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S.M. SHIN*, D.-W. LEE**, J.-Y. YUN***, CH.-Y. KANG****, J.-P. WANG****,♯

A STUDY ON THE FABRICATION OF IRON POWDER FROM FORGING SCALE USING HYDROGEN

PRÓBY WYTWARZANIE PROSZKU ŻELAZA METODĄ REDUKCJI ZGORZELINY POCHODZĄCEJ Z PROCESÓW KUCIA ZA POMOCĄ WODORU

This study was conducted to investigate the effect of hydrogen content, temperature, reaction time for the reduction of forging scale which is mainly composed of hematite (Fe_2O_3). All reductive reactions were performed over the temperature range of 700 to 1200°C as well as 0.1 to 1 atm of hydrogen partial pressures. The results showed that the mechanism for the reduction of iron oxides using hydrogen gas was not a simple process, but proceeded in multiple reduction stages thermodynamically. The iron oxide was almost completely reduced to metallic iron powder with 91 wt.% of iron content in the forging scale at 0.1 atm of hydrogen partial pressure. The content of iron was however found to be increased with increasing hydrogen partial pressure from 0.1 to 1 atm with regardless of temperatures. The metallic iron powder was obtained with the mean size of 100 μm and more porous structure was observed.

Keywords: forging scale, hydrogen partial pressure, hematite, iron powder

1. Introduction

Forging is the process that deforms metal into a predetermined shape using localized compressive forces. As the metal is shaped during operation, deformation is always accomplished using hot, cold, or even warm forging processes. Generally, hot forging process has been recommend for the fabrication of industry components with a high formability ratio, low stress, low work hardening, and increased ductility. On the other hand, hot forging process will also rise to a large amount of loss of the main component due to spalling off of oxide scale when oxidation reaction takes place between the surrounding atmosphere and the metal. The oxide scale taken away from a main body during heat treatment is called as a forging scale. Unfortunately, the forging scale has not been attempted yet to be recycled and reused by many researchers and manufacturer. Therefore, this study was conducted to produce iron powder from forging scale using hydrogen gas.

The reduction of iron ore by hydrogen was widely studied and most of the reaction features were very similar to those of the reduction by carbon monoxide and many mechanisms are common to both of them [1-5]. In this study, a forging scale of industrial waste was employed as a raw material to fabricate metallic iron powder using hydrogen gas. The effect of temperature, reaction time, and hydrogen partial pressure was widely studied to determine the kinetics of iron oxide reduction by hydrogen. The characteristics of final species were examined by scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD).

2. Materials and methods

Forging scales were obtained from a manufacturer of forged metal products in Korea and their chemical composition and phase were examined by X-ray diffraction (XRD) and Energy dispersive X-ray spectroscopy (EDX) shown in Fig. 1. It is noted that the forging scale is composed of three different types of iron oxides, and main peak from XRD result are shown to be hematite (Fe_3O_4). In addition, EDX analysis indicated that iron shows a large portion accounting for about 68%, and 28% for oxygen of the forging scale. The small amounts of impurities were also observed such as silicon, manganese, chromium, aluminum, etc which takes up about 4% out of total amount. Therefore, reduction reaction of iron oxides by hydrogen should be taken into account for three different oxides and other impurities of the forging scale.

A schematic diagram of experimental apparatus for the reduction of iron oxides using a gas mixture of hydrogen and argon gas is shown in Fig. 2. The powder of forging scale was put on the alumina tray that was placed on the center of an alumina reactor. Copper turning furnace was installed in front of ultra high purity (UHP) argon gas to eliminate humidity from the gas. Two flask bottles are located at the end of re-

* MINERAL RESOURCES RESEARCH DIVISION, KOREA INSTITUTE OF GEOSCIENCE & MINERAL RESOURCES (KIGAM), KOREA

** TITANIUM DEPARTMENT, KOREA INSTITUTE OF MATERIALS SCIENCE (KIMS), KOREA

*** POWDER TECHNOLOGY RESEARCH GROUP, KOREA INSTITUTE OF MATERIALS SCIENCE (KIMS), KOREA

**** DEPARTMENT OF METALLURGICAL ENGINEERING, PUKYONG NATIONAL UNIVERSITY (PKNU), KOREA

♯ Corresponding author: jeipil.wang@gmail.com

actor to safely handle wasted gas and finally extra hydrogen gas completely was burned out. The sample tray with forging scale particles was placed in the reactor and UHP argon gas was kept to flow into the reactor until desired temperature was reached. The mixture of hydrogen and argon gas was introduced into the reactor, and then the reactor was cooled down to the room temperature under UHP argon atmosphere at each reaction time.

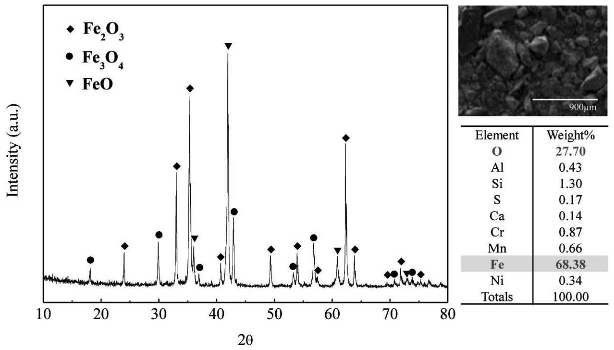

Fig. 1. Chemical composition and phase of forging scale

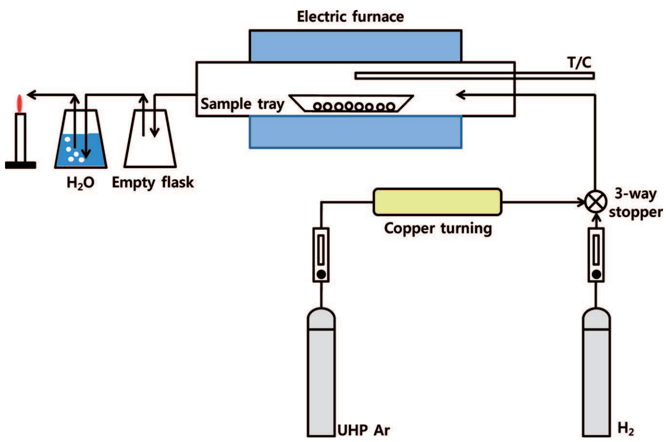

Fig. 2. A schematic diagram of experimental apparatus

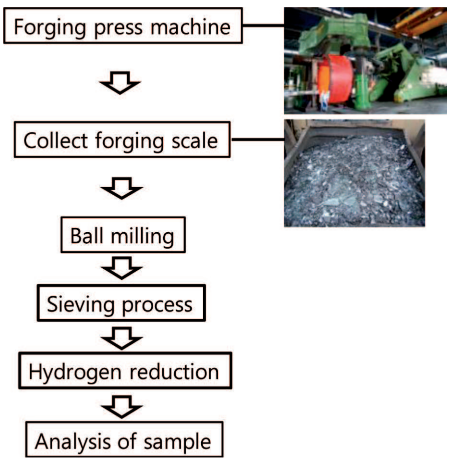

Fig. 3. Process flow of fabrication of iron powder by hydrogen reduction

The overall process to fabricate metallic iron powder from the forging scale is illustrated in Fig. 3. The forging scale was spontaneously taken apart from forged metal products during operation. The scale particles collected were ball-milled for 3 hours with tungsten carbide balls leading to fine size of particles. Consequently, sieving process was conducted to screen rough particles and the mean particle size was found to be around 100 μm which is suitable in powder metallurgical process. The oxide particles were reduced by hydrogen gas on the effect of temperature, reaction time, and hydrogen content. The final species when reduction was completed were examined by XRD, EDX, and SEM to determine whether reduction reaction was successful or not.

3. Results and discussion

The reduction of iron oxides by hydrogen is known as a gas-solid reaction which occurs in various stages depending on the temperature and oxygen content shown in Fig. 4. For the temperature higher than 570°C, hematite (Fe_2O_3) is first transformed into magnetite (Fe_3O_4), then into wüstite ($Fe_{1-y}O$), and finally into metallic iron (Fe). On the other hand, at temperature below 570°C, magnetite is directly transformed into iron, since wüstite is not thermodynamically stable [6].

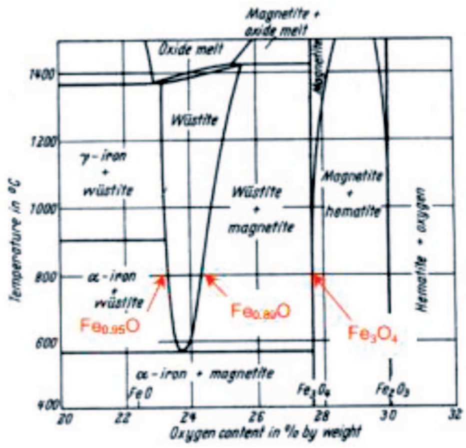

Fig. 4. Stability diagram of the different iron oxides as a function of temperature and oxygen content [7]

Multiple step processes for the reduction of iron oxides by hydrogen were proposed and their data of Gibbs free energy (G) were calculated by thermodynamic program of HSC Chemistry 5.1. As stated below, hematite can be directly reduced to metallic iron, and only water vapor (H_2O) evolved in one-step process. In case of two-step process, hematite can be transformed into magnetite and metallic iron in order, and in three-step process hematite can be reduced to wüstite that is decomposed into magnetite and iron. Consequently, magnetite can be reduced to iron, and water vapor was generated at the same time. In a multiple-step process, hematite can be transformed into magnetite and it is again reduced to wüstite. The wüstite can be decomposed to magnetite once again that means the phase transformation of magnetite into wüstite will be possible to take place in a cycle leading to finally them become metallic iron.

■ [U+25FC] One-step process [$Fe_2O_3 \rightarrow Fe$]

$Fe_2O_3 + 3H_2(g) \rightarrow 2Fe + 3H_2O(g)$ ΔG_{600C} = -1.96kcal

■ [U+25FC] Two-step process [$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$]

$Fe_2O_3 + H_2(g) \rightarrow 2Fe_3O_4 + H_2O(g)$ ΔG_{700C} = - 23.30kcal

$2Fe_3O_4 + H_2(g) \rightarrow 3Fe + 4H_2O(g)$ ΔG_{1100C} = -1.54kcal

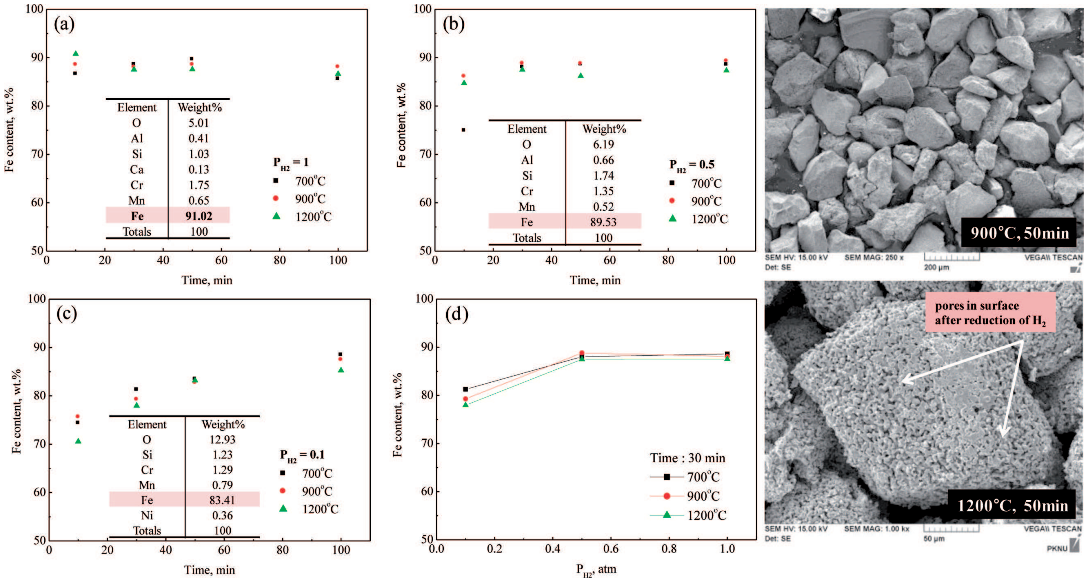

Fig. 5. Fe content in forging scale and particle size of iron powders after reduction of hydrogen gas

■ [U+25FC] Three-step process [$Fe_2O_3 \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow Fe$]

$Fe_2O_3 + H_2(g) \rightarrow 2FeO + H_2O(g)$ $\quad \Delta G_{600C} = -5.62$kcal
$4FeO \rightarrow Fe_3O_4 + Fe$ $\quad \Delta G_{600C} = -0.21$kcal
$2Fe_3O_4 + H_2(g) \rightarrow 3Fe + 4H_2O(g)$ $\quad \Delta G_{1100C} = -1.54$kcal

■ [U+25FC] Multiple-step process [$Fe_2O_3 \rightarrow$ **$Fe_3O_4 \leftrightarrow FeO$** $\rightarrow Fe$]

$Fe_2O_3 + H_2(g) \rightarrow 2Fe_3O_4 + H_2O(g)$ $\quad \Delta G_{700C} = -\ 23.30$kcal
$2Fe_3O_4 + H_2(g) \rightarrow 3FeO + H_2O(g)$ $\quad \Delta G_{800C} = -0.16$kcal
$4FeO \rightarrow Fe_3O_4 + Fe$ $\quad \Delta G_{600C} = -0.12$kcal

The reduction of iron oxide was conducted on the effect of temperature, reaction time, and hydrogen content and the results are shown in Fig. 5. It shows in (a) of Fig. 5 that iron oxides were almost reduced to metallic iron less than 10 minutes using a pure hydrogen gas regardless of temperatures. It can be expected that reduction rate of iron oxides to metallic iron was so fast and took place less than 10 minutes. The iron content in forging scale was increased from 68.38 to 91.02 wt.% and its content was not found to be variable on the effect of reaction time, which means reduction of iron oxides was almost finished. At a 0.5 atm of hydrogen partial pressure in (b) of Fig. 5, the iron content in forging scale was found to be about 89.53 wt.% and its content showed almost constant value except for its content in 10 minutes at 700°C, since reaction time might not be enough. On the other hand, the iron content was increased with increasing reaction time in a 0.1 atm of hydrogen partial pressure at each temperature shown in (c) of Fig. 5, and the iron content was also found to be increased with increasing hydrogen partial pressure from 0.1 to 0.5 atm. However, hydrogen content was no longer in effect of increasing reduction of iron oxides after 0.5 atm of hydrogen partial pressure. The powder of metallic iron after hydrogen reduction was observed by scanning electron microscopy (SEM), which shows many pores were detected on the surface of iron powder due to reduction of oxygen by hydrogen and an average size of iron particle was shown to be approximately 100 μm.

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4. Conclusions

The reduction of iron oxides by hydrogen was conducted on the effect of temperature, reaction time, and hydrogen partial pressure, and the multiple-step of reaction proposed above was thermodynamically considered. The reduction of iron oxides by hydrogen was found to be so fast less than 10 minutes using a pure hydrogen gas, and the study of reaction kinetics was therefore recommended to be measured less than 10 minutes in the further study. Moreover, iron content in the forging scale was shown to be increased with increasing hydrogen partial pressure at each temperature. Finally, the metallic iron powder reduced was observed to have an average size of 100 μm and has a porous structure due to reduction of oxygen by hydrogen.

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