Elaboration of iron powder from mill scale

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Abstract

This work refers to the study of the conditions of mill scale reduction, a by-product of iron and steel formed during the hot rolling of steels, with a reducing gas (carbon monoxide) in order to produce iron powder having characteristics required by powder metallurgy. The reduction was carried out at various temperatures (750-1050°C) during different times ranging between 40 and 180 min in an atmosphere of pure CO. The produced iron powder was characterized by chemical analysis, x-rays diffraction, optical microscopy and scanning electron microscopy. These methods of investigation confirm the presence of iron, graphite and iron carbide (Fe_3C) as the products of reactions. The maximum iron content (98.40% Fe) in the iron powder was obtained by reduction of mill scale at 1050°C for 180 min. A reduction annealing under hydrogen makes it possible to decrease carbon and oxygen content of the reduced iron powder up to acceptable values.

Keywords: recycling, mill scale, reduction, carbon monoxide, iron powder.

1. Introduction

The steelmaking by-products such as dust and mill scale, very rich in iron (≈ 72% Fe), are currently produced in large quantities and represent a potential of almost 5 millions tons in the world [1]. Generally, these by-products are recycled by the metallurgical processes such as the blast furnace or the direct reduction reactors that uses coal as reducing agent to produce pre-reduced pellets intended for the remelt in electric steel plant. Besides the steelmaking, recycling part of these by-products is already supported by the powder metallurgy where the economic recovery is more favorable. During the last twenty years, powder metallurgy has presented a continued expansion in all its aspects and in all of its applications to the industry. Powder metallurgy comprises a set of processes of forming having for common denominator a raw material in a powder form.

The reduced iron powder is the most widely used material in powder metallurgy industry. The direct reduction process has commonly been used by many companies (such as Hoeganas in Sweden, Kawasaki in Japan and Pyron in US) to obtain metallic iron powder by the reaction of iron oxide (magnetite, hematite ore or mill scale) and reducing gases (CO/H_2) under high temperatures (> 1000°C) [2].

The reduction of iron oxides and various ores containing iron oxides have been studied in the past [3-8]. Their researches are conducted using as reducing agents solid carbon and reducing gas (CO and/or H_2). When the reduction is carried out by solid carbon or carbon monoxide the final process of reduction is always written as follows:

$$Fe_nO_m + mCO_{(g)} = nFe + mCO_{2(g)} \quad (1)$$

The necessary CO is provided directly or by the Boudouard reaction:

$$mC_{(s)} + mCO_{2(g)} = 2mCO_{(g)} \quad (2)$$

The Boudouard reaction, regenerating reducing gas CO, keeps the P_{CO}/P_{CO_2} ratio always great and therefore the reduction process according to (1) will be maintained at a constant level. In the event of reduction occurring by circulation gas over or through a bed of particles of iron oxides (fixed or mobile) the CO_2 formed by the reaction (1) will be carried away by gas flow, which allows to reach the quasi-complete reaction of a bed of oxide particles [9]. In addition to the reduction to metallic iron, disintegration of carbon monoxide by the reverse Boudouard reaction (2) and carburization are expected to occur simultaneously. This is confirmed by thermodynamic studies which indicate that relatively low temperatures (less than 1000°C) and high concentrations of CO along with the presence of metallic iron, which acts as a catalyst, lead to carbon deposition [10]. The increase in temperature and CO concentration leads to reduction in iron oxides without carburizing.

Other parameters can greatly affect the kinetics of reduction of iron oxides. The rate of reduction of iron oxides depends on several factors that can vary from one process to another, especially the grain size, porosity and specific surface, mineralogy (Fe_2O_3 and Fe_3O_4 are not reduced in the same way), pressure, gas flow and the gangue constituents such as silica, alumina and silicates which may alter the equilibrium [11]. The aim of this work is to study:

(a) The optimal conditions for the reduction of mill scale to obtain iron powder with acceptable purity for the use in powder metallurgy industry.

(b) The effect of carbon deposition on the reduction of iron oxides by pure CO.

2. Experimental

2.1. Materials Used

Mill scale generated in a hot rolling step (Fig. 1) was heated to 400°C to remove the oil and crushed to the desired particle size distribution. Three fractions of particles were used in this study: 2-3.15, 6.3-10 and 10-16 mm. Sieves were standardized. Chemical analysis of the mill scale is given in Table 1. Analysis by X-ray diffraction (Fig. 2a) and microstructure of the mill scale particles (Fig. 2b) shows the presence of hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO) phases. Oxidation at 1000°C converts the iron oxides that are present in the mill scale, FeO and Fe_3O_4, to ferric oxide (Fe_2O_3).

Figure 1. Raw mill scale

Table 1. Chemical compositions of mill scale

Compounds	Fe_{total}	FeO	CaO	SiO_2	MnO
%	72.13	56.70	0.42	0.14	0.37

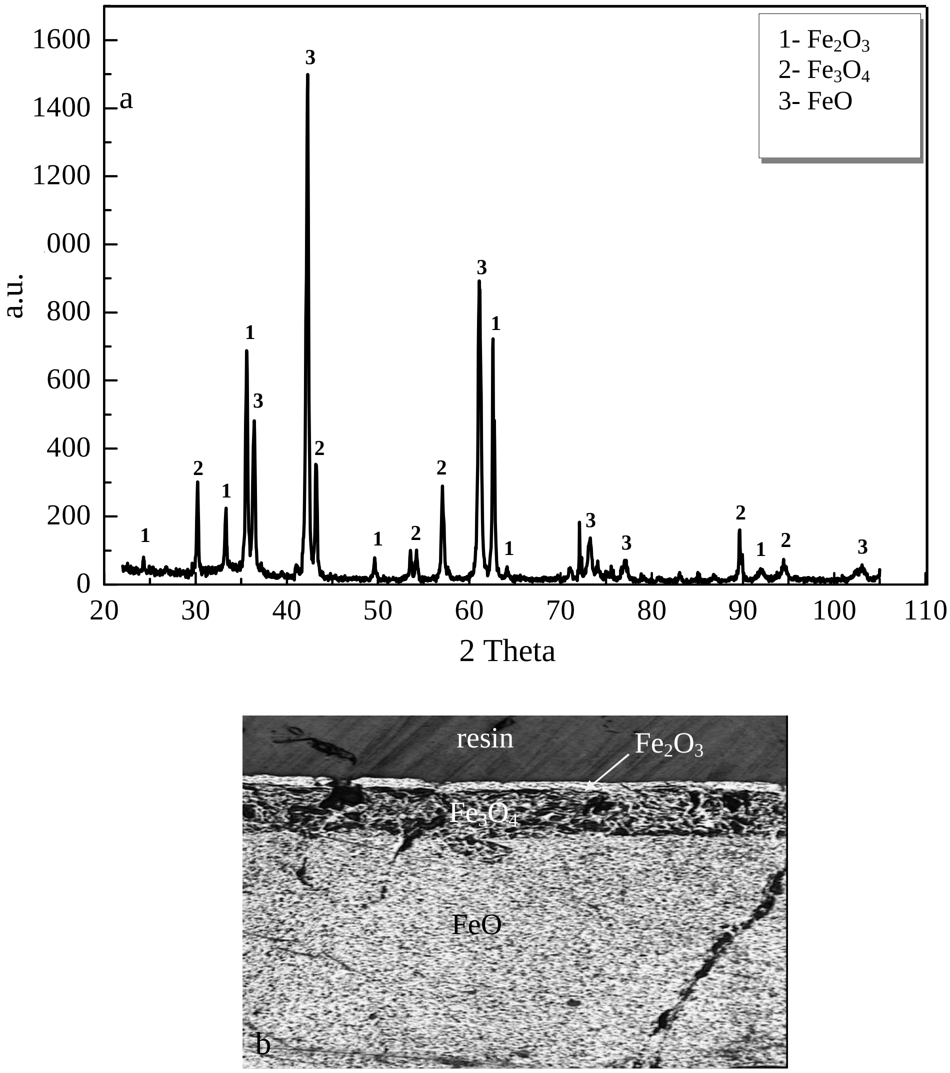

Figure 2. Oxide scale formed on the mill scale: (a) XRD spectra, (b) cross-section microstructure.

2.2. Reduction System and Procedure

The reduction tests were performed at the center of applied research in metallurgy and steel (URASM), Annaba. The reduction device and the method used to perform these tests are described in several works [12, 13]. In this method, where reduction was done in fixed bed, the sample was placed in a vertical reduction shaft which was introduced into an electric furnace maintained at a fixed temperature of up to 1600°C. As long as the sample had not reached test temperature, it was kept under nitrogen to prevent oxidation. When the temperature was stabilized, purified CO was passed at fixed rate during a fixed time. Preliminary reduction tests were carried out at 1000°C to determine the optimal gas flow rate which does not significantly affect the rate of reduction. As a result of these tests, a 1000 l/h gas flow of CO gas was used in all the reduction experiments. The reduced samples were cooled to room temperature in a nitrogen gas atmosphere for subsequent examination and chemical analysis. The tests were performed in two steps: (a) To study the effect of particle size, the CO/N_2 ratio and oxidation of mill scale on its reducibility at 1000°C and 60 min. (b) Extending the study to investigate the influence of various temperatures (750-1050°C) and different reduction times (40-180 min) under an atmosphere of pure CO.

The evolution of the reduction rate was calculated on the basis of data obtained by chemical analysis. The scanning electron microscope (SEM), light microscope (LM) and X-ray technique were used to characterize the structure and the different phases formed in each reduced sample. The total amounts of carbon deposited in the reduced samples were determined according to ISO 437 [14]. The oxygen content was also measured in accordance with ISO 4491-2 [15].

3. Results and discussion

3.1. Effect of Some Parameters on the Rate of Reduction

Preliminary tests were carried out in order to study the effect of CO rate in the CO-N_2 mixture, particle size and oxidation of mill scale on the evolution of reduction at fixed time (60 min) and 1000°C. The results are presented in Table 2.

The mill scale sample reduced in the conditions of test N1 has low total iron content and a low rate of reduction, 78.85 and 34.48% respectively. These two indexes evolve in the same direction (80.30 and 41.80%) when the fraction 6.3-10 mm was used, keeping the same CO/N_2 ratio. For the same fraction (6.3-10 mm), increasing the CO/N_2 ratio from 40 to 100% (corresponding to pure CO), while maintaining the other parameters unchanged, increases significantly the rate of reduction (41.80 to 68.06%) and total iron content (80.30 to 88.59%). The amount of metallic iron (Fe^0) increased and that of Fe^{2+} decreased with decreasing particle size and increasing CO/N_2 ratio. Test N5 shows the effect of prior oxidation of the mill scale on its reducibility. The mill scale has undergone an oxidation at 1000°C. The rate of reduction and the total iron content of reduced iron powder increases to 86.21 and 92.96% respectively. The maximum iron content (94.74%) and rate of reduction (90.78%) was obtained when we used sample of particle size 2-3.15 mm (test N6).

Table 2. Effect of CO/N_2 ratio, particle size and mill scale oxidation on the rate of reduction and chemical composition of reduced iron powder at 1000°C and 60 min.

Tests	Size mm	Gas CO/N_2	Rate of reduction %	Chemical composition, %			
				Fe_{tot}	Fe^{2+}	Fe^0	Fe^{3+}
N1	10-16	40/60	34.48	78.85	54.32	18.04	6.49
N2	6.3-10	40/60	41.80	80.30	51.10	24.63	4.57
N3	6.3-10	60/40	49.38	85.68	48.38	33.60	3.60
N4	6.3-10	100	68.06	88.59	34.93	53.53	0.13
N5	6.3-10	100	86.21	92.96	17.18	75.66	0.12
N6	2-3.15	100	90.78	94.74	12.10	82.54	0.10

The most important result to be drawn from these tests is the strong influence of the rate of CO in the CO-N_2 mixture, the oxidation of the mill scale and the particle size on the rate of reduction and the total iron content of reduced iron powder. The total amount of iron reaches its maximum value (94.74%) when oxidized mill scale with particle size 2-3.15 mm is reduced with pure CO at 1000°C and 60 min.

3.2. Effects of Temperature and Reduction Time

Another series of tests were performed by varying the temperature (750 to 1050°C) and reduction time (40 to 180 min). Mill scale with particle size 2-3.15 mm undergoes an oxidation at 1000°C. The reducing gas used was pure CO.

The results of reduction tests are presented in Figure 3. At 750°C it was found that with the increase reduction time from 40 to 180 min the total iron content of reduced iron powder decreases from 88.5 to 75.3% respectively. At the same time interval, the amount of metallic iron increases (40.6 to 56.9%) and that of Fe^{2+} decreases (47.8 to 19%). The decrease in total iron content can be explained as follows: along the reduction of iron oxides by pure carbon monoxide to wustite and metallic iron a disintegration of carbon monoxide takes place according to the reverse Boudouard reaction [10]:

$$2(CO)_{ads} \rightarrow (CO_2)_g + C \tag{3}$$

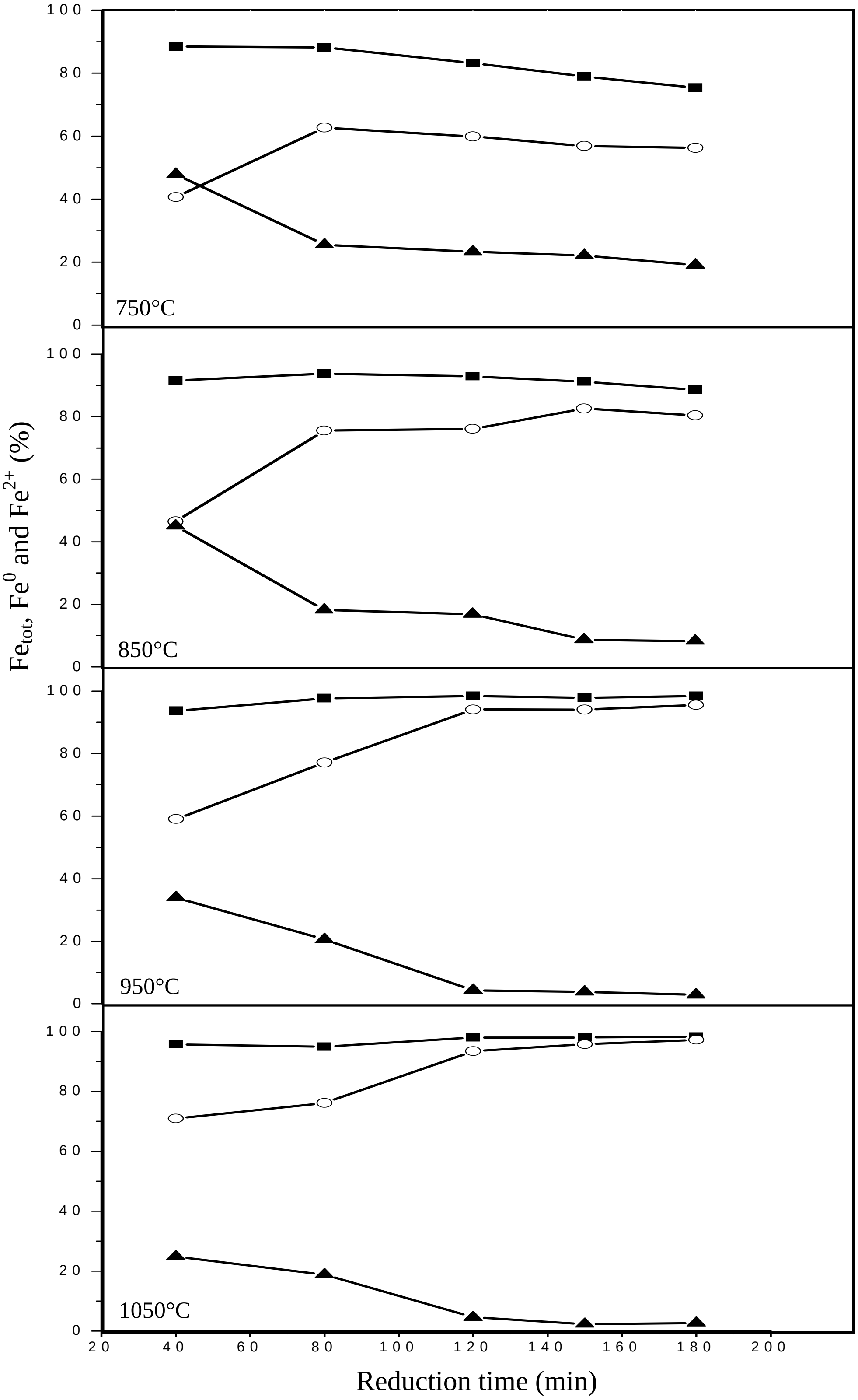

Figure 3. Evolution of ■ Fe$_{total}$, ○ Fe^0 and ▲ Fe^{2+} in reduced iron powders with temperature and reduction time.

and accordingly the carbon deposition and its reaction with metallic iron and wustite leads to the formation of iron carbide. Carburization of the reduced iron or wustite grains can take place according to the following reactions:

$$3Fe + C \rightarrow Fe_3C \tag{4}$$

$$3Fe + 2CO \rightarrow Fe_3C + CO_2 \tag{5}$$

$$3FeO + 5CO \rightarrow Fe_3C + 4CO_2 \tag{6}$$

Carbon monoxide, adsorbed (reaction 3) onto the surface of metallic iron grains disintegrates more easily than when it is free. The metallic iron acts as a catalyst [16]. Thus, as shown in figure 3 at 750°C, the decrease in total iron content is attributed to the increase of amount of carbon deposition with the increase of reduction time and amount of metallic iron. This carbon increases the weight of the sample and consequently the total iron content is increased. The total amount of carbon in reduced iron powder at various temperatures and reduction times is presented in Figure 4.

It shows that the carbon content in the reduced iron powders decreased with rise in temperature and with decrease in the reduction time. At 850°C, as shown in Figure 3, the amount of total iron, metallic iron and Fe^{2+} evolve in the same direction as the tests at 750°C. However, the decrease of amount of total iron content with reduction time is less pronounced. As a result, the amount of carbon deposition with reduction time is lower at 850°C. For reduction tests at 950°C and 1050°C there is already a significant improvement in the content of total iron and metallic iron with increasing reduction time. At 180 min, the content of total iron and metallic iron increases up to 98.30 and 95.50% at 950°C and up to 98.40 and 97.20% at 1050°C respectively. As shown in Figure 4, the carbon content in the reduced sample decreased up to 1% at 1050°C and 180 min.

The different phases formed in the reduced iron powders at 750-1050°C and at 180 min, as identified by X-ray diffraction technique, are shown in Figure 5. The diffraction pattern of the reduced iron powder at 750°C shows the presence of metallic iron (Fe^0), wustite, graphite and iron carbide (Fe_3C). At 850 and 950°C, it was observed the presence of metallic iron and graphite and at 1050°C only metallic iron phase was obtained.

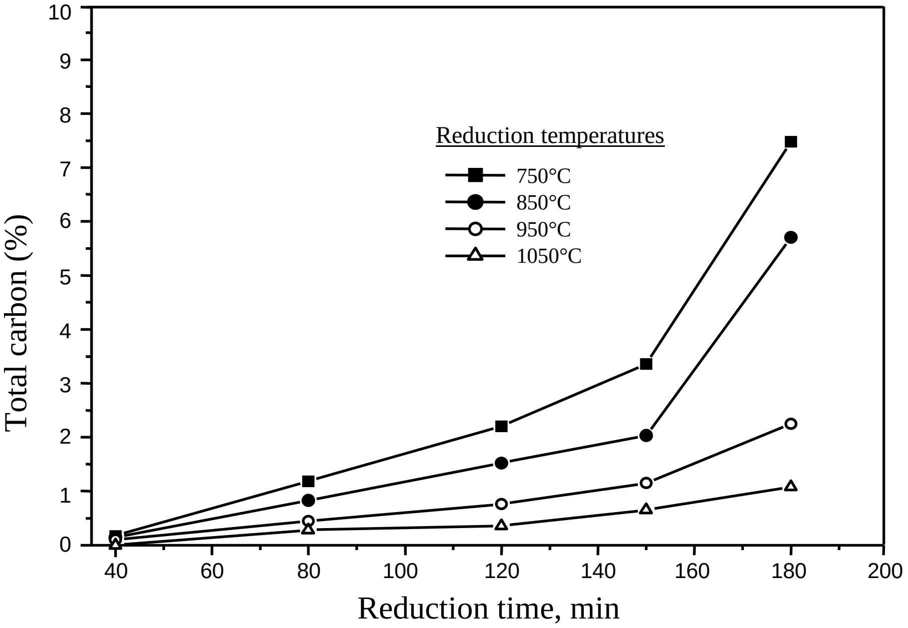

Figure 4. Evolution of total carbon content in reduced iron powders with temperature and reduction time.

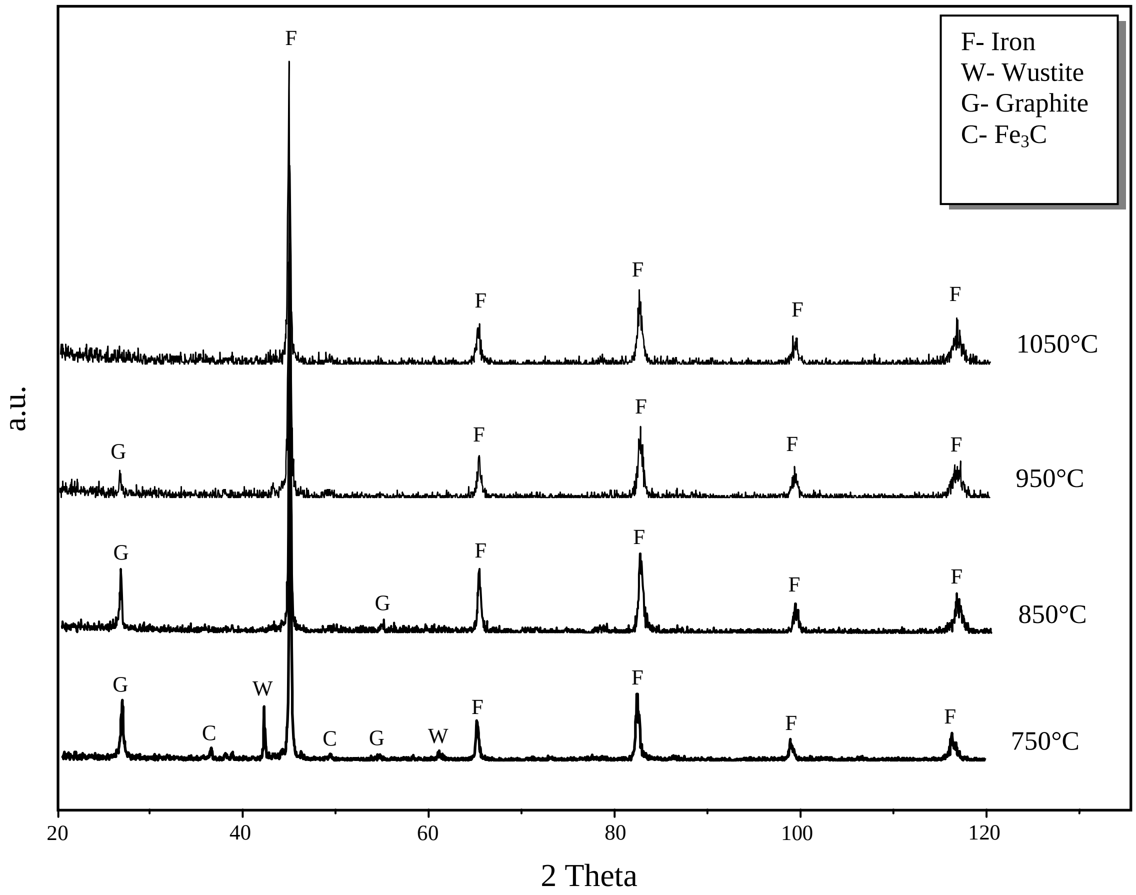

Figure 5. X-Ray spectra of the reduced iron powders at various temperatures and 180 min.

Microscopic examination of polished sections of reduced samples at various temperatures and at 40 min and 180 min are given in Figures 6 and 7 respectively.

Figures 6a to 6d, shows the photomicrographs of partially reduced samples at 40 min and at 750 to 1050°C. The four photomicrographs show frontal reduction of oxides particles into magnetite (Figs. 6a, b) or wustite (Figs. 6c, d) in an envelope of metallic iron. At 180 min and at lower temperatures (750 and 850°C), metallic iron dominated with a minor phase of wustite were observed as shown in Figures 7a and 7b. For reduced samples at 950 and 1050°C, iron oxides are completely converted to metallic iron as shown in Figures 7c and 7d. SEM photomicrographs of reduced samples at 1050°C and 180 min are presented in Figures 8a and 8b. Irregular shape of the particles surfaces and particle porosity are visible. This morphology is the typical form of particles of iron powder obtained by reduction with carbon monoxide [17, 18].

The results presented in Figures 3 to 7 shows that the best reduction conditions for reduced iron powder are 1050°C and 180 min. Chemical analysis of these powders are presented in the Table 3. To reduce the carbon and oxygen content, the iron powder is annealed in an atmosphere of hydrogen at 850°C for 1 hr. During annealing the carbon and oxygen content is considerably reduced and the strain hardening of particles is removed [16, 19, 20]. After annealing, the contents of carbon and oxygen in iron powder increases to 0.23 and 0.28% respectively.

Table 3. Chemical compositions of reduced iron powder at 1050°C and 180 min.

Compounds	Fe_t	Fe^0	C	Si	Mn	P	S	O
%	98.40	97.20	1.08	0.028	0.32	0.039	0.01	0.49

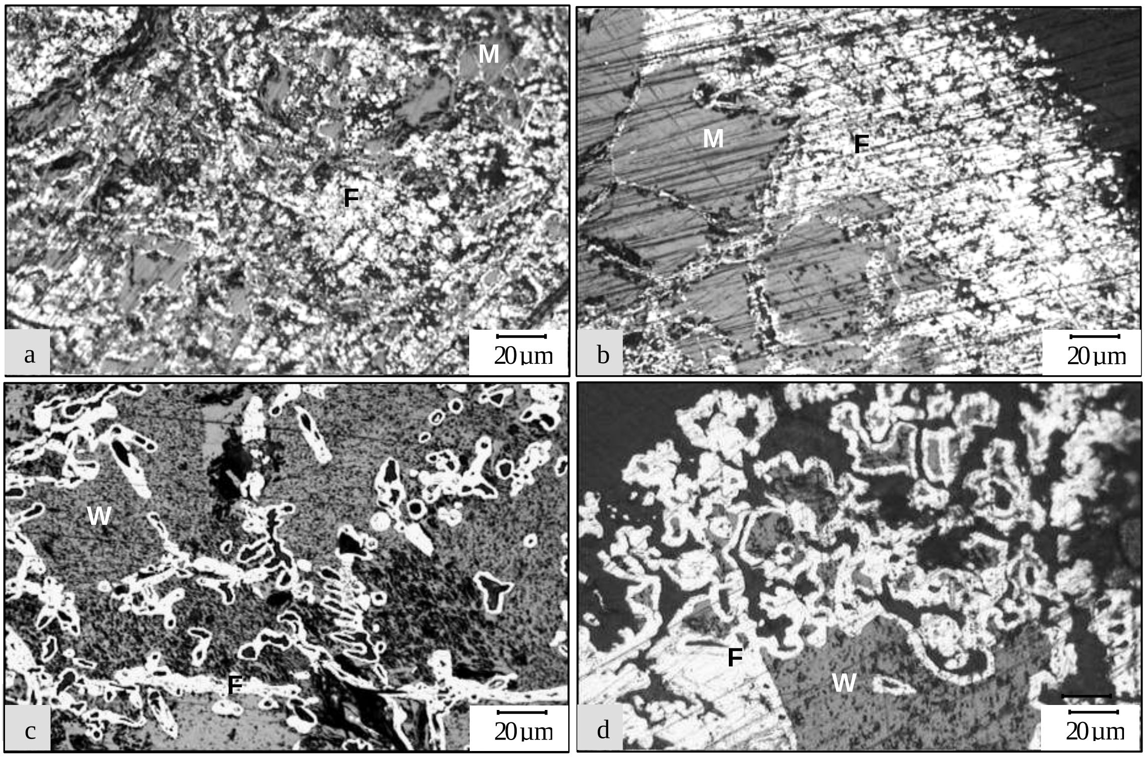

Figure 6. Photomicrographs of reduced iron powders at 40 min and at (a) 750°C, (b) 850°C, (c) 950°C and (d) 1050°C. M: magnetite W: wustite F: iron

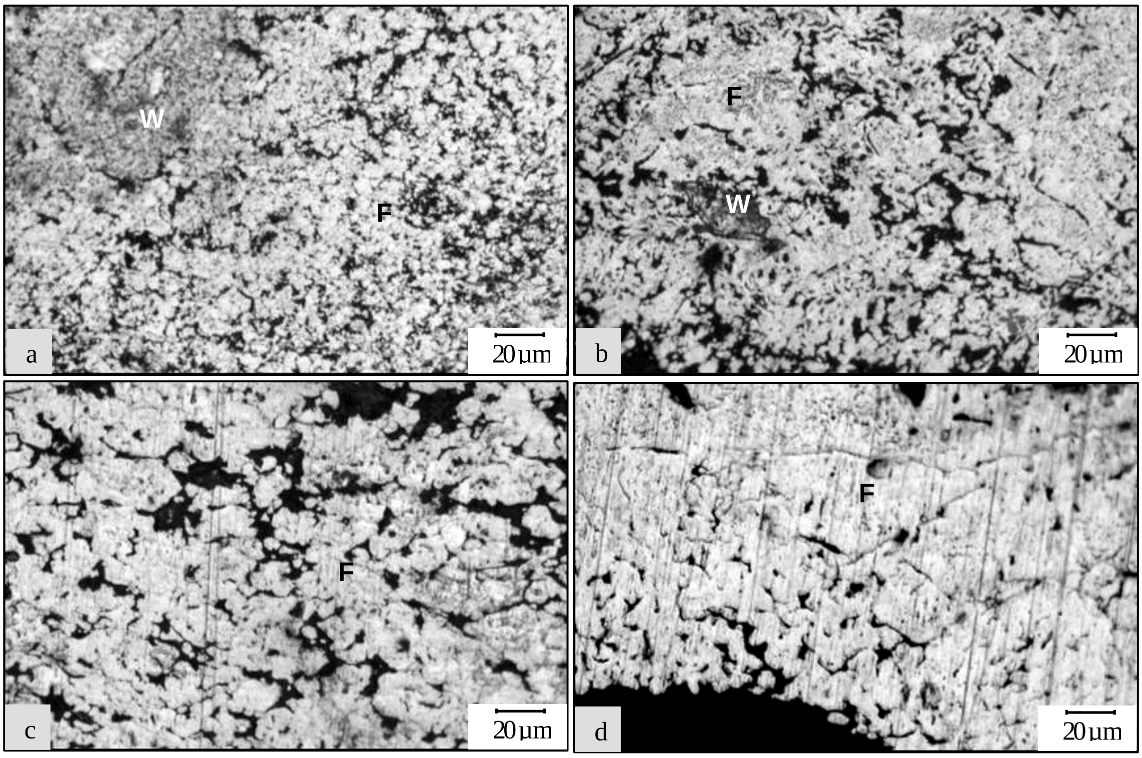

Figure 7. Photomicrographs of reduced iron powders at 180 min and at (a) 750°C, (b) 850°C, (c) 950°C and (d) 1050°C. W: wustite F: iron

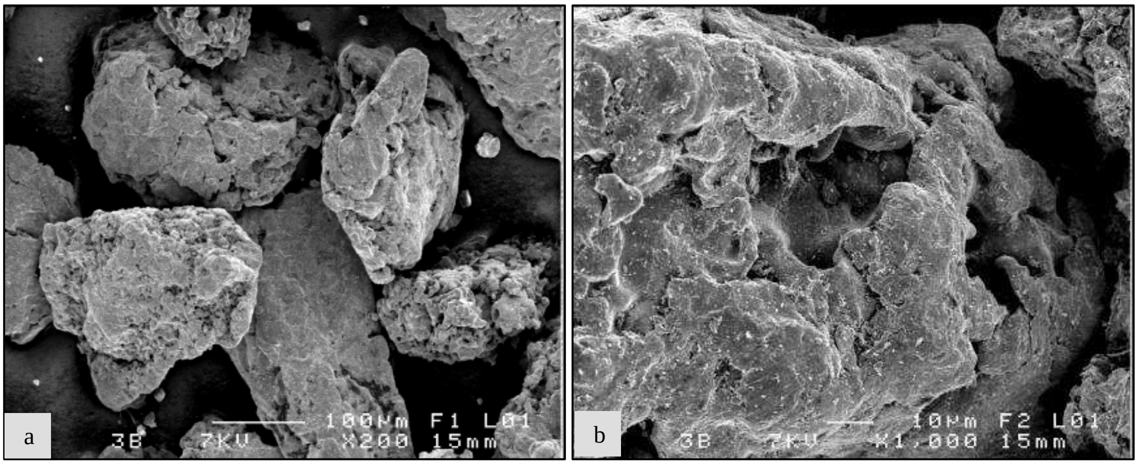

Figure 8. SEM photomicrographs of completely reduced iron powder at 180 min and at 1050°C.

4. Conclusion

The results presented and discussed in this study can be summarized in the following points:

(1) Different parameters for the reduction of the mill scale with carbon monoxide were studied to obtain the best conditions for the production of iron powder with physico-chemical properties required by powder metallurgy.

(2) The best reduction was obtained at 1050°C and 180 min in pure CO atmosphere. This is confirmed by chemical analysis, X-ray diffraction and light microscope. The content of total iron and metallic iron in the reduced iron powder is 98.4 and 97.2% respectively.

(3) Annealing by hydrogen reduces considerably carbon and oxygen content in the iron powder up to the desired values.

(4) The iron powders obtained by the process of reduction of mill scale can be used in the powder metallurgy industry.

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