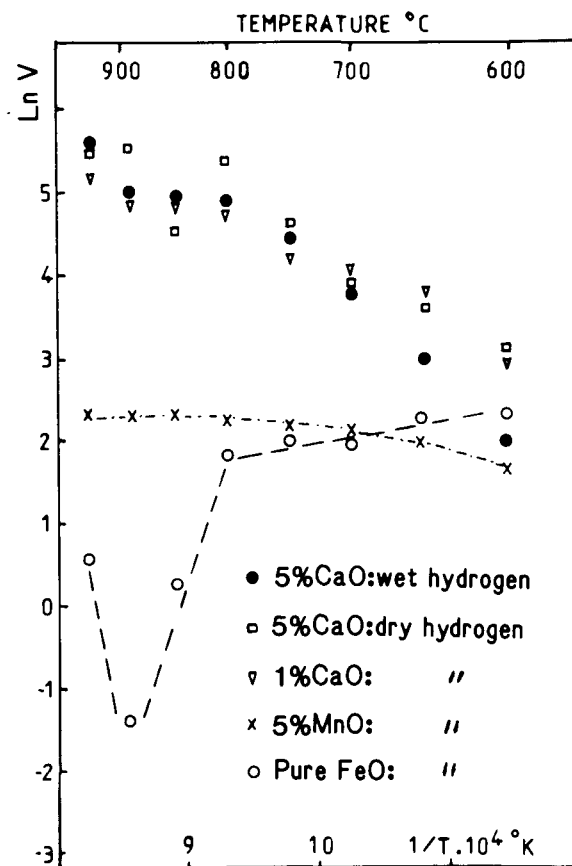


Fig. 8—Reduction of Ca-doped particles: Arrhenius diagram (V means average reduction rate between $\alpha = 0.05$ and $\alpha = 0.75$).

mately topochemical. At high temperature many crystals show noticeable cracking; see Figure 12.

In order to clarify the influence of Si, another preparation has been made with a lower content:

2. Crystallization with 1 mol pct SiO_2

No fayalite crystals are found in this case. However, with dry hydrogen the kinetics are nearly the same as with 5 pct SiO_2 and are just a little less accelerated at high temperature. With wet hydrogen (20 torrs H_2O), the "rate minimum" is even more pronounced leading to a quasi-blocking of the reduction to an $\alpha \sim 0.05$ value. As expected, the micrographs show a very dense and rather

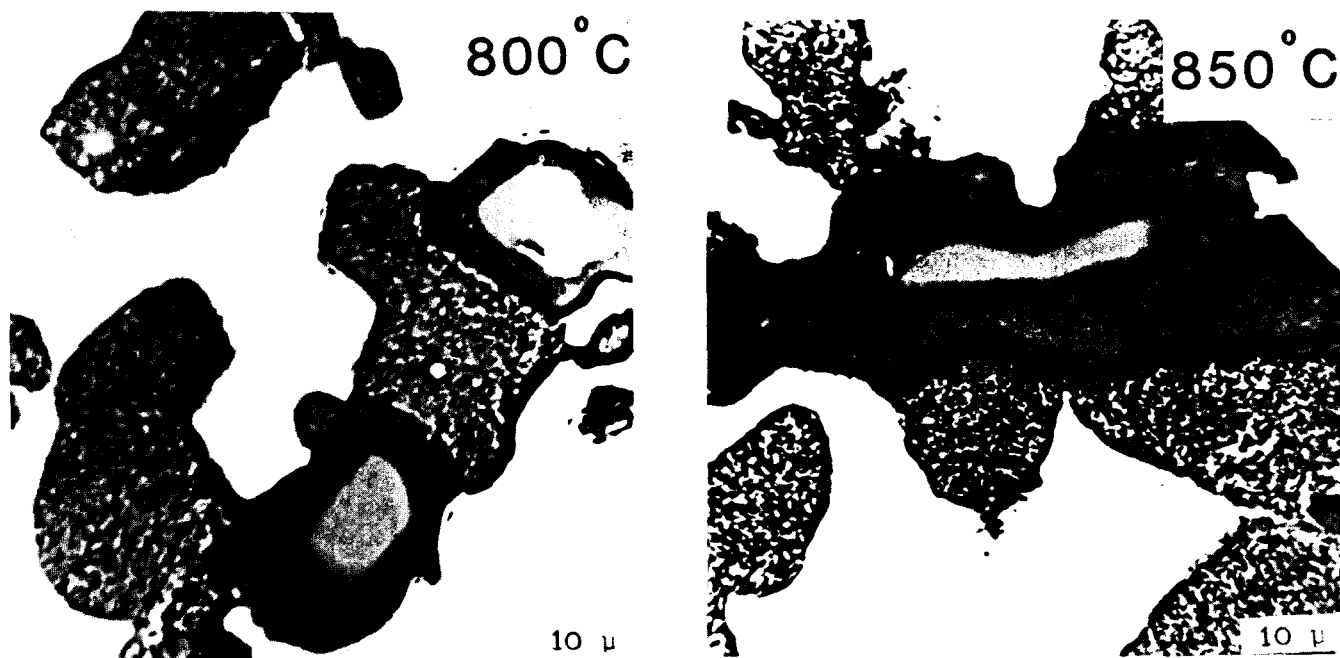


Fig. 9—Micrographs of Ca-doped particles (5 pct molar CaO) after reduction in dry hydrogen. Reduction time: 800 °C: 20 sec; 850 °C: 30 sec.

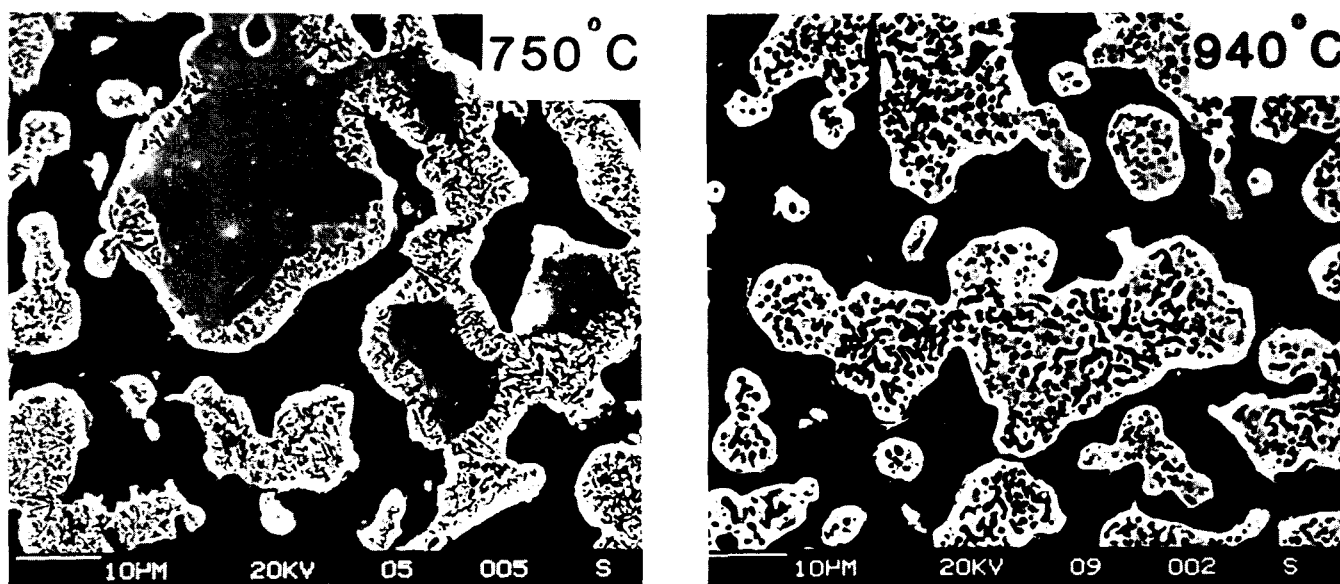


Fig. 10—Micrographs of Ca-doped particles (1 pct molar CaO) after reduction in dry hydrogen. Reduction time: 750 °C: 30 sec; 940 °C: 10 sec.

uniform iron layer at 700 °C and a finely porous metal region at 940 °C, without any noticeable cracking.

V. DISCUSSION

A. The "Rate Minimum"

1. The case of Mg, Mn, and Ca

It is clear that with these elements, giving rise to solid solutions derived from wustite, the reduction is much faster and the rate minimum is more or less attenuated: completely suppressed with pure hydrogen and, with wet hydrogen, suppressed by Ca only. As it has been said above, the

substituted elements may play a role in the adsorption, nucleation, and recrystallization processes. However, Figure 6 shows conclusively that, whereas the iron porosity displays a maximum at the "rate minimum" for pure wustite,¹ this maximum has disappeared at the same time as this "rate minimum." In other words, this is a confirmation of the relation between kinetics and texture of the reduced phase, which has already been put forward by us¹ as well as by Szekely and Evans, for instance,¹⁸ which leads us to consider mainly the role of additives on the iron texture.

It seems reasonable to suggest that the distribution of small inclusions of different oxides in the metal slows down its recrystallization *via* sintering. Then the question is: why

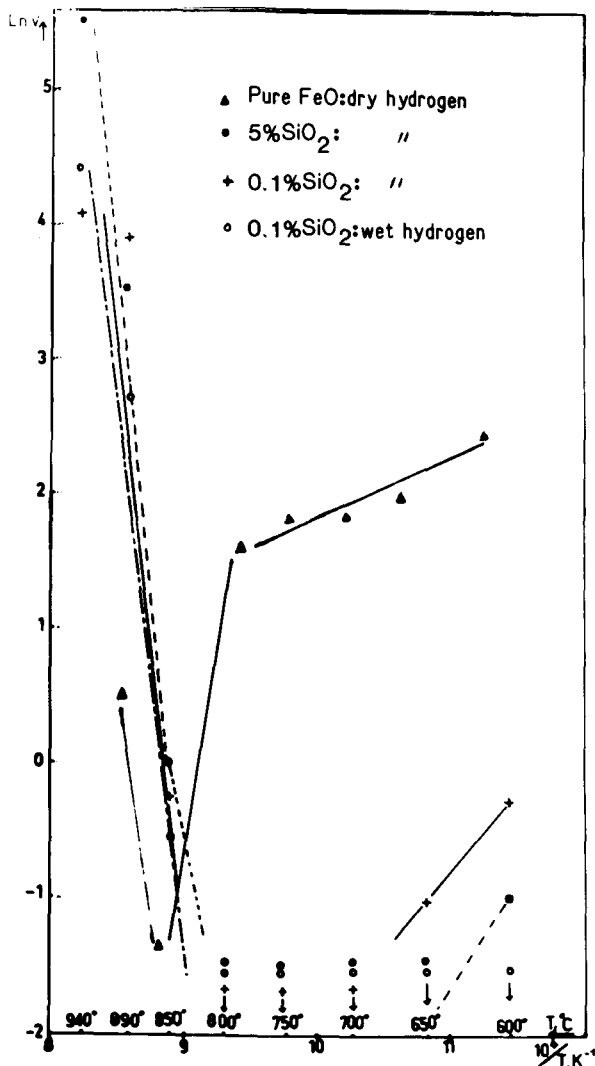


Fig. 11—Reduction of Si-doped particles: Arrhenius diagram (V means average reduction rate between $\alpha = 0.05$ and $\alpha = 0.75$). The arrows mean that the reduction has not reached the expected rate of progress when the experiment is stopped.

does the calcium seem to be more efficient than the two other cations? However, such inclusions are certainly more efficient if they are smaller and, hence, more regularly distributed. This involves diffusion of the ions which constitute the inclusions (MgO , MnO , CaO) and/or plentiful nucleation of these oxides, these two aspects being actually correlated. Now, these conditions are met by Ca^{2+} , which is of considerably greater size than Mg^{2+} or Mn^{2+} (1.00 Å, 0.72 Å, and 0.83 Å, respectively, according to Reference 19). Hence, it diffuses less easily and is associated with higher stresses favorable to nucleation, more especially as the solubility of CaO in wustite is limited. Although, as far as we know, there is no theoretical description of the situation schematically illustrated on Figure 13, we can assume that there is a competition between the chemical reaction which produces free Ca^{2+} ions and the diffusion of these ions. This diffusion may use not only the classical intragranular gradients of concentration, but also some faster surface pathways toward CaO nuclei. The faster the reduction process, the smaller will be the CaO inclusions. Hence, the sizes of these inclusions should be related

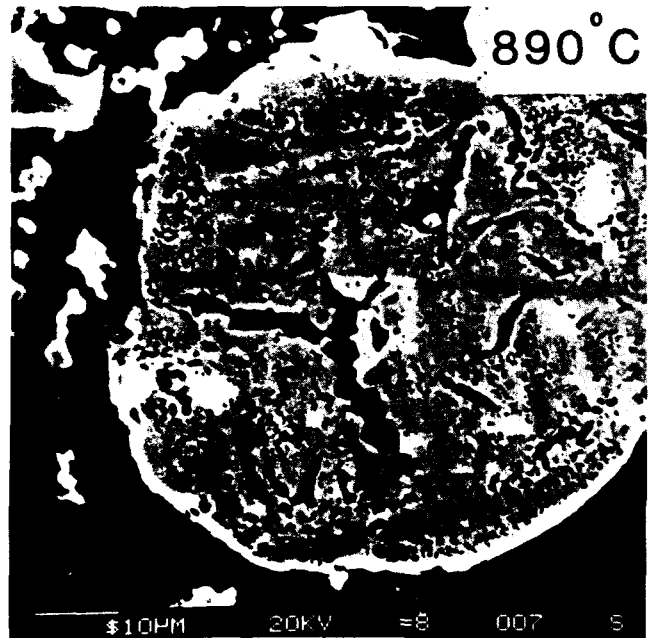


Fig. 12—Micrograph of Si-doped particles (5 pct molar SiO_2) after reduction in dry hydrogen. Reduction time: 50 sec.

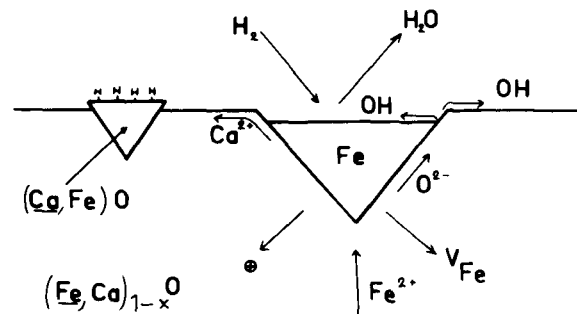


Fig. 13—Diagram of the species transfer when two nuclei are present (the shape of each nucleus is assumed to be the same as for Ni in the reduction of NiO^{20}).

through the following equation to the phenomenological parameters:

$$s \sim \frac{D_M}{k(p_{H_2} - p_{H_2^e})}$$

where D_M is the diffusion coefficient of cation M^{2+} in wustite, k is the kinetic constant of reaction, and $(p_{H_2} - p_{H_2^e})$ the departure from equilibrium $Fe/Fe_{1-x}O$.

Finally, these considerations should not rule out the possibility that Ca could also play a role in the chemical reaction step itself, for instance in the reduction of wustite inside its homogeneity range. Of interest is the fact that, as shown by Figure 9, the $CaFe_5O_7$ blocks, which are, of course, richer in Ca than the substituted wustite, display a rather slow reduction. This reveals an influence of Ca more complex than that assumed above, possibly linked with the nucleation and growth of iron, as El Moujahid has emphasized in the case of pure wustite,² or due to the transient formation of other calcium ferrites which may be more difficult to reduce.

2. The case of Al and Si

It was expected that these elements would play a very limited role as they are mainly involved in separate phases as aluminate or silicate. However, it was observed that Al slows down the reduction process at any temperature, which proves that it is effective at a content of 0.5 pct in wustite. Still more remarkable is the action of Si which is present in the wustite lattice at most in a concentration of 0.01 pct, and yet has a marked effect as shown in Figure 11 in that it slows down the reduction at low temperature, and accelerates it, to the same extent as Ca, at high temperature.

Such low levels of concentration for Al and particularly for Si, raise the question of their presence at the surface of wustite, which, especially for Si, is a more reasonable location to postulate. It has been shown by Dufour,²⁰ in the case of NiO, that tiny amounts of Si form a bidimensional compound of the phyllosilicate type. No such data are available for wustite where another interpretation, partly suggested by Dufour,²¹ suggests a blocking of diffusion paths by Si, for instance the clustering of Si at the emergence of dislocations at low temperatures, whereas when the temperature is high enough the volume diffusion overcomes the problem of finding easy ways of diffusion, and, at the same time the accelerating effect could be due to adsorption and nucleation effects of the silicon present on the surface.

Such an interpretation should not prevent us from taking into account the possibility that annealing of wustite crystals in the presence of Si modifies the morphology of the particles. Of course, this applies generally to any pretreatment needed for incorporating the additives.

B. Other Features

1. The role of water vapor

It is worth reemphasizing that Mg and Mn suppress the "rate minimum" only with pure hydrogen. As the iron sintering is not accelerated by traces of water vapor, it must be concluded that, in our experimental conditions, H₂O blocks some favorable nucleation sites and, as a consequence, more time is available for the metal for sintering and, thus, to slow down the reduction rate. But this assumes that continuous nucleation is needed, probably due to the fact that, at the atomic level, epitaxy is not really obtained or, if it is, un-sticking of the iron layer occurs. However, El Moujahid has shown, for pure wustite, that a dense iron layer may be obtained when the oxygen pressure in the gas is increased, and this is an alternative explanation.

2. Oxygen diffusion

At temperatures above the "rate minimum", when a dense iron layer protects the remaining wustite from the gas, the reaction can proceed only through diffusion of oxygen across the metal, as established by different authors.^{3,22-24}

In the case of MgO, for instance, this means that the MgO particles, embedded in the metal, slows down its sintering but cannot prevent it when temperature is high enough, constituting then a kind of composite material without microcracks through which gas diffusion could take place.

3. Comparison with previous authors

This is limited by the fact that previous authors have not paid special attention to the situation at a high degree of reduction, where the metal texture is of great importance.

It is, however, interesting to note that Iguchi and Inouye²⁴ report very little influence of 2.4 mol pct MgO or Al₂O₃ in

wustite reduction with H₂ at 795 and 985 °C at a reduction degree of 0.30 to 0.35. However, it must be stressed that they dealt with wustite particles ten times smaller than ours, and this minimizes, of course, the texture effects on the course of reduction. On the other hand, they observe a favorable influence of CaO, and this gives food for thought about a role of calcium not only in sintering of iron, but also in the chemical step of the reduction, as noticed in other respects with potassium.²⁵

In the same way, Piepenbrock *et al.*¹¹ mainly investigate the first 50 pct of reduction, and it is of interest to call attention to the fact that their hierarchy of doping (from acceleration to slowing down) is: K, Ba, Ca, Mn, Fe, Al, and Si at 0.1 for the reduction degree, and K, Mn, Ba, Ca, Si, Al, and Fe at 0.5, whereas our own classification would be Ca, Si, Mg-Mn, Fe, and Al at 940 °C.

Let us also mention that, very recently, Inami *et al.*²⁶ have briefly reported on the influence of Ca, Mg, Ba, and Si on the reduction of wustite at 900 and 1200 °C with CO although they do not specify the doping content nor the degree of reduction. They observed a favorable influence of all these elements at 900 °C and of Mg and Si only at 1200 °C. These results are difficult to compare with ours because of lack of detailed information.

Finally, it seems clear that the interpretation of Khalafalla and Weston⁵ based upon the diffusion in wustite, more or less favored by doping elements, is certainly debatable insofar as elements such as K or Ba, which are very active in the wustite reduction process, are practically insoluble in the lattice, indeed as is Si at every temperature.

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