Abstract

Rolling mill scale is a solid by-product of the steelmaking industry that contains metallic iron, 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 using coke at 1100 ºC and different times. 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.

Keywords: Rolling Mill Scale, Reduction, Sponge Iron Powder, Coke

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: FeO, α-Fe₂O₃ and 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 (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 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. Depending on the process and the nature of the product, the weight of mill scale can vary between 20 and 50 kg/t of hot rolled product. The average specific production of this by-product is 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 [1,3], while 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 [4,5].

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 [4,6].

Industrially, iron ore is placed with coal and lime in rotary furnaces at a rate that is controlled by the rotation speed. The interior of the furnace is coated with a refractory material. Carbon dioxide, produced by the effect of combustion, promotes the reduction of the iron ore. In order to control the temperature, fans are situated throughout the oven to provide the air necessary for combustion of the coal. The sponge iron obtained subsequently passes into a rotary cooler where it is cooled with water [7-9].

EXPERIMENTAL

The rolling mill scale used in this work was provided by an electric steelshop in northern Spain [10]. The
mineralogical composition was determined by X-ray diffraction (XRD) using a Philips X’Pert diffractometer with a Cu anode (Cu Kα radiation) and a Ni filter to remove Kβ 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 min, 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 hours cycles of 1 h milling and 1 hour rest. The balls used were 10 mm diameter stainless steel. The mill scale 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 1100 ºC and for different reaction times (3, 6 and 12 hours). Calcium oxide was used as fluxing agent.

The final treatment of the samples was performed in an oven with a H2 atmosphere belonging to the company Höganäs AB, at 900 ºC for 0.5 hours with 1 hour of subsequent cooling in H2.

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 O was performed by combustion with oxygen in a LECO model TC-436 induction oven, with subsequent detection by infra-red absorption.

The particle size distribution of the resulting sponge iron powder was carried out with a MALVERN Instruments Mastersizer.

RESULTS AND DISCUSSION
A. Characterisation of rolling mill scale

Mill scale is comprised mainly of metallic iron and a mixture of the iron oxides wustite (FeO), hematite (α-Fe2O3) and magnetite (FeO - Fe2O3) (Figure 1a). The analysis of the oxidation states of iron contained in the mill scale is: 48.70 % (Fe2+), 12.41 % (Fe3+) and 7.09 % (Fe) [10]. The morphology of the mill scale (70.7 % of the accumulated weight presents a particle size of ≥ 0.125 mm) [10] is preferentially lamellar with a heterogeneous surface formed basically by a matrix of iron oxides (Figure 1b).

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

B. Mill scale reduction tests
B.1. Reduction tests with coke

Reduction of the iron oxides was achieved with coke by means of the “direct reduction” process [4] according to equation (1):

\[ \text{Fe}_n\text{O}_m + m\text{C} \rightarrow n\text{Fe} + m\text{CO} \]  (1)

As can be seen in Figure 2(a), in the reductions carried out for 6 hours the diffraction maxima corresponding to wustite (FeO) disappear (according to equation (1)). 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 (3 and 6 hours).

![Figure 2. X-ray diffraction patterns for the reduced mill scale by coke. (a) t = 6 hours, (b) t = 12 hours.](image)

Figure 3 shows image of the mill scale after the thermal treatment (6 hours). The “EDS” analyses confirm the existence of Fe in most zones of the mill scale samples reduced for 3 and 6 hours and the existence of areas with mainly O and Fe in the sample reduced for 12 hours.
Of the three treatments carried out the most favoured is that performed for a reaction time of 6 hours, with a final O content of 6.47 % (Table 1).

Figure 3. Secondary electron image of the reduced mill scale and "EDS" analysis (t = 6 hours).

**B.2. Final treatment in hydrogen atmosphere furnace**

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 (Figure 4(a)).

Table 1. Oxygen content

<table>
<thead>
<tr>
<th>Reduction treatment (T/t)</th>
<th>% O (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rolling mill scale</td>
<td>20.85</td>
</tr>
<tr>
<td>1100 °C / 3 h</td>
<td>8.53</td>
</tr>
<tr>
<td>1100 °C / 6 h</td>
<td>6.47</td>
</tr>
<tr>
<td>1100 °C / 12 h</td>
<td>10.17</td>
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</tbody>
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Figure 4(b) 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 %. The sponge iron powder particle size distribution is illustrated in Figure 5, 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.

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

Figure 4. X-ray diffraction patterns for the reduced mill scale (a) and secondary electron image of the reduced mill scale (b), after of treatment in H₂ furnace. t = 6 hours.

Figure 5. Particle size distribution of obtained sponge iron.

**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.

**REFERENCES**


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