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Production of Sponge Iron Powder by Reduction of a By-product of the Steelmaking Industry

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Abstract

Rolling mill scale is a solid steelmaking by-product that contains metallic iron (Fe), wustite (FeO), hematite (α -Fe₂O₃) and magnetite (Fe₃O₄). It also contains traces of non-ferrous metals, alkaline compounds and oils from the rolling process. A study is made of the reduction of mill scale to sponge iron, in covered crucibles, using coke at different temperatures (1050°-1150°C) and times (3-12 h). The final treatment of the samples was carried out in a hydrogen atmosphere furnace at 900°C for 0.5 h. The reduced samples are studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Oxygen analysis is carried out by combustion in a LECO oven. The reduction of mill scale allows the new use and development of this material to obtain sponge iron that can be re-used to the electric furnace as metallic load in steel manufacturing or as a raw material in the production of iron-base powder metallurgy parts.

Key Words: Powder production, Sponge iron, Solid by-product.

1. Introduction

Mill scale is a steelmaking by-product from the rolling mill in the steel hot rolling process. Mill scale contains both iron in elemental form and three types of iron oxides: wustite (FeO), hematite (α -Fe₂O₃) and magnetite (Fe₃O₄). The iron content is normally around 70 %, with traces of non-ferrous metals and alkaline compounds. Mill scale is contaminated with remains of lubricants and other oils and greases from the equipment associated with rolling operations. The oil content usually ranges between 0.1 and 2.0 %, but can reach up to 10.0 %. Mill scale is formed by flaky particles of a size of generally less than 5.0 mm. The size distribution depends on the point in the process where the mill scale is generated. The smallest particles (< 0.1 mm), known as mill scale sludge, are normally collected in the process water treatment units located close to the rolling machines. The average specific production of this by-product is typically around 35 - 40 kg/t. In Spain some 44,000 tons of mill scale are generated each year [1,2].

Coarse mill scale is practically 100 % recycled via the sintering plant, while finer mill scale or mill scale sludge, which is more heavily contaminated with oils, ends up in landfills. Mill scale with a particle size of between 0.5 and 5 mm and an oil content of less than 1.0 % is considered returnable via sintering without any pretreatment. Mill scale sludge cannot be recycled via sintering since its fine particles contain a high oil level (5.0-20.0 %) and is normally treated as a landfill waste [3,4].

The reduction of rolling mill scale to sponge iron powder is a new way to take advantage of a cheap by-product of the steelmaking industry, yielding sponge iron that can be re-used to the electric furnace as metallic charge for steelmaking to obtain a product with a lower residual content and improved properties [3,5].

High purity sponge iron powder is currently manufactured from high purity iron ore following the basic steps of magnetic separation and milling, primary reduction process, hydrogen annealing, and final milling and classification.

2. Materials and methods

The rolling mill scale used in this work was provided by an electric steelshop in northern Spain [6]. The mineralogical composition was determined by X-ray diffraction (XRD) using a Philips X'Pert diffractometer with a Cu anode (Cu K_{α} radiation) and a Ni filter to remove K_{β} radiation due to the sample's Fe content.

Coke was used to reduce the mill scale. The mill scale with coke was firstly subjected to conventional mixing in a turbula for 30 minutes, followed by high energy mechanical milling in a Pulverisette 6 planetary mill with a ball to load weight ratio of 10:1 at a speed of 400 rpm, in all cases using an Ar atmosphere, in 2 hour cycles of 1 hour milling and 1 hour rest. The mill scale ($d(0.5) = 45 \mu\text{m}$, after of milling) then underwent thermal treatment in an air atmosphere, in covered porcelain crucibles, in a CHESA brand muffle furnace using a mill scale/coke ratio of 100/50 at various temperatures in the 1050° to 1150°C range and for different reaction times (3, 6 and 12 hours). Calcium oxide (reagent grade) was used as fluxing agent. The final treatment of the samples was performed in an oven with a H_2 atmosphere belonging to the company Högånäs AB, at 900°C for 0.5 hours with 1 hour of subsequent cooling in hydrogen.

Morphological analysis of the mill scale samples was performed by scanning electron microscopy (SEM) using a Philips XL30 microscope equipped with back-scattered and secondary electron detectors and an EDAX brand "EDS" detector. The samples were prepared by depositing the mill scale on an adhesive tape and subsequently sputtered them with graphite.

Analysis of the samples for oxygen was performed by combustion with oxygen in a LECO model TC-436 induction oven, with subsequent detection by infra-red absorption.

The particle size distributions of the mill scale after of milling and the resulting sponge iron powder were carried out with a MALVERN Instruments Mastersizer 2000 analyzer.

3. Results and discussion

3.1. Characterisation of rolling mill scale

Mill scale is comprised mainly of metallic iron and a mixture of the iron oxides wustite (FeO), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite ($\text{FeO} - \text{Fe}_2\text{O}_3$) (Figure 1a).

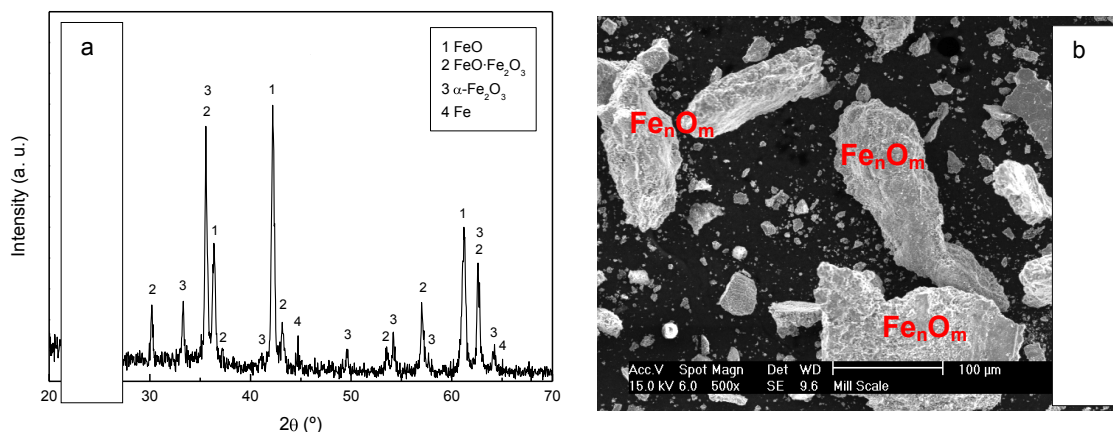


Figure 1. (a) X-ray diffraction patterns of the mill scale (500x), (b) Secondary electron image of the mill scale.

The analysis of the oxidation states of iron contained in the mill scale is: 48.70 % (Fe^{2+}), 12.41 % (Fe^{3+}) and 7.09 % (Fe) [6].

The morphology of the mill scale (70.7 % of the accumulated weight presents a particle size of $\geq 0.125 \text{ mm}$) [6] is preferentially lamellar with a heterogeneous surface formed basically by a matrix of iron oxides (Figure 1b).

3.2. Mill scale reduction tests

3.2.1. Reduction tests with coke

Reduction of the iron oxides was achieved with coke by means of the “direct reduction” process [3] according to equation (1):



Milled mill scale reduction experiments were carried out using a mill scale/coke ratio of 100/50, treatment temperatures of 1050°, 1100° and 1150°C, and three different reaction times (3, 6 and 12 hours). Figure 2 shows X-ray diffraction spectra for the mill scale reduced with coke at 1100°C for various reaction times.

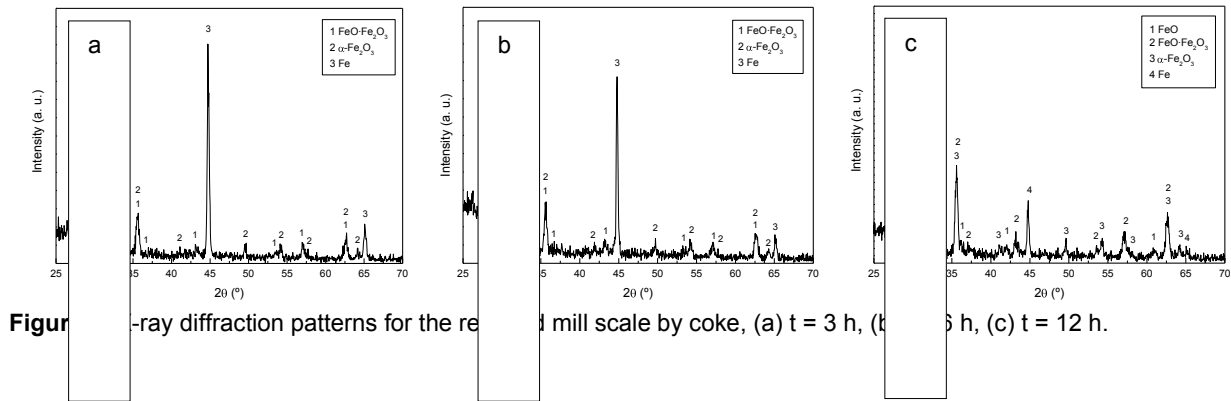


Figure 2. X-ray diffraction patterns for the reduced mill scale by coke, (a) t = 3 h, (b) t = 6 h, (c) t = 12 h.

As can be seen, in the reductions carried out for 3 and 6 hours (a and b) the diffraction maxima corresponding to wustite (FeO) disappear (according to equation 1), compared to the as-received mill scale composition (Figure 1a). The diffraction peaks corresponding to metallic iron (Fe) increase with thermal treatments. Therefore, the reduction of mill scale to sponge iron is favoured in the two treatments carried out for a shorter time in covered crucibles.

Figure 3, shows images of the rolling mill scale after thermal treatments at 1100°C and corresponding “EDS” analyses. These analyses confirm the existence of metallic iron in most zones of the mill scale samples reduced for 3 (and 6 hours) and the existence of areas with mainly oxygen and iron in the sample reduced for 12 hours (b).

XRD results for the reduction of mill scale with coke at 1050° and 1150°C for reaction times of 3 (a and c) and 12 (b and d) hours are shown in Figure 4. As can be seen, the diffraction maxima for metallic iron (Fe) increase with all four thermal treatments while the maxima for wustite (FeO) disappear (according to equation (1)) in the two treatments performed at 1050°C, compared to the as-received mill scale composition. In the treatments carried out at 1150°C wustite continues to be present after 12 hours. Therefore it may be observed that the reaction time does not generally have any influence in the mill scale reduction process at 1050°C, but is influential in the treatments performed at higher temperatures (1150° and 1100°C) (Figures 4 and 2, respectively), since in these processes small diffraction maxima appear for wustite after 12 hours, indicating that the mill scale may undergo a reoxidation process after long reaction times.

Table 1 shows the oxygen content of the mill scale samples as-received and after the reduction process with coke. It can be seen that the most favoured reduction process, with the lowest oxygen content after the thermal treatments with coke, is that performed at 1100°C. Of the three treatments carried out at this temperature, the most favoured is that performed for a reaction time of 6 hours, with a final oxygen content of 6.47 %.

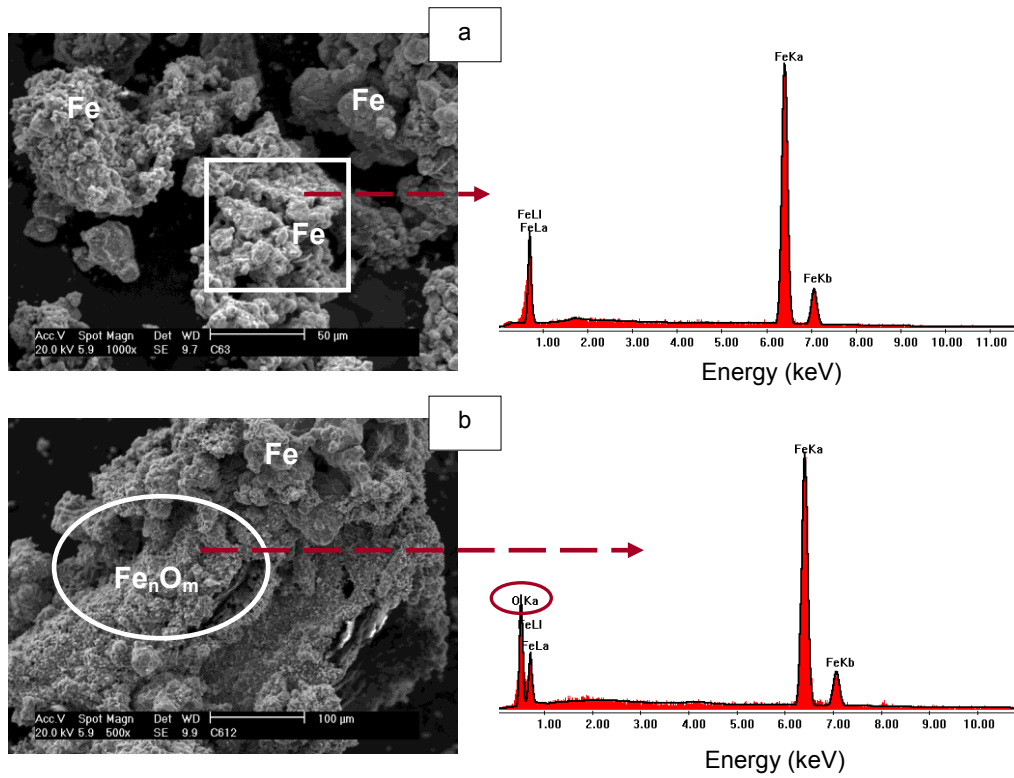


Figure 3. Secondary electron images of the reduced mill scale and “EDS” analysis, (a) $t = 3$ h, (b) $t = 12$ h.

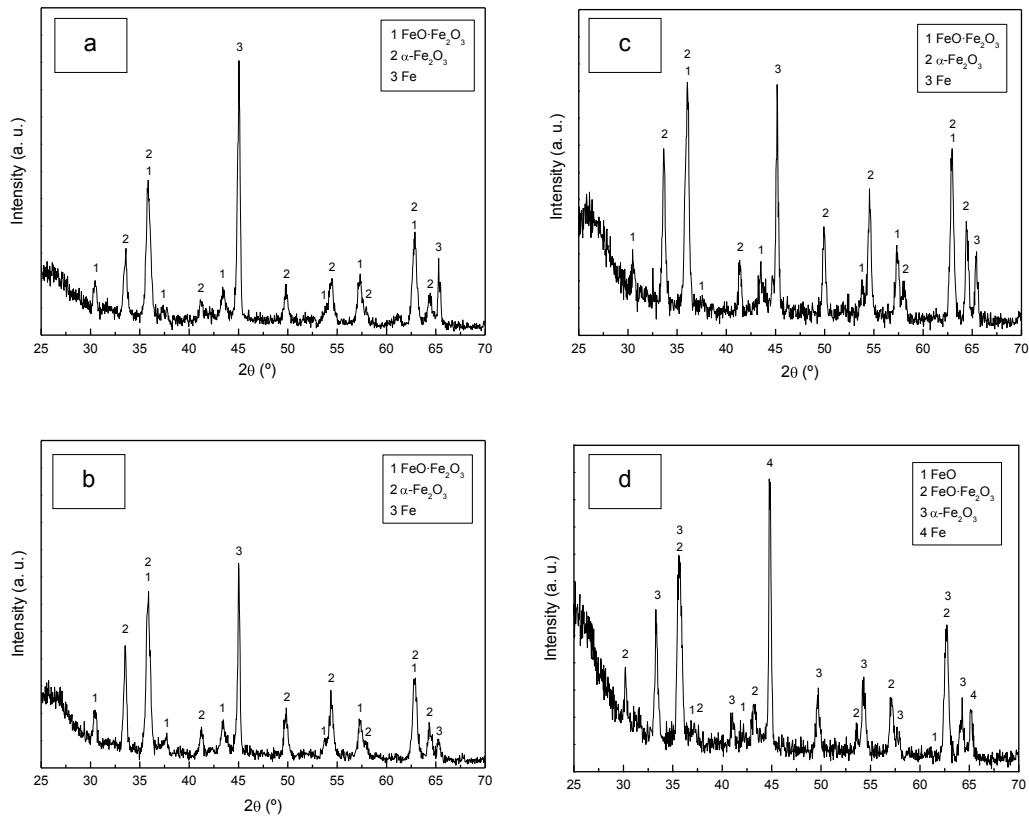


Figure 4. Secondary X-ray diffraction patterns for the reduced mill scale, (a), (b) $T^a = 1050^\circ\text{C}$; (c), (d) $T^a = 1150^\circ\text{C}$.

Reduction treatment (Temperature / time)	% O (w/w)
Rolling mill scale	20.85
1050°C / 3 h	12.08
1050°C / 6 h	10.20
1050°C / 12 h	13.91
1100°C / 3 h	8.53
1100°C / 6 h	6.47
1100°C / 12 h	10.17
1150°C / 3 h	14.90
1150°C / 6 h	12.90
1150°C / 12 h	15.45

Table 1. Oxygen content.

3.2.2. Final treatment in hydrogen atmosphere furnace

The final treatment of the samples was carried out in a hydrogen atmosphere furnace at 900°C for 0.5 hours, followed by 1 hour of cooling in hydrogen. Figure 5a shows the X-ray diffraction spectrum of the mill scale treated at 1100°C for 6 hours after thermal treatment in the H₂ atmosphere furnace. Only diffraction maxima corresponding to metallic iron are observed, which confirms that in this case the reduction of the mill scale to sponge iron powder has been completed. The figure 5b shows a powder with a spongy appearance, irregular but rounded, with a high specific surface area that makes it highly suitable for powder metallurgy applications. The oxygen content in these samples was 0 %.

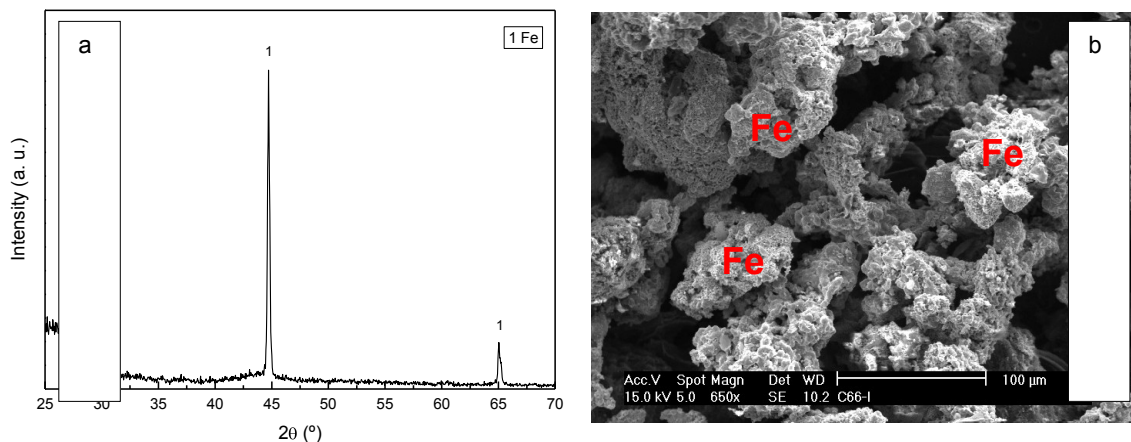


Figure 5. X-ray diffraction patterns (a) and secondary electron image of the reduced mill scale (b).

The sponge iron powder particle size distribution is illustrated in Figure 6, showing an average particle size of 157 μm. The obtained sponge iron can be used for produce powder metallurgy parts by pressing and sintering because it size distribution can assure a good flow behaviour.

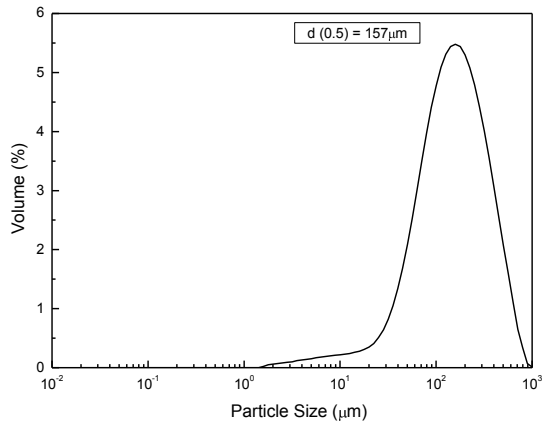


Figure 6. Particle size distribution of obtained sponge iron.

The mill scale reduced at a temperature of 1100°C for a reaction time of 3 hours has been treated identically, yielding similar test results.

Conclusions

Sponge iron powder has been obtained by reducing rolling mill scale with coke via thermal treatment in an air atmosphere furnace and subsequent final treatment in a H₂ atmosphere furnace.

The most effective thermal treatments in the air atmosphere furnace have been those performed at 1100°C for reaction times of 3 and 6 hours, which yielded the lowest oxygen contents in the treated samples.

The proposed process allows the obtainment of a sponge iron powder of an irregular morphology with an average particle size of 157 µm and great purity, making use of a cheap by-product of the steelmaking industry which is currently largely disposed of in landfills.

The iron powder obtained may be used in conventional steelmaking processes or as a raw material in powder metallurgy processes.

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References

- [1] International Iron and Steel Institute, The Management of Steel Industry By-products and Waste, Committee on Environmental Affairs, Brussels, 1987, chapter 6.
- [2] International Iron and Steel Institute, The Management of Steel Plant Ferruginous By-Products, Committee on Environmental Affairs and Committee on Technology, Brussels, 1994, chapters 6, 7.
- [3] L. Camci, S. Aydin, C. Arslan, Reduction of iron oxides in solid wastes generated by steelworks, Turkish J. Eng. Env. Sci., 26 (2002) 37-44.
- [4] European Commission, Reference Document on Best Available Techniques in the Ferrous Metals Processing Industries, IPPC Directive European Commission, Institute for Prospective Technological Studies, Directorate-General Joint Research Centre, Seville, Spain (2001) 161-162.
- [5] J.-W. Park, J.-C. Ahn, H. Song, K. Park, H. Shin, J.-S. Ahn, Reduction characteristics of oily hot rolling mill sludge by direct reduced iron method, Resour. Conserv. Recy. 34(2) (2002) 129-140.
- [6] M.I. Martín. 2004. Tesis Doctoral. Universidad Complutense de Madrid, Madrid, España.