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RESEARCH ARTICLE

Preparation and Characterization of Mill Scale Industrial Waste Reduced by Biomass-Based Carbon

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Abstract
Utilizing locally based and renewable biomass resources are challenging. This work aims to understand the role of the utilization of solid byproduct of Indonesian mill scale, formed during the cold rolling process, and abundant local resources of coconut coir wastes. Mill scale has a fairly high total iron content with the dominant phase being hematite, while pure Fe content is insignificant. In this study, we utilized coconut coir-based carbon (CCC) for direct reduction of mill scale via a carbothermic process to enhance its metallic Fe content. The reduction was carried out by mixing mill scale/CCC at 6:1 wt% ratio in high energy milling for 2 min. The mixture was pressed (100 MPa for 1 min) into pellets and sintered at 900 °C for 1 h and 1000 °C for 1 and 2 h under inert gas atmosphere. After cooling, the sintered pellets were crushed into powder and separated from impurities by magnetic separation. The results show that the reduction process is dominated by carbon gasification–diffusion from CCC. The improved metallization and better reducing process was more pronounced at 1000 °C for 2 h than that for 1 h with over 80 wt% being separated into metallic Fe and lesser CO_2 trapped within the sample. X-ray diffractometry revealed that the intimate contact of mill scale/CCC was more increased in solid than that in powder state and indicated that the obtained phases are Fe, Fe_3O_4, and CO_2. The presence of CO_2 can be expected due to incomplete evacuation within the sample. These results suggest that mill scale/CCC has some promising potential on certain technical-industrial-scale applications, which might enhance their economic value after further research investigation and evaluation.

Keywords Industrial waste · Mill scale · Coconut coir-based carbon · Direct reduction · Carbothermic

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Introduction

Optimizing the use of available local-based resources and utilizing the waste materials are necessary in today's world. The management of waste generated by hot metal and steel has become an important issue due to ever-stringent environment regulations. Furthermore, the depletion of iron ores necessitates extensive research work to reuse the secondary raw materials produced as a solid byproduct in the steelmaking industry and considered as waste materials. In Indonesia, there are a large number of steelmaking companies producing tons of mill scale every day. For instance, the hot rolling mills are producing more than 800 thousand tons per year [1]. Meanwhile, coconut coir (coconut fiber) wastes are produced every day in Indonesia. Based on the data from Asian and Pacific Coconut Community (APCC), the average production of coconut coir is 31.972 million tons per year [2]. The coconut coir waste is abundantly available in the local area but is not fully utilized. In this study, mill scale

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is reduced by coconut coir-based carbon (CCC), which was previously prepared in our group using a pyrolitic carbonization process [3].

During the hot rolling of steel, iron oxides form on the surface of the metal as scales. In general, a scale comprises layers of wustite (FeO), magnetite (Fe_3O_4), and hematite (Fe_2O_3). The scale is accumulated as a waste material in all steel companies. In an integrated steel plant, a portion of mill scale, the large size one, was recycled in sintering plants [4]. However, a study on recycling mill scale of steel in the sintering process showed that the sinter productivity decreased with the increase in mill scale addition due to decreased permeability of the sinter bed. In recent years, steelmakers used this mill scale as an oxidizer in a conventional electric arc furnace steelmaking process [5]. However, the modern electric arc furnaces are equipped with an oxygen lancing system to enhance melting and oxidation processes with higher efficiency than the mill scale practice [6]. A small portion of mill scale has been used by cement plants. However, the mill scale does not uniformly blend with the other feedstock materials due to its higher density than any of the blending components and thus causes a greater variation in the blend of the kiln feed [7].

At the same time, the amount of mill scale used by cement plants, as a raw material in the manufacturing of clinker, is still small. A study on laboratory scale was made to use mill scale waste to prepare iron powder. Benchiheub et al. [8] used CO followed by H_2 as a reducing agent. When the reduction was carried out by CO, the maximum iron content (98.40 wt% Fe) in the iron powder was obtained at 1050 °C after 180 min. A reduction annealing under hydrogen makes it possible to decrease carbon and oxygen contents of the reduced iron powder within acceptable values (0.23 and 0.28 wt%, respectively). Another recent study [9] reports the reduction of mill scale to sponge iron using coke at different temperatures and process times. Sponge iron was successfully produced for reuse in electric furnaces as part of the metallic charge or as a raw material in the production of iron-based powder metallurgy parts. Unfortunately, no technology has been implemented to recover and use such materials [10]. In some steel manufacturing companies, the bulk of mill scale waste was dumped in landfills, and this resulted in heavy metals leaching into soil and groundwater, thus posing a threat to the environment.

The continuous production of landfills and their adverse effect on the environment highlight the need for more effective methods of productive utilization of mill scale. In general, the reduction of iron oxide or various ores containing iron oxides has been investigated in the past [11–18]. To the best of our knowledge, studies in this area are mainly conducted using a reducing agent based on gas (mostly H_2 and CO) and some of them by solid carbon (usually based on coal and graphite). In this work, the mill scale was recycled into valuable products, for instance, iron powder, using solid carbon from coconut coir as a reductant via direct reduction of carbothermic process. The use of CCC as reducing agent makes it possible to decrease the oxygen content of mill scale within acceptable values of the product. This is important to improve upon the existing mill scale (iron oxide) reduction technology for energy saving compared to the conventional carbon source and develop new technology using coconut coir-based carbon as a renewable carbon source.

Methods

In this study, the chemical composition of mill scale as raw material includes Fe_2O_3: 93.339 wt%, MgO: 0.182 wt%, Al_2O_3: 3.093 wt%, SiO_2: 0.982 wt%, CaO: 0.123 wt%, TiO_2: 0.018 wt%, MnO: 0.345 wt%, P_2O_5: 0.024 wt%, NiO: 0.206 wt%, Cr_2O_3: 0.043 wt%, SO_3: 1.153 wt%, and WO_3: 0.492 wt%, which was analyzed by X-ray fluorescence (XRF, VF-320 A, Shimadzu). Figure 1 shows the micrograph of the as-received CCC and mill scale examined by scanning electron microscopy (SEM), which were used in this study as the main raw materials. Mill scale size was first reduced by means of ring mill process down to 150 mesh. The fraction of raw materials (mill scale and carbon) used in this study was calculated based on Gibbs free energy method leading to the optimal formation of Fe metal. From the calculation, the mixing ratio of mill scale to carbon (CCC) is found as 6:1 (in wt%). Thus, the blend was mixed using a shaker mill for 2 min. As for the second approach, to prepare the pellet, the milled powders were added to 3 wt% of polyfinilidene fluoride (PVDF) to agglutinate the mixture, and then compressed at a load of 100 MPa at room temperature to form the mold with a diameter of 20 mm. The CCC composite cylindrical pellets were loaded into a horizontal resistance furnace under a flow of UHP N_2 gas (99.9999 vol%) at 200 sccm and reduced at target temperatures of 900 °C for 1 h, and of 1000 °C for 1 and 2 h. The reduced samples were then ground in a mortar and pestle to make a fine powder. The resulting powder was separated from the impurities by magnetic separation method. The phase and composition analyses were carried out using X-ray diffraction (XRD Smartlab, Rigaku) equipped with Cu anode X-ray tube and 2θ from 10° to 90° using a 0.01° step size and 0.25 s count time. Micrograph analysis was performed using scanning electron microscopy (SEM, SU3500 Hitachi) equipped with energy dispersive X-ray spectroscopy (EDX, EMAX Evolution X-Max, Horiba).

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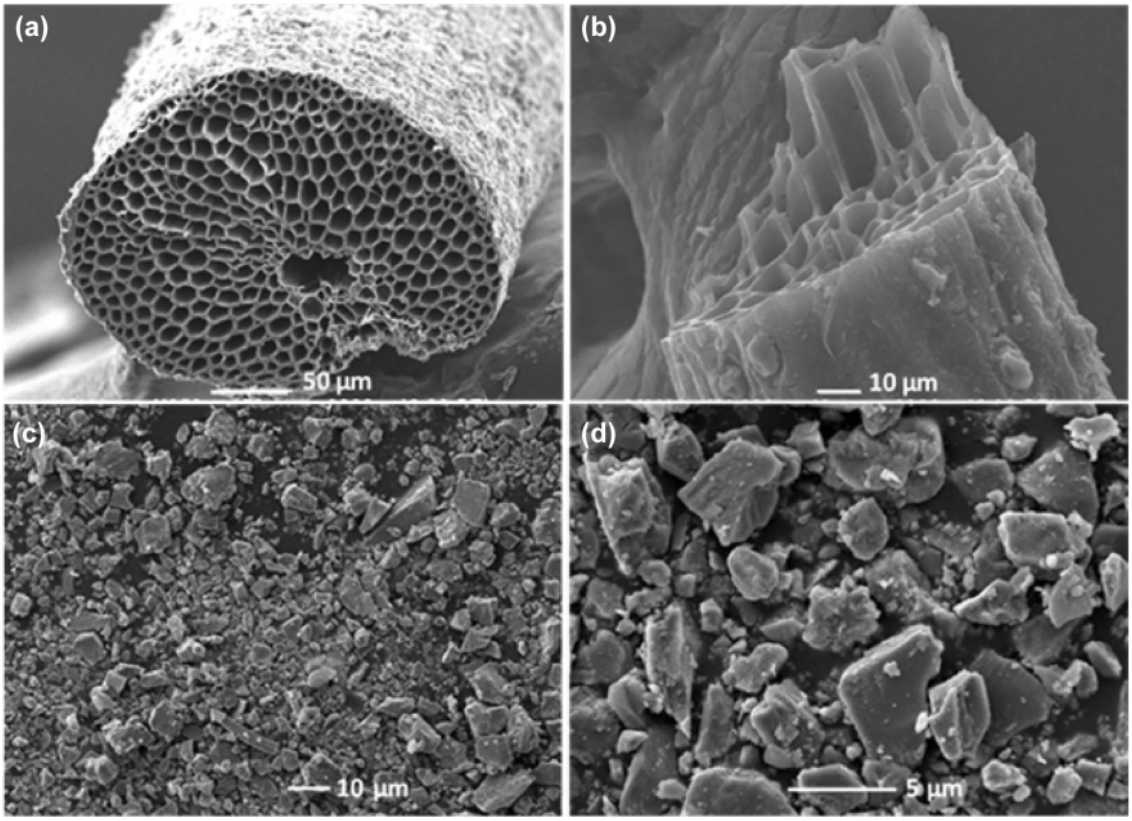

Fig. 1 SEM micrograph of raw material used in this experiment: **a**, **b** CCC and **c**, **d** mill scale

Results and Discussion

Mill Scale Phase Identification

XRD and Rietveld analyses were performed to study the existing phase which depends on the composition of the sample before and after the reduction process. Figure 2 shows the XRD peaks' profile of mill scale sample in the powder state (with the size down to 150 mesh) before reduction process. It can be seen that the dominant phases are FeO (wustite) and Fe_3O_4 (magnetite), while, the amount of Fe metallic is insignificant. Under this condition, the Fe phase is still dominantly of the oxide-based phase, typical of mill scale, as also previously confirmed by XRF analysis.

When the reduction of the iron oxides is carried out by any carbon sources (solid carbon or gas), in this case, with CCC by means of direct reduction process, the final process of reduction can then be expressed as follows:

$$Fe_nO_m + mC_{(s,g)} \rightarrow nFe + mCO_{(g)} \quad (1)$$

or

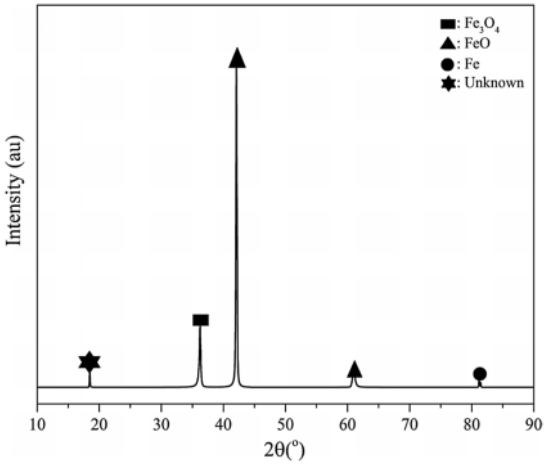

Fig. 2 XRD patterns of cold rolling mill scale (sieved under 150 mesh)

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$$2Fe_nO_m + mC_{(s,g)} \rightarrow 2nFe + mCO_{2(g)} \quad (2)$$

As an example, we consider hematite (Fe_2O_3) phase (its existence is confirmed by XRF); thus from Eq. 2, the direct reduction of the hematite can take place according to the following reaction:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2 \quad \text{with } \Delta G = 104{,}840 - T^{*}122.68 \text{ cal/mol } O_2 \quad (3)$$

In order to confirm whether the reaction is possible, the obtained Gibbs free energy should have negative in values (more spontaneous reaction). From Eq. 3, the minimum required temperature for direct reduction of hematite/carbon to take place should be 1173 K or 900 °C. In reality, the mill scale contained other iron oxide phases. However, we consider here only the hematite (Fe_2O_3) based on the assumption that the reaction takes place homogenously in all cases of iron oxide presence in mill scale and to simplify the analysis.

Reduction Analyses at Solid and Powder States

Mill scale reduction experiments were then carried out using a mill scale/CCC ratio of 6:1 (this value is obtained from the molar ratio calculations according to Eq. 3), treated at temperatures of 900 and 1000 °C with two different dwell times of 1 and 2 h. Figure 3 shows the XRD spectra of the reduced mill scale using CCC as a reducing agent at 900 °C for 1 h in nitrogen atmosphere for two different states of treated samples, i.e., solid (pellet) and powder states. The original (before reduction) mill scale powder is also included in Fig. 3 for comparison purposes of the phase evolution.

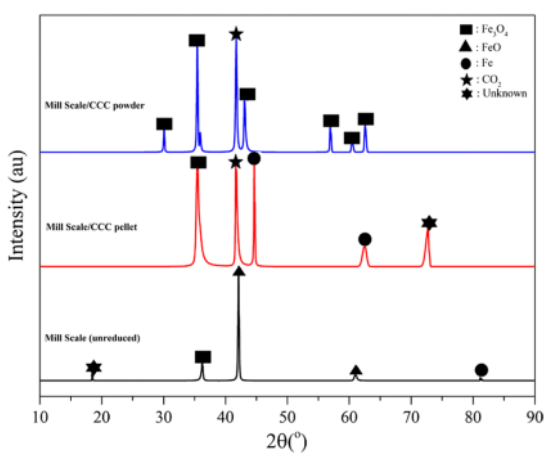

Fig. 3 XRD patterns of the samples reduced at 900 °C for 1 h in N_2, in powder and solid states (Color figure online)

Experiments were performed for pellet samples which were compressed at a load of 100 MPa with the addition of PVDF binder of 3 wt%. For reduction under solid-state condition, the metallic iron (Fe) phase peaks are observed clearly. Meanwhile, in the powder state, there is no peak detected for the metallic Fe phase. It is clear that the different states of the sample (solid and powder) affect the effectiveness of the reduction process. This may be due to the fact that the compaction (pelleting) contributes to realizing much better contact interface and that consequently the van der Waals forces of the mill scale/CCC increased [1]. Therefore, the contact interface (local reaction) as well as their atomic bonding interaction of pelletized mill scale/CCC leads to better progressive reduction process than the one realized in the case of their mixture in powder state.

It is seen in Fig. 3 that the plot for the powder state shows the diffraction maxima mainly shifted to the phase corresponding to magnetite (Fe_3O_4). The presence of magnetite (Fe_3O_4) is more dominantly detected in powder than in solid state. This can be explained as follows: in the reduction process of mill scale by CCC in powder state, the interfacial CCC–mill scale powder is not as good as that of CCC–mill scale pellet. Therefore, the disintegration (local reaction) of iron oxide does not occur completely in the powder state as the one observed in the solid-state substrate.

Another series of phases present are both in powder and pellet states. Furthermore, the X-ray peak corresponding to wustite (FeO) disappears (according to the reaction FeO + C → Fe + CO) in the reduced mill scale composition. This can be explained using the Fe–O phase diagram [19], shown in Fig. 4. FeO undergoes eutectoid transformation and turns into Fe_3O_4 at or less than 560 °C during the cooling process.

Further, the XRD shows that the CO_2 phase is still detected during reductions of samples under both solid and powder conditions. This can be explained as follows: CO_2 is not entirely evacuated due to its being trapped within the sample in the reduction at 900 °C. In this case, the nature of interaction of mill scale/carbon during the reduction process causes many micro/nano 'pockets' within the material, which trap CO_2. The reduction mechanism is illustrated in Fig. 5. The XRD spectrum shows that the CO_2 peaks occurred more often for the samples in the solid state than for those in the powder state since the interatomic bonding is probably better in the solid state than that in the powder state. Based on this fact, it is possible that, under 900 °C operating conditions, mill scale/carbon composite does not undergo reduction completely. Thus, further thermodynamics and heat-transfer control (for instance, higher operating temperature, longer residence time, or faster cooling rate) are highly recommended in order to obtain the optimal reduction of mill scale/carbon as well as to evacuate CO_2 completely.

The three-step sequence of reduction of iron oxides by carbon can be expressed as follows: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow$

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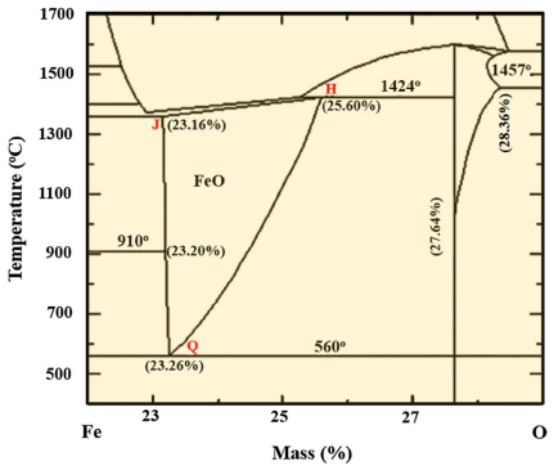

Fig. 4 Fe–O phase diagram [19] (Color figure online)

FeO → Fe. These three steps are in accordance with the Gaussner–Bouduard diagram [20], as shown in Fig. 6 (and also illustrated in a different manner after being modified, in Fig. 5). This diagram is referred to as a basic for the direct reduction based on carbon. The reduction kinematics in a direct reduction furnace is normally (first) controlled by the reduction of gas diffusion that originates from the carbon. In this proposed process, the reduction reaction occurs inside the carbon composite pellet made up of mill scale and CCC (as illustrated in Fig. 5) by means of carbon gasification. Once the composite pellets are heated, carbon (as CO) inside them, promotes the reduction of iron oxide. Thus, the reduction reaction proceeds faster in the carbon composite pellets than the reduction reaction happening in the powder. The coupling basic reduction reactions (inset in Fig. 5) are considered to be occurring during the processes.

In general, direct reduction is the reaction that takes place below the melting point of iron (≪ 500 °C, avoiding the liquid phase reaction). Under this condition, there is hardly any direct reaction with the solid carbon of CCC, and hence the reaction as given in Eq. 1 dominates the reaction kinematics. Therefore, the sequence reaction that promotes the reduction of hematite (Fe_2O_3) into magnetite (Fe_3O_4) is dominant, as observed in previous XRD results shown in Fig. 3. This occurs mainly for reductions under powder-state condition.

From Gaussner–Bouduard diagram (Fig. 6), it is observed that for the reaction (carbon gasification) of CO (dash line with red color) to take place at 100% CO a temperature of 1000 °C or more is required. When the temperature is decreased, such equilibrium does not occur, and thus, CO is dissociated into CO_2 and C. This means that the amount of CO gas (reductant) is less. The Bouduard reaction is an endothermic reaction; therefore, it requires high temperature for the reaction to take place. This also explained the high X-ray peaks of CO_2 that appear during reduction at a temperature of 900 °C (Fig. 3), both in powder and pellet states. Hence, for promoting the reaction, it is essential to supply the heat required for the reaction to take place inside of the carbon composite, specifically for pellet sample, at the elevated temperature of 1000 °C or higher.

Figure 7 shows the XRD results for the reduction of mill scale/CCC composite pellet at 1000 °C for 1 h, and the reduced sample at 900 °C is shown alongside for the comparison purpose. As seen from the peaks of reductions at 1000 °C, the numbers of magnetite (Fe_3O_4) and CO_2 peaks become less compared to those at 900 °C. The diffraction

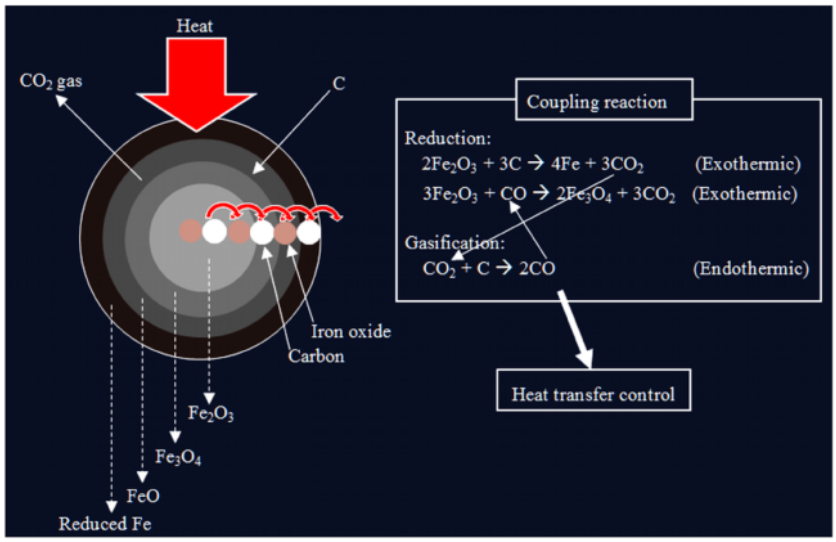

Fig. 5 Schematic direct reduction mechanism of carbon composite pellet (Color figure online)

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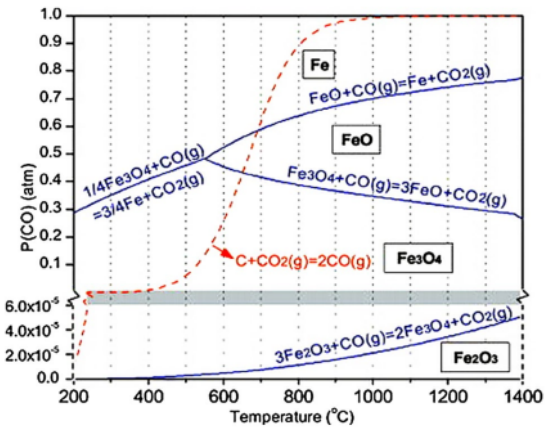

Fig. 6 Gaussner–Bouduard diagram [20] (Color figure online)

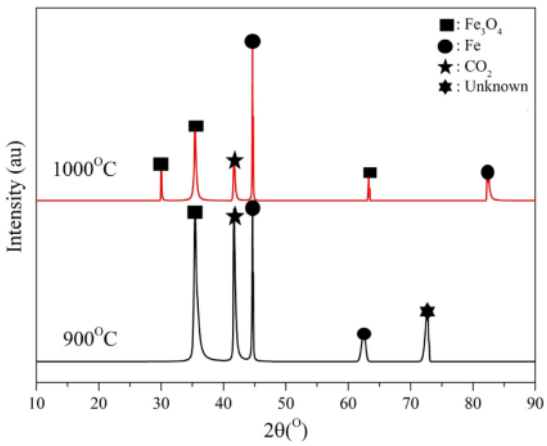

Fig. 7 XRD patterns of the reduced samples at 900 and 1000 °C for 1 h in N_2 for pellet (Color figure online)

maxima corresponding to the dominant metallic Fe phase are observed, which confirms that, in this case, the reaction of the generation of CO by the loss of carbon solution as per Equation (CO_2 and C → 2CO) and the reduction of iron oxide by CO as per Eq. ($3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + 3CO_2$) take place in series inside the carbon composite pellets, which are schematically shown in Fig. 6. This reducing atmosphere promotes formation of more metallic Fe (as well as magnetite). In the above reactions, the CO gas generation controls the reaction kinematics with its highly endothermic nature. This also explains why the CO_2 peak at 1000 °C is smaller: higher heat is transferred efficiently to evacuate more CO_2 from such trapping ('pockets') within the sample.

Figure 8 shows the XRD patterns for different residence times (reduction reaction) of mill scale with CCC composite pellet reduced at 1000 °C. The diffraction pattern of the reduced samples over 2 h shows similar results as the one for 1 h: except that the presence of metallic iron (Fe) is more pronounced than that for 1-h residence time. From the XRD pattern for 2 h, the X-ray peaks of magnetite (Fe_3O_4) and CO_2 are found to decrease more than those at 1 h. The metallization achieved for 2 h process is more than 80 wt%. This means that longer residence time promotes more effective evacuation of the CO_2 from trapping ('pockets') within the sample and better reducing process into forming metallic iron (Fe). This also means that the generation of carbon monoxide due to the loss of carbon solution taking place in series inside the carbon composite pellets is better in the case of treatment for 2 h. From the residence-time treatment results, it is observed that the reaction time does have influence on the metallization process.

Metallographic Analysis

In this study, we further evaluated the microstructure of the reduced sample at 1000 °C for 1 and 2 h in powder state by the SEM/EDX micrograph analysis, as shown in Fig. 9. From the SEM observation, it is clearly shown that various phases are detected from each grain after reduction. It detected Fe element from each grain, followed by the detection of O element with different percentages. For the reduced sample at 1000 °C for 1 h (Fig. 9a), from point #1, the Fe element is about 60.01%; however, from the same grain (point), the oxygen element is also detected with the percentage of 31.67%. For point #2, the oxygen element (54.77%) is more pronounced compared to Fe (32.85%). For instance, from the atomic comparison at this point (point #2), it is clear that the iron oxide phase is formed with phase

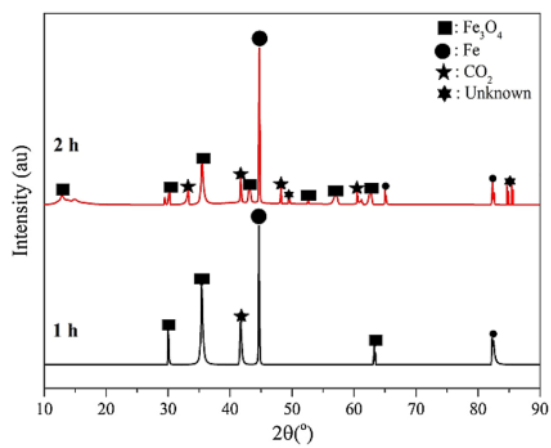

Fig. 8 XRD patterns of reduced sample at 1000 °C for 1 and 2 h in N_2 atmosphere for pellet (Color figure online)

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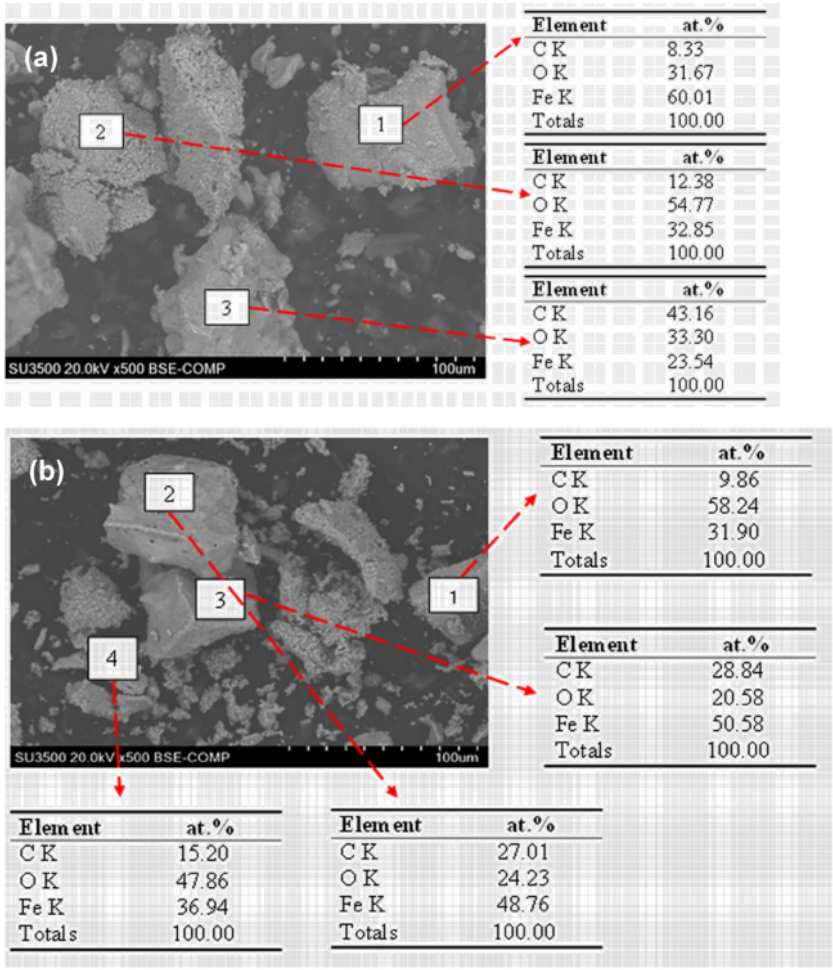

Fig. 9 SEM metallography and EDX point analysis of reduced sample at 1000 °C for **a** 1 h and **b** 2 h, in powder state (Color figure online)

composition of $Fe_{32.85}O_{54.77}$ or in the simplified form close to Fe_3O_4 (magnetite). At point #3, the main formed element is carbon, followed by oxygen and Fe metal. This means that at this grain (point #3), the carbon element is the dominant one. This can be correlated with the previous XRD analysis (Fig. 8) of the reduced sample at 1000 °C for 1 h, which showed quite a high CO_2 peak.

For the reduced sample at 1000 °C for 2 h (Fig. 9b), we observe better and homogenous results compared to those at residence time of 1 h. It shows that, at every point, the carbon is not the dominant phase. For instance, at point #1, the oxygen element (58.24%) is the dominant phase, followed by Fe metal (31.90%). Consequently, at this point, the formed phase is the iron oxide with composition of $Fe_{31.90}O_{58.24}$ or in the simplified form close to that of Fe_3O_4 (magnetite). From points #2 and #3, the compositions of C and O elements are similar, which is probably related with the low CO_2 peaks as shown in the XRD result (Fig. 8) of residence time of 2 h. However, at the same points, the Fe metal is shown to be the highest one. Thus, considering the differences in grain morphology (shape) as well as their composition number, the observed grain is closely related to Fe metal. From point #4, the percentage of oxygen element is shown to be higher than that of Fe; from their compositions at this point, this is determined as $Fe_{36.94}O_{47.86}$ phase, or in the simplified form, it is Fe_3O_4 (magnetite).

Further results of analyses of EDX mapping are shown in Fig. 10. One can see that the intensity of the Fe element (purple color) for the residence time of 2 h is stronger than that for 1 h. Once the mapping is scanned, the C element (red color) is mainly scattered from the carbon tape background (for attaching powder sample). The residence time of 2 h shows brighter red color than that of 1 h; however, it is scattered only on their background (carbon tape). Meanwhile, for residence time of 1 h, the brightness of C element is also detected on their sample (for instance, as

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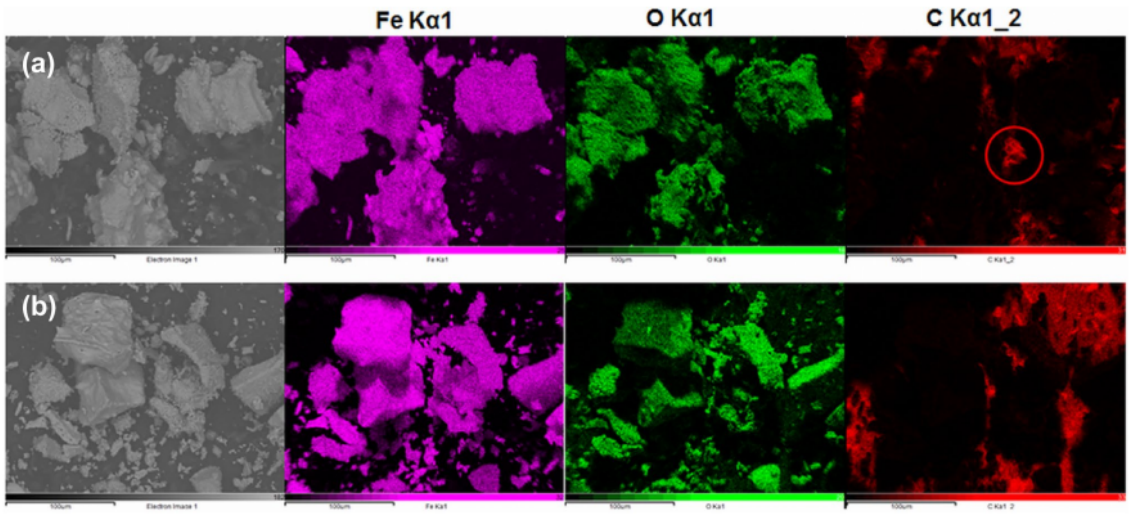

Fig. 10 SEM/EDX mapping analyses of reduced sample at 1000 °C for **a** 1 h and **b** 2 h, in powder state (Color figure online)

denoted by the red circle). This indicates that the carbon content for the residence time of 2 h is far less than that for 1 h, as previously confirmed by their XRD peaks. From these evaluations, indeed, the residence time of 2 h shows much better results (Fe metal phase with lesser amount of C) compared to those for 1 h. This means 2-h residence time promotes better evacuation of the CO_2 from the trapping within the sample and better process of reduction into metallic iron (Fe) than that of 1 h.

The steps of the reduction process, as illustrated in Fig. 5, are as follows: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. However, from the XRD and EDX evaluations, FeO is not detected after reduction. This is due to the fact that FeO undergoes eutectoid transformation (based on Fe–O phase diagram) and forms Fe_3O_4 (at 560 °C or less during the cooling). Meanwhile, from the reduction reaction ($2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$), the CO_2 is generated, and then during the gasification reaction (endothermic), some of CO_2 is reduced into CO ($CO_2 + C \rightarrow 2CO$). The CO gas then converted Fe_2O_3 into Fe_3O_4 (from the reaction: $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + 3CO_2$). Therefore, from this study, the main obtained phase, other than metallic iron (Fe), is Fe_3O_4 (magnetite). At this step, the reduced mill scale indeed can still be considered for many applications, for instance, applications in bipolar plate material of PEMFC [21], soft magnetic toner, and radio antenna material. However, other strategies should be carried out in order to enhance the yield of the metallic iron content (or other specific phase) from mill scale, as well as to achieve their suitable economic value.

Conclusions

In this study, a series of reduction processes of mill scale were successfully developed by using solid carbon CCC as a reductant via direct reduction of a carbothermic process. The influences of reduction temperature and residence time were also investigated. We used powder and solid states for reduction conditions with the mixing ratio of mill scale to carbon (CCC) of 6:1 wt%, which is calculated based on Gibbs free energy. We then calcined them at 900 and 1000 °C for 1 and 2 h under inert gas atmosphere. The crystallographic analysis by XRD, as also confirmed by SEM/EDS analysis, revealed that the obtained phases are Fe (metallic iron), Fe_3O_4 (magnetite), and CO_2 (this phase obtained tentatively due to not being totally evacuated/converted within the sample). Thus, under this condition, the reduction is mainly controlled by gas diffusion. However, the generated CO_2 actually also acts as a reductant; and at a higher reduction temperature of 1000 °C, the coupling reaction occurred where the CO (from gasification of CO_2 and solid solution of C) also acted as another sequence reductant to obtain more Fe_3O_4 (magnetite). Therefore, under this condition, the carbon content in the sample is lesser, specifically at 1000 °C for 2 h, and thus at this stage, the reduction is dominated by carbon gasification. XRD also revealed that the intimate contact of the carbon/mill scale increases more in their metallization result for the solid than that in powder state. From this study, the metallization achieved in solid-state sample at 1000 °C for residence time of 2 h is more than 80 wt%. However, such a solidification condition should be considered more carefully for the sake of further works, for instance, binder-to-powder ratio and their pressures, in order to increase their

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metallization factor as well as CO_2 evacuation. These results suggest that the mill scale combined with coconut coir waste has some potential for technical/industrial applications that might meet their economic value for commercialization after further research investigation and evaluation.

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Author Contributions DSK conceived, directed the project, and analyzed the results. IC prepared and pre-treated the raw material, calcined and sintered sample; carried out XRD and SEM/EDS experiments and data analysis. DSK and FD supervised the preparation of mill scale and CCC material as a proper carbon source. DRI carried out CCC material preparation and mass of balance calculations. DSK, SA and AP supervised the XRD and SEM/EDS characterizations. DSK wrote and edited the manuscript (with the help of IC, SA and AP). All the authors discussed the data and contributed in the manuscript.

Compliance with Ethical Standards

Conflict of interest On behalf of all authors, the corresponding author declare that there is no conflict of interest regarding the publication of this article.

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