APPLYING THE VAPOR DEPOSITION TECHNIQUE IN STUDYING THE KINETICS OF REDUCTION OF IRON OXIDES

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Abstract:

Thin films of Fe, Ca and Mg were deposited on high purity wustite surfaces to study the mode of nucleation and growth of iron also to investigate the influence of impurities on the kinetics of metallization. The specimens were examined after reduction using the SEM to observe the shape of iron.

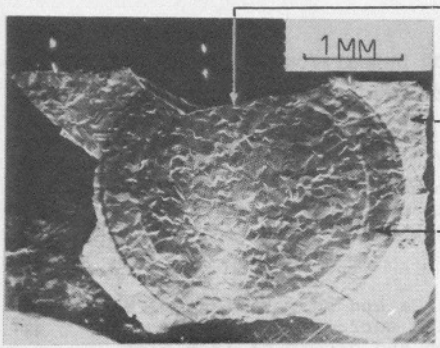
The results suggests that early nucleation followed by rapid growth causes the iron to grow outside the surface. CaO could promote the outer growth when it is concentrated in certain sites. On the other hand MgO seems to have no pronouced effect.

I. INTRODUCTION

This paper is presented to show how the vapor deposition technique, in its simplest form was used to confirm certain mechanisms of metallization of iron during reduction of iron oxides.

Metalographic examination of partially reduced iron oxides showed different mode of metallizations, depending on the reduction conditions and specimens characteristics(1). In some cases iron is shaped as filaments or whiskers while on the others a layer of sponge iron is formed. The mode of metallization can be related to: the degree of wustite surface heterogenity(2), the presence of minor impurities (like CaO(3), or alkali oxides(4)), and more important the distribution of these impurities in the wustite lattice structure prior to metallization(5,6).

The influence of CaO and its distribution was investigated using the electron probe microanalyzer, but with mixed results(1,5). The main difficulty was to locate the CaO on exact sites and follow the specimen history before and after reduction.



The openings of the grid screen

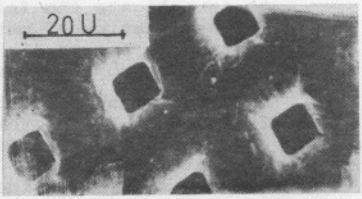


Figure 1: Appearance of the wustite specimen after iron film deposition

II. HOW THE VAPOR DEPOSITION TECHNIQUE IS USED

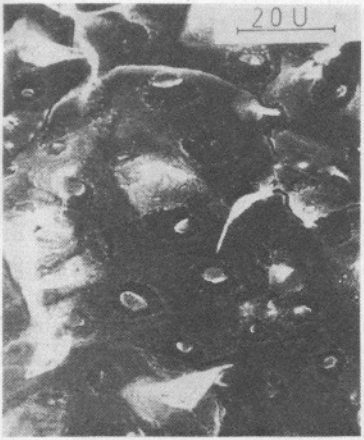
Briefly, employing the vapor deposition technique in investigating the kinetics of reduction and the mode of metallization, can be recapitulated in the following steps:

- Preparing wustite specimens with regular surfaces.
- Depositing a thin film of Fe, Ca or Mg on the wustite surface, under high vacuum.
- In cases of Ca or Mg films, they were first oxidized to CaO or MgO prior to reduction.
- Reducing the wustite under controlled conditions of temperature and reducing gas mixture.

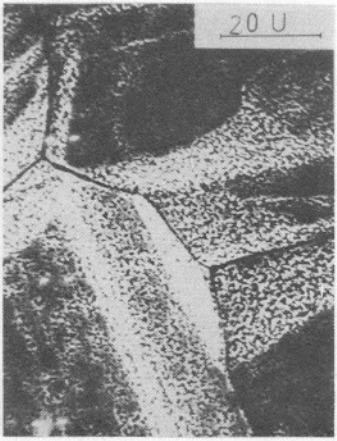
The distribution of impurities, deposited on the wustite surface, is detected and related to the metallization mode, using the SEM examination before and after carrying the reduction experiments. Also, some of the specimens were cutted and examinaded by optical microscope, to determine the thickness of the iron layer formed during reduction.

III. EXPERIMENTAL WORK AND RESULTS

Wustite specimens of regular surfaces were prepared by



Outer growth of iron from the 12x12 μm iron deposited films (The bright and sharp images are irregularities).



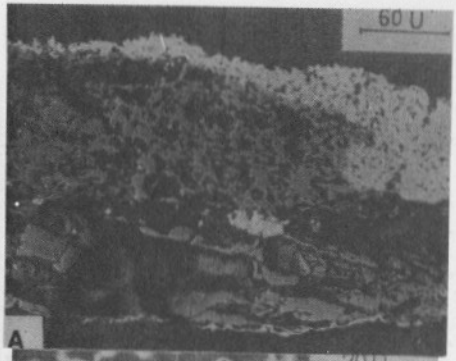
Sponge formation of iron, similar for both uncoated or completely coated zones on the surface.

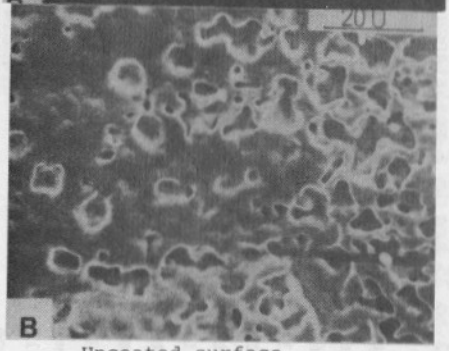
Figure 2: Appearance of the metallized specimens with iron film deposition, after reduction for 1hr. at 700°C

oxidizing high purity ARMCO iron foil (99.85 wt% Fe). The oxidizing conditions were: 1000°C, using gas mixture of $CO:CO_2$ and N_2 of 100: 100 and 300 CC(STP)/min. respectively, for 22 to 25 hrs in a resistance-heated tubular furnace. After oxidation the specimens were examined to confirm the oxidation of all the iron and the formation of two dense layers of wustite free from pores, one in each side of the specimens.

3.1 - Depositing the thin films

The surface of the wustite was coated with a thin film of the desired substance, which was first evaporated then deposited on the surface by fusion in a conical shaped tungsten filament, heated by passing electrical current under vacuum of 10^{-4} to 10^{-5} mm.Hg. The hickness of the deposited film could be calculated by weighing the substance prior to carry out the evaporation and deposition, and measuring the normal distance from the tungsten filament to the wustite surface.

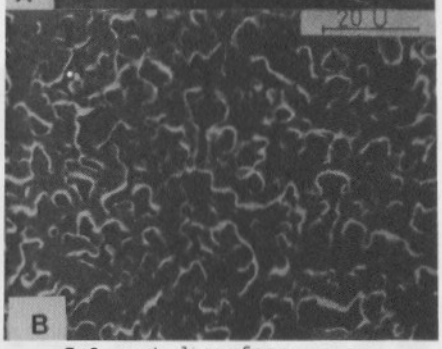




Uncoated surface

A: are photographs of Optical Microscope.

B: are photographs of SEM.



CaO coated surface

Figure 3: The effect of CaO on the morphology of iron during reduction of treated wustite specimen reduced at 900°C.

Assuming the evaporations is equal in all directions, the tickness of the deposited film may be determined from the mass balance as follows.

$$t = \frac{m}{4\Pi r^2 \rho}$$

where: t is the film thickness in Cm.
r is the normal distance between the wustite surface
ρ is the density of the deposited substance in gms/cc
m is the weight of the evaporated substance in gms.

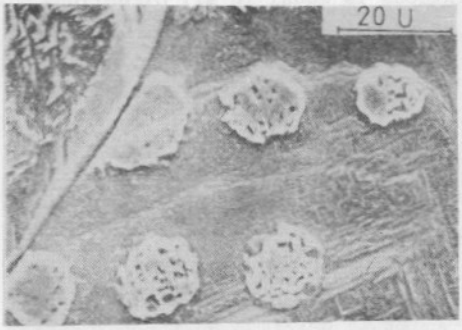
Unfortunately, the vapor is not usually radiated with spherical symmetry. The error in determining the thickness using the above equation may be as high as $\pm$ 50%(7). The thickness of the deposited films was in the order of about 200°A.

To facilitate the research, microscopic grids were used to cover the wustite surface. After film deposition, there were three zones on the wustite surface to be considered. The uncovered surface which had a continual deposited film. The covered surface, underneath the gridrim, which was not affected by the evaporation and deposition. The third is the region, which is covered by the screen of the microscopic grid, it result in a regular spaced pattern of deposited film with the same dimensions of the screen openings. Figure 1 shows the appearance of a wustite specimen after depositing a thin film of iron, the grid used of 1000 mesh and resulted in a regular spaced pattern of 12x12 micron.

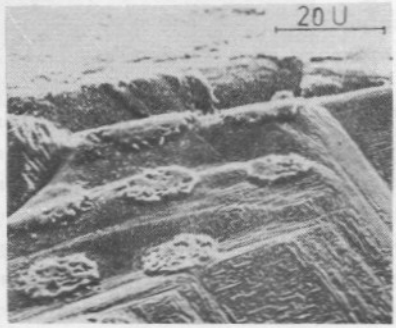
3.2 - Some results of reduction experiments

Figures 2 to 4 illustrate some of the SEM and optical microscope photographs, taken of the partially reduced specimens. The reduction was carried in the same tubular furnace of 4 cm inside diameter used for oxidizing the iron to wustite. The reducing gas mixture was $CO:CO_2$ and N_2 of 160:40 and 300 CC(STP)/min. respectively. Most the experiments were carried out at 700 and 750°C except very few at 900°C.

As shown in Figure 2, with high purity wustite specimens the metallization of iron appeared to depend on the presence of the Fe film which was deposited prior reduction on the surface. Short but definite outward growth of iron was originated from the 12x12 micro iron films, the morphology of



Specimen as positioned horizontally under the SEM



Specimen as tilted 30° under the SEM

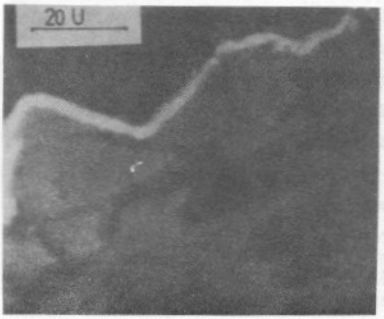
Figure 4: Effect of CaO on the outward growth of iron, the specimen was reduced at 750°C.

the other two zones (with continuous iron film and the uncoated region) was almost the same and a sponge layer of iron with very fine pores was observed after reduction.

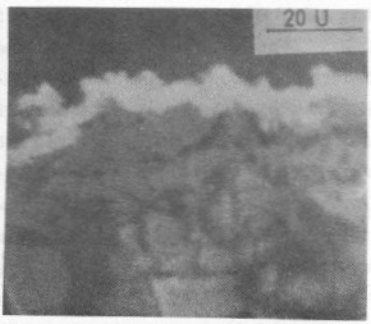
The influence of CaO on the kinetic of reduction is illustrated in Figure 3. CaO enhance the rate of reduction and a porous iron layer was formed from the wustite surface coated with CaO. The effect of CaO as a promoter for outward growth of iron is shown in Figure 4. On the other hand, Figure 5 demonstrates that MgO has much less effect on the kinetics of reduction compare to that of CaO.

IV. DISCUSSIONS AND SOME CONCLUSIONS

The results suggest the morphology of iron to depend on the state of wustite surface during metallization. The outward growth and iron whiskers formation during reduction



Wustite specimen without coating, reduced for 2 hr.



Wustite specimen coated with MgO film, reduced for 2 hr.

Wustite specimen coated with CaO film, reduced for 1 hr.

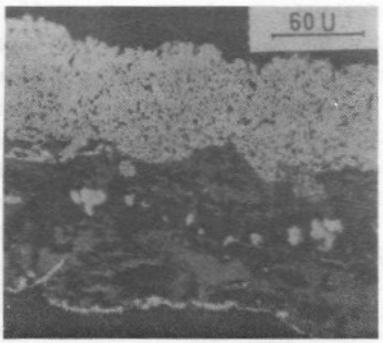


Figure 5: The optical photographs show the difference in effect between CaO and MgO on the morphology of iron formed during reduction at 900°C.

seem to be related to the wustite surface heterogeneity. It could be physical heterogeneity or chemical heterogeneity, due to the uneven distribution of impurities in the wustite lattice structure.

As shown in Figure 2, the deposition of the 12x12 μm. films prior to reduction enhances the tendency of outward growth during metallization. When there is a continuous film or no film the result is almost the same i.e. a layer of sponge iron, because in both cases the surface is more or less homogeneous.

The influence of CaO on the outward growth is illustrated in Figure 4, when the specimen was tilted under the

SEM it could be seen that the iron patches were about 2 μm. tall. The shorter iron patches may be the result of two factors i.e., the bigger metallic base area (compare to that of whiskers) which needs more iron to graw for same lenght, and the presence of CaO prior to metallization which makes nucleation much easier so that the extent of supersaturation (capacity to store more iron) would be less(6).

The results given in Figure 3 support the idea that CaO promotes the reduction kinetics. This pronounced effect seems to be due to its influence on forming a porous iron layer. On the other hand MgO has little effect on the porosity and the thickness of the iron layer as illustrated in Figure 5. The explanation offered regarding the difference of the ionic size between Ca^{++}, Mg^{++} and Fe^{++}, may suggest that MgO to distribute more uniformly in very short time compare to CaO, hence its influence to be very limitted (1,6).

The main conclusion is the success of the vapor deposition technique in our research. It is obvious that in employing the technique a very simple approach was used and there are many steps to be taken to improve its use.

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