



Experimental Investigation on Reduction of High Combined Water Contained Iron Ore by Ammonia-Methane-Mixed Gas

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Abstract

Reducing CO₂ emissions in the steel industry, which contributes 7% of global emissions, is crucial. Ammonia, as a hydrogen-based reducing agent offers one promising solution to address the decarbonization challenge in primary ironmaking process due to its high hydrogen storage density and ease of transport. However, for subsequent steelmaking process, the lack of carbon in the reduced ore from the ammonia-hydrogen iron reduction system must be addressed. In this study, we reduced iron ore using an ammonia-methane mixed reducing gas to introduce carbon into the reduced ore, from the raw material of porous ore prepared from a high combined water, goethite ore. We varied the reduction conditions to investigate how the reaction and carbon content would change, aiming to optimize the reduction process and enhance carbon content in the reduced iron. The results show that ammonia is primarily consumed for iron reduction, facilitated by hydrogen from its decomposition, while methane decomposes into carbon and hydrogen. Methane decomposition begins around 800°C, significantly increasing the ore's carbon content. Higher temperatures accelerate both reduction and carbon incorporation. The ammonia-methane mixing ratio influences reduction efficiency and carbon content, with a higher ammonia ratio expediting these processes. At 850°C, a 1:1 ammonia-methane mixture yields higher carbon content than higher ammonia ratios. This study highlights the potential of ammonia-methane mixed gases for sustainable steel production by enhancing the reduction and carbonization of high-CW-content iron ores.

Keywords : Ammonia, Goethite, Hydrogen, Iron reduction, Methane, Carbon

INTRODUCTION

Reduction of greenhouse gas emissions, especially CO₂ emissions, is a global challenge, as mentioned in the Paris Agreement 2015 [1]. The steel industry directly emits 2.6 gigatons of CO₂ per year, which is 7% of the total energy system [2]. Steel production in 2020 was 1,878 million tons, an increase of about 31% from 2010 [3]. It is also expected to increase to 2,500 million tons by 2050 [4]. In order to achieve both sufficient steel supply and climate change protection, CO₂ emissions during steel production must be significantly reduced. In the steel industry, ironmaking process uses a large amount of cokes, and there is a large potential for reducing CO₂ emissions. The use of hydrogen as a reducing agent is an important means of reducing CO₂ emissions in the ironmaking process [5].

The electrolysis of water to produce hydrogen is one of the most important methods of renewable energy conversion [6]. On the other hand, there are some problems with transport and storage of hydrogen, so various hydrogen carriers, such as hydrogen storage alloys, inorganic chemical hydrides, carbon materials, and liquid hydrides have been studied [7]. There is also the Power to Gas, which produces hydrogen from renewable energy, stored as methane [8]. Conversion to methane has a significant advantage in that it allows the use of existing natural gas infrastructure. Recently, ammonia has also been attracting attention as a hydrogen carrier.

Ammonia is a hydrogen carrier with high hydrogen storage density, 17.8 mass%. It can also be easily liquefied at a pressure of 1 MPa at room temperature, and the volumetric hydrogen density at this condition is 107 kg m⁻³. To remove hydrogen from ammonia, catalysts such as Ru, Ni, and Fe have been studied [9-11]. Ammonia Solid Oxide Fuel Cell (SOFC) and ammonia combustion are also being studied as a way to use ammonia directly as a fuel [12, 13].

Ammonia has also been proposed as a reducing agent for the ironmaking process [14]. Since iron decomposes ammonia, ammonia can be fed directly into the process. One of the features of this method is that ammonia reacts with iron to form iron nitrides. When a layer of iron nitride is formed, corrosion of iron is inhibited [15]. It may be possible that by nitrides formation, reduced iron ore can be transported over long distances without re-oxidation. For example, Australia is a major supplier of iron ore to Japan and has high renewable energy potential [16]. It may be possible to transport iron nitrides as an iron source if ammonia derived from renewable energy sources is used locally to make iron nitrides. In a previous study, products containing a large number of nitride phases were reported when the reduction was performed at low reduction temperature or when the ammonia concentration in the reducing gas was high [17].

On the other hand, high combined water (CW) contained iron ore has recently been studied as a raw material for ironmaking. Goethite (FeOOH), the main component of high CW contained iron ore, is known to change nano-porous hematite (Fe₂O₃) by dehydration [18, 19]. High CW contained iron ore also changes nano-porous hematite ore by dehydration [20]. In vacuum conditions, pore generation can be faster [21]. Generated pores can improve the reduction reactivity of ore due to the nano-contact between iron oxides and reducing agents [22-24]. It can also improve catalytic activities [25-27]. Some studies that goethite ore is used as a catalyst for ammonia decomposition have been reported [28-31].

N. Yasuda et al. demonstrated that the reduction rate of iron oxides by ammonia is limited by the hydrogen flow rate, suggesting that a higher reduction rate could be achieved if iron oxides can decompose more ammonia [17]. This indicates that iron ore with high combined water (CW) content holds promise as a raw material for reduction by ammonia. However, while the utilization of ammonia as a reducing agent in ironmaking has been studied using hematite reagent, there are no known examples of iron ore reduced by ammonia. In the previous study [32], we aimed to fill this gap by investigating the reduction of iron ores by ammonia and examining the effects of different ores on reduction behavior. Additionally, we analyzed the reactions and generated phases under varying reduction conditions such as temperature, time, and reducing gas components. It showed that iron ore with higher CW content exhibited a greater ammonia utilization rate and reduction rate when reduced with ammonia. We also examined the impact of reduction temperature and the post-reduction process on the resulting phases.

However, iron ore reduced by ammonia lacks the necessary carbon content for steelmaking, where pig iron typically contains about 4.5 mass% carbon, and the final product, steel, contains 0.02-2.14 mass% carbon. Even in the direct reduced iron (DRI) process, most DRIs contain carbon from reducing agents. Therefore, carbon addition to reduced iron ore is necessary, even with ammonia reduction. However, on the other hand, D. Nuber *et al.* showed the advantages of carbon-free DRI [33]. Nevertheless, iron ore reduced by ammonia may not need to contain carbon depending on the steelmaking process.

As an approach, methane is proposed as a source for carbon addition to iron ore reduced by ammonia. Methane, already used in the DRI process as a reducing agent, can be decomposed by iron catalysts into hydrogen and carbon without CO₂ emission [34, 35]. J. Zhang et al. produced cementite by reducing iron ore with hydrogen-methane mixed gas [36], indicating that it is possible to introduce carbon into the reduced ore as carbon or carbides by mixing methane with the reducing gas.

In this study, we reduced iron ore using an ammonia-methane mixed reducing gas to introduce carbon into the reduced ore, from the raw material of porous ore prepared from a high combined water,

goethite ore. We varied the reduction conditions to investigate how the reaction and carbon content would change, aiming to optimize the reduction process and enhance carbon incorporation in the reduced iron.

METHODS

Samples preparation

High CW contained iron ore A and low CW contained iron ore B were employed. Table 1 shows the compositions of each ore. The original ores were crushed and sieved so that a particle size ranged from 0.3 to 0.6 mm and dehydrated at 300°C under vacuum condition. During dehydration, the temperature profile was heated from room temperature to 300°C at a rate of 10°C min⁻¹ and held for 1 h. This method is a similar preparation method in the previous study [21]. The ore structure before and after dehydration was analyzed using X-ray diffraction (XRD, Miniflex 600, Rigaku), shown in Figure 1, and the change of their appearances.

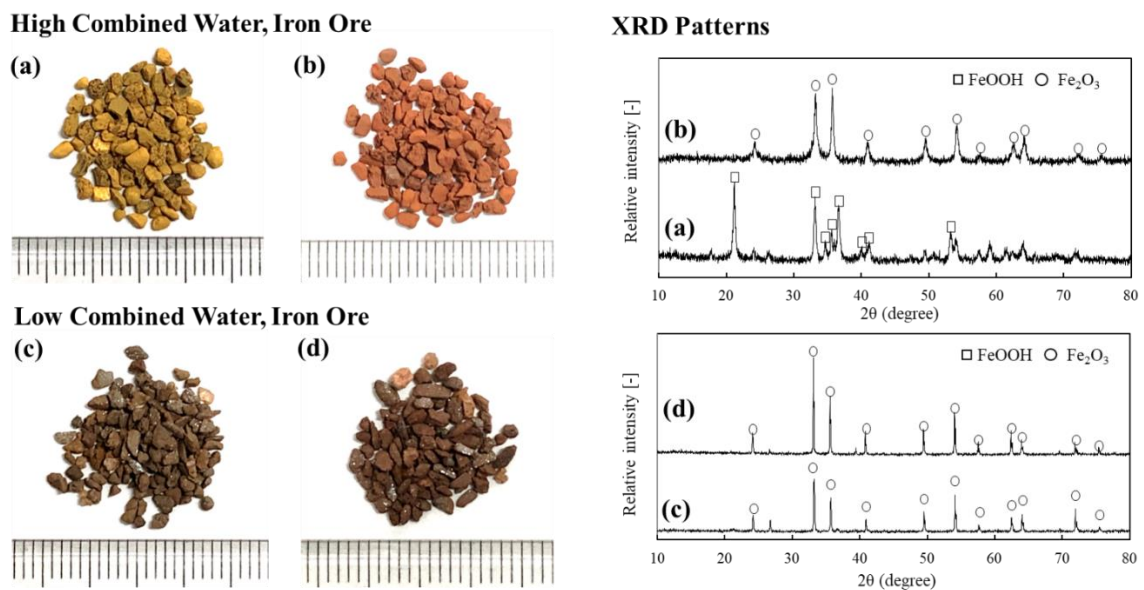


Figure 1. Pictures (in mm-scale) and XRD patterns of each samples, (a) raw ore A, (b) dehydrated ore A, (c) raw ore B, (d) dehydrated ore B.

There were some peaks in the XRD patterns that seemed to be other than Fe compounds in ores. Ore A showed a significant change in color, and the component changed from FeOOH to Fe₂O₃, but the ore B did not show significant changes in both appearance and XRD patterns.

Table 1. The properties of Ore A and Ore B employed in this study.

Ore	CW* [mass%]	T. Fe** [mass%]	FeO [mass%]	SiO ₂ [mass%]	Al ₂ O ₃ [mass%]
A	6.36	61.92	0.14	2.83	1.73
B	0.77	64.99	0.10	4.68	0.98

*CW: Combined Water

**T. Fe: Total Fe

Reduction of iron ore by ammonia-methane-mixed gas

The effect of high combined water (CW) content in iron ore on its reduction in an NH₃ reducing gas, on comparison between Ore A and B, has been extensively discussed in our previous study. In the current study, we focused exclusively on Ore A, which exhibits high CW content, to further elucidate its reduction behavior in an ammonia-methane mixed reducing gas. This targeted approach allows us to build upon our prior findings and provides a deeper understanding of the role that high CW content plays in enhancing reduction and carbon incorporation processes. Figure 2 shows the experimental apparatus scheme in this study.

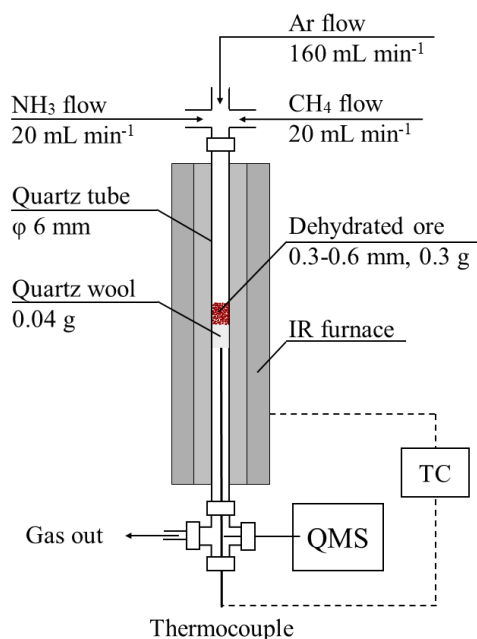


Figure 2. Schematic figure of the reduction experiment.

The apparatus is similar to that used in previous studies [14, 17, 32]. The apparatus consists of mass flow controllers, a fixed-bed reactor, a temperature controller, and a quadrupole mass spectrometer (QMS, Prisma QMS200, Pfeiffer Vacuum) for analyzing gaseous compounds at the reactor downstream. The mass flow controllers were connected to Ar and NH_3 . A gas line was also connected to the inlet reactor allowing CH_4 to flow simultaneously with NH_3 . The fixed-bed reactor was a transparent quartz tube with an inner diameter of 6 mm and heated in a vertical infrared (IR) furnace. The fixed bed was 0.3 g of dehydrated iron ores. This was supported by 0.04 g of quartz wool. The fixed-bed temperature was monitored and controlled using a K-type thermocouple placed underneath the quartz wool.

A reducing gas containing the mixture of 10% NH_3 -10% CH_4 with a total flow rate of 200 mL min^{-1} was used in this experiment. In this case, Ar, NH_3 , and CH_4 flowrates were set at 160, 20, and 20 mL min^{-1} , respectively. After the atmosphere was replaced with reducing gas, the reactor was heated from room temperature to different final temperatures (700-900°C) at a rate of 10°C min^{-1} . This heating method is known as Temperature Programmed Reduction (TPR). In another experiment, the reactor was heated from room temperature to different final temperatures (700, 750, 800, and 900°C) in 1 min and held for 5-30 min to reduce. After reduction, the samples were quenched under fast Ar flow (> 4,000 mL min^{-1}). The quenching gas was switched to Ar flow (200 mL min^{-1}) and cooled to room temperature when the temperature fell below 350°C.

Reduction tests were also conducted by changing the mixing ratio of NH_3 and CH_4 . One was Ar-15% NH_3 -5% CH_4 reducing gas with NH_3 and CH_4 flowing at 30 and 10 mL min^{-1} , respectively, and the other was Ar-5% NH_3 -15% CH_4 reducing gas with NH_3 and CH_4 flowing at 10 and 30 mL min^{-1} , respectively.

Table 2. Sample names and the mixture condition of reducing gas.

Sample Name	Gas Composition	Air (mL min^{-1})	NH_3 (mL min^{-1})	CH_4 (mL min^{-1})
NH ₃ -rich	15% NH_3 - 5% CH_4	160	30	10
Control	10% NH_3 - 10% CH_4	160	20	20
CH ₄ -rich	5% NH_3 - 15% CH_4	160	10	30

Sample characterization

In order to calculate carbon content in the reduced ore, the following method was used as similar to [24]. The amount of carbon is calculated based on the change in mass of the reduced ore and after combustion at 1000°C for 1 h in an air atmosphere.

$$X_C = \left(1 - \frac{w_{sb}}{w_{sa}} \left(1 - \frac{23.99 X_{Fe0} X_{RDa}}{55.85 (1 - X_{CW})} \right) \right) \times 100\% \quad (1)$$

where X_C is the fraction of carbon content in the sample after reduction test [mass%]. w_{sa} and w_{sb} are the sample weight after reduction test and after combustion in air, respectively [mg]. X_{Fe0} and X_{CW} are the mass fraction of total Fe and the combined water (CW) content in raw material, respectively [-]. X_{RDa} is the reduction degree (RD) of the sample after reduction test. In addition, nitrides may be present in the sample after reduction in this study. Therefore, Eq. (1) should be modified to become Eq. (2) by considering the mass loss of nitrogen during combustion.

$$X_C = \left(1 - \frac{w_{sb}}{w_{sa}} \left(\left(1 - \frac{23.99 X_{Fe0} X_{RDa}}{55.85 (1 - X_{CW})} \right) + \left(\frac{X_{Fe0} X_{Na}}{(1 - X_{CW})} \right) \right) \right) \times 100\% \quad (2)$$

where X_{Na} is the mass fraction of N to Fe in the sample after reduction [-], calculated from the quantitative analysis by XRD as well as the RD.

RESULT AND DISCUSSIONS

Reduction behaviors in ammonia-methane-mixed gas

Figure 3 shows the result of gas analysis during the temperature was raised to 900°C at 10°C min⁻¹ under reducing gas mixture NH₃ and CH₄ of 1:1 ratio.

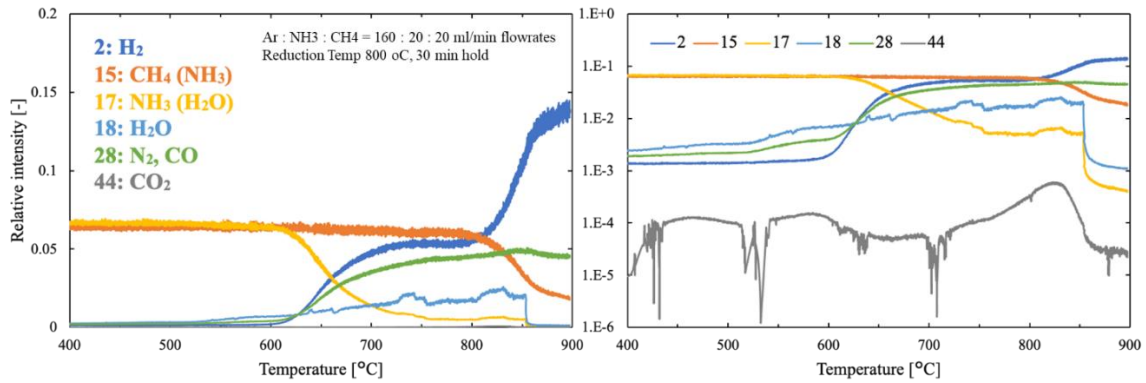


Figure 3. Changes in the relative intensities of ions of each mass during heating at a rate of 10°C min⁻¹ to 900°C under reducing gas mixture NH₃ and CH₄ of 1:1 ratio.

The detected ion masses using Quadrupole Mass Spectrometry (QMS) and their corresponding gases are presented in Table 3. Between 520 and 600°C, there was an increase in the concentrations of H₂O and N₂ without corresponding rise H₂ concentration, indicating that direct reduction by NH₃ occurred. Post 600°C, the production of H₂ was observed, suggesting the onset of NH₃ decomposition. Around 700°C, the influence of H₂O on NH₃ value became pronounced, leading to the inference that NH₃ was almost completely decomposed after this temperature.

The concentration of CH₄ began to decrease around 800°C. Concurrently, a slight increase in CO (and N₂) concentration was noted, implying that some CH₄ may have been utilized for reduction. However, the increase in the H₂ concentration was more significant, which suggests that most of the consumed CH₄ has been decomposed into C and H₂. The sudden drop in H₂O concentration seen around 850°C is considered as the end of reduction. This phenomenon would imply that the direct reduction occurred at 520~600°C, and NH₃ decomposition started at 600°C, similar to previous study's result [17]. On the other hand, CH₄ consumption is considered to have occurred before 800°C.

Table 3. List of ion masses and corresponding gases analyzed in QMS

Ion Mass	Corresponding Gas
2	H ₂
15*	CH ₄ (~detected as CH ₃ *)
17	NH ₃
18	H ₂ O
28	N ₂ , CO
44	CO ₂

Note: *ion mass of 15 was selected for CH₄ is to distinguish from Oxygen (O* with mass of 16)

In addition, to confirm the effect of CH_4 in iron reduction, Figure 4 provides a detailed gas analysis of the changes in the relative intensities of various ions as the temperature was increased to 900°C at a rate of 10°C per minute under a reducing gas condition containing 20% CH_4 , without NH_3 .

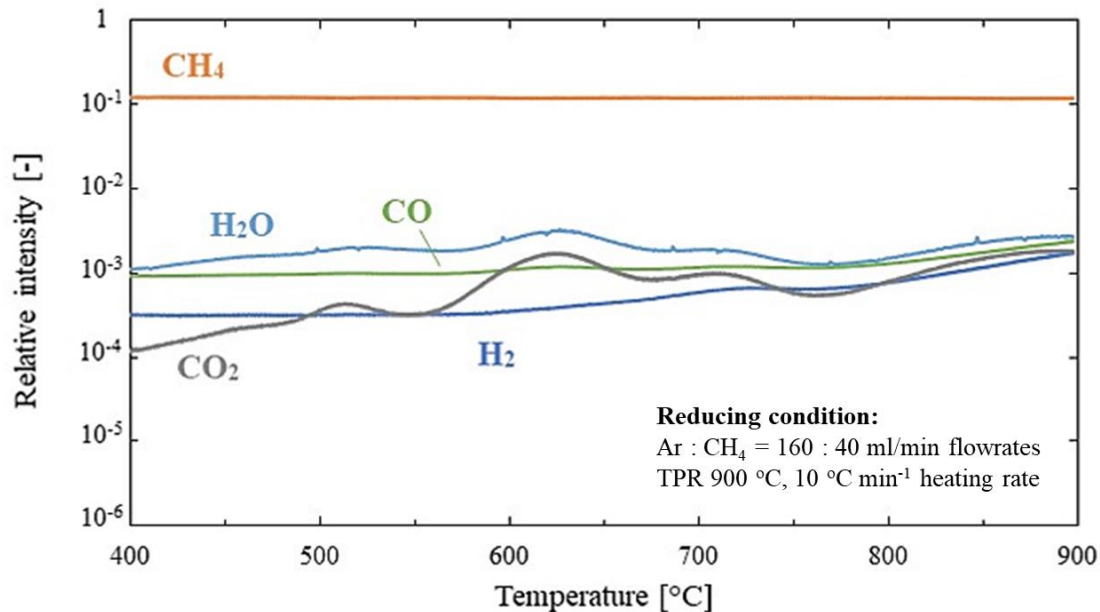


Figure 4. Changes in the relative intensities of ions of each mass during heating at a rate of $10^\circ\text{C min}^{-1}$ to 900°C under reducing gas containing 20% CH_4 (without NH_3) condition.

The data show that the concentrations of H_2O , CO , and CO_2 increased slightly during the heating process. This indicates that Fe_2O_3 in the iron ore was reduced either by CH_4 directly or by gases produced from CH_4 decomposition. The relatively low reduction degree (RD) of 22.3% for this sample (preliminary measured), when compared with our previous studies utilizing reducing gas mixtures containing NH_3 [32], highlights the significant impact of NH_3 on the reduction process. NH_3 facilitates iron reduction primarily through the generation of hydrogen from NH_3 decomposition. This suggests that NH_3 plays a critical role in enhancing the reduction efficiency, underscoring its importance in the reduction mechanism observed in this experiment.

Figure 5(a) presents the X-ray diffraction (XRD) patterns of samples subjected to reduction at various temperatures ranging from 700°C to 900°C . At 700°C , the presence of the nitride phase was observed, which subsequently disappeared after 750°C . By 800°C , concurrent with the onset of CH_4 decomposition, the formation of iron carbide (Fe_4C) was noted. Following the reduction process beyond 850°C , the reduction was deemed complete, with Fe_3C also being detected. Figure 5(b) illustrates the reduction degree and carbon content of each sample. The circular, triangular, and square markers represent the reduction degrees, the carbon contents calculated via Equation 2, and the carbon contents as carbides in the samples, derived from quantitative XRD analysis, respectively. The differences between the triangular and square markers indicate the amount of carbon present as deposited-C in the sample. A significant increase in carbon content was observed following the confirmation of CH_4 decomposition. For samples reduced at 700°C and 750°C , where no carbide phase was detected, the calculated carbon content was found to be comparable to that at 800°C . This suggests that the carbon content is unlikely to increase further even if the reduction process continues. The carbon contents might differ due to the discrepancies of the quantitative analysis since the calculation result of Eq. 2 strongly depends on the values (X_{RDa} , X_{Na}) calculated from XRD. On the other hand, from the result of Figure 4, there is a possibility that a small amount of CH_4 was consumed simultaneously with the reduction by NH_3 . Thus, the samples of 700°C and 750°C are possible to contain carbon before the CH_4 decomposition was confirmed.

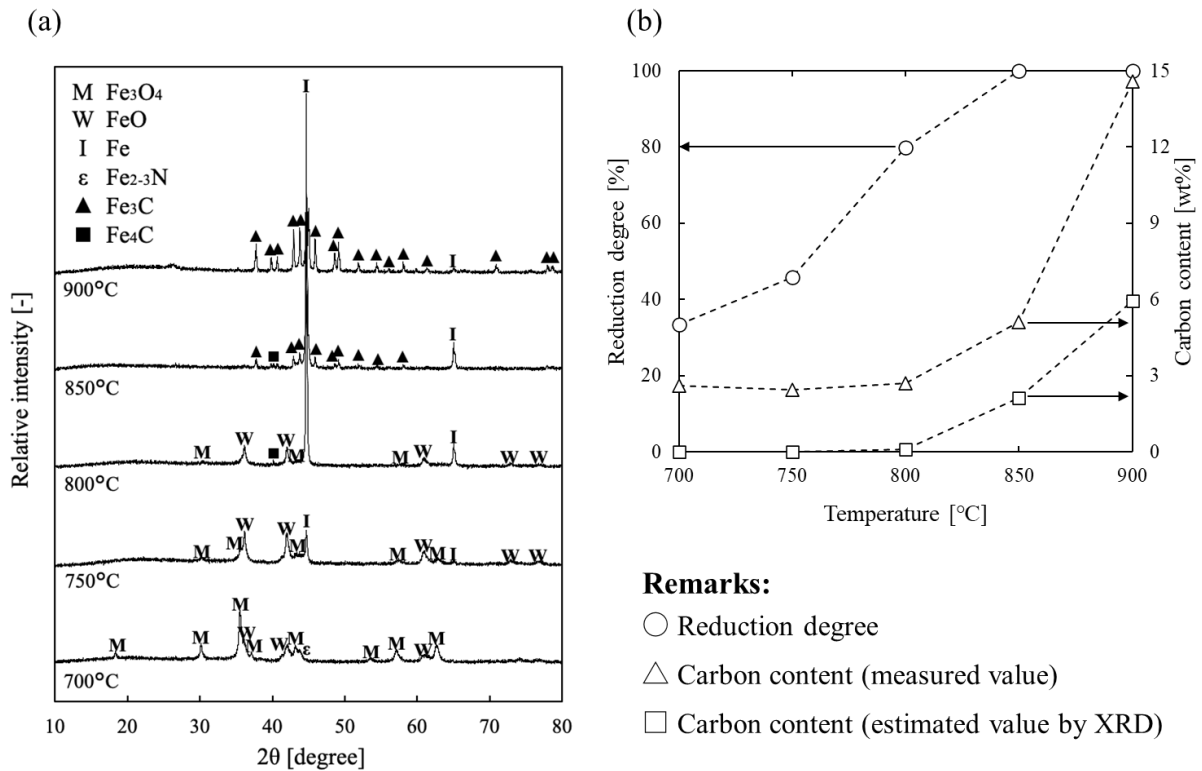


Figure 5. (a) XRD patterns of dehydrated ore A after reduction at various temperatures. (b) Reduction degree and carbon content of each sample at various temperatures under gas mixture of 10%NH₃-10%CH₄.

Reduction behaviors at different temperatures

Figure 6 presents the gas analysis results obtained when the temperature was rapidly increased to 800°C within one minute and subsequently held for 30 minutes. Despite the confirmation of CH₄ decomposition at 800°C in Figure 5, the CH₄ concentration did not exhibit a noticeable decrease for the first 10 minutes.

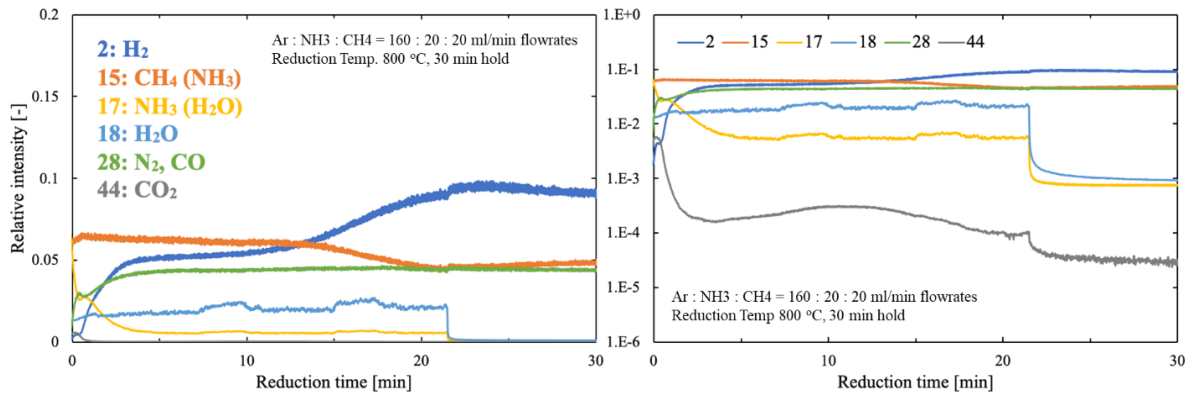


Figure 6. Changes in the relative intensities of ions of each mass at 800°C holding for 30 min under gas mixture of 10%NH₃-10%CH₄.

This observation indicates that the reduction by NH₃ and the H₂ produced from NH₃ decomposition occurred initially. After 20 minutes, the CH₄ concentration began to increase while the H₂ concentration decreased, suggesting a decline in CH₄ decomposition. This implies that the reduction process by NH₃ occurred first at 800°C, the temperature at which CH₄ decomposition was confirmed in Figure 5. Consequently, CH₄ decomposition followed the reduction process. Therefore, it can be inferred that the factor driving CH₄ decomposition is not solely the temperature but also the reduction process.

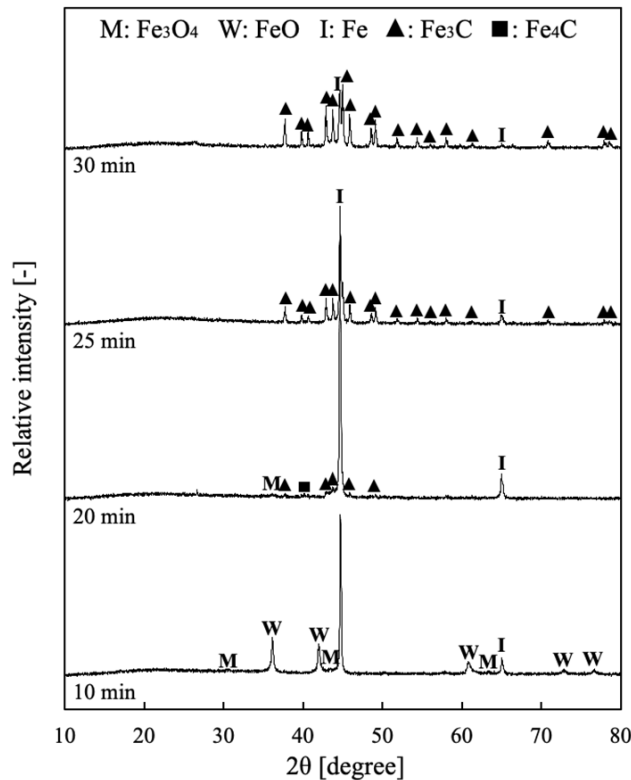


Figure 7. XRD patterns of dehydrated ore A after reduction at 800°C held for different times under gas mixture of 10%NH₃-10%CH₄.

Figure 7 shows the XRD patterns of the samples following reduction at 800°C. At the 10-minute mark, when CH₄ decomposition was confirmed, a substantial amount of metallic iron (Fe) had already formed. By 20 minutes, the percentage of metallic Fe reached its peak. Beyond 20 minutes, the percentage of metallic Fe decreased due to the formation of carbides. Those behaviors indicate that a significant amount of metallic Fe was present when CH₄ decomposition was confirmed. Given that Fe is known to act as a catalyst for CH₄ decomposition, it is suggested that the quantity of metallic Fe produced influences the initiation of CH₄ decomposition. After 20 minutes, as CH₄ decomposition slowed, the amount of metallic Fe diminished due to carbide formation. This implies that the quantity of metallic Fe affects both the initiation and the rate of CH₄ decomposition. However, as shown in Figure 3, CH₄ decomposition did not decline even after most of the phases had transformed into carbides. Therefore, the decrease in CH₄ decomposition is likely due to factors other than the reduction in metallic Fe. One such factor could be the disappearance of pores in the dehydrated ore when it is maintained at 800°C, as reported in previous studies [18]. The observed decline in CH₄ decomposition when the sample was held at 800°C and 900°C may thus be attributed to the disappearance of these pores.

Figure 8 illustrates the reduction degrees and carbon contents of samples subjected to reduction at various temperatures and durations. The results indicate that higher reduction temperatures correlate with faster reduction rates and an accelerated increase in carbon content. The increasing discrepancy between the triangular and square markers over time suggests that the amount of carbon present as deposited-C in the ore increases with prolonged reduction. The observed trend of faster reduction and increased carbon content at higher temperatures can be attributed to the more rapid occurrence of reduction facilitated by NH₃ at elevated temperatures. This demonstrates the temperature-dependent kinetics of the reduction process and the deposition of carbon within the ore.

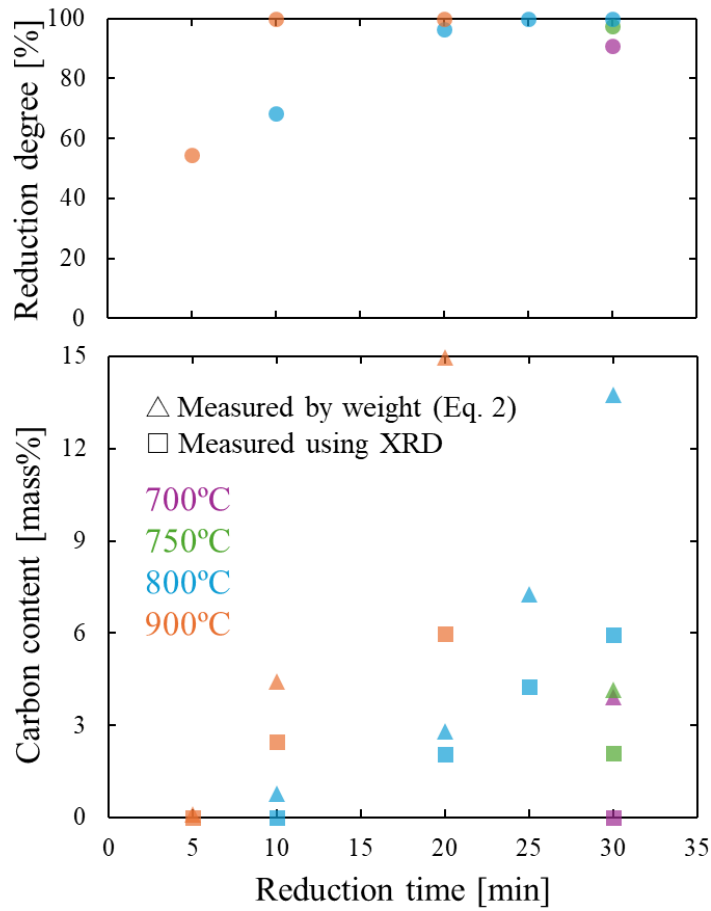


Figure 8. Reduction degrees and carbon contents over reduction time of dehydrated ore A after reduction at various temperatures under gas mixture of 10%NH₃-10%CH₄.

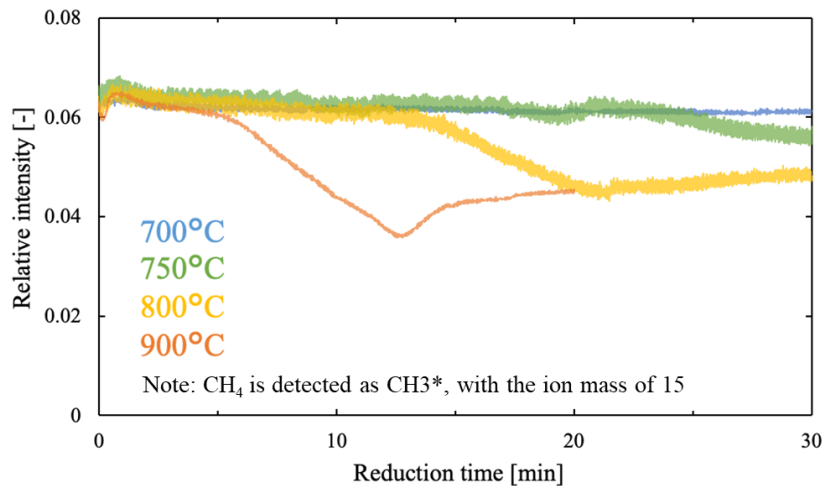


Figure 9. Changes in the relative intensities of methane ion on The reduction of dehydrated ore A holding at various temperatures under gas mixture of 10%NH₃-10%CH₄.

Figure 9 depicts the variation in CH₄ concentration, represented as relative intensities, during the reduction process at different temperatures. The results demonstrate that the decrease in CH₄ concentration commenced more rapidly at elevated temperatures. Notably, the increase in concentration observed at 800°C was also evident at 900°C; however, the reaction duration was shorter at 900°C, and the concentration increase was less pronounced compared to 800°C. The reduced time required for the CH₄ concentration to diminish, further corroborates that the reduction

process accelerated at higher temperatures. It also indicates a more substantial rate of CH_4 decomposition at elevated temperatures. Consequently, the samples subjected to reduction at higher temperatures exhibited increased carbon content due to two primary factors: firstly, the accelerated reduction process that initiates CH_4 decomposition more swiftly, and secondly, the greater extent of CH_4 decomposition.

Effects of ammonia-methane mixing ratio

Figure 10 presents the changes in H_2 concentration as the temperature was increased to 900°C at a rate of $10^\circ\text{C min}^{-1}$ under different reducing gas mixture conditions: NH_3 -rich, control ($\text{NH}_3:\text{CH}_4 = 1:1$), and CH_4 -rich. It illustrates two distinct increases in H_2 concentration for each condition. The initial increase corresponds to the decomposition of NH_3 , while the subsequent increase is attributed to the decomposition of CH_4 . The data reveal that higher NH_3 concentrations result in an earlier onset of both increases in H_2 concentration. Specifically, the decomposition of NH_3 and CH_4 occurs at lower temperatures when the ratio of NH_3 is higher. This phenomenon can be explained by the kinetics of NH_3 decomposition, which follows direct reduction.

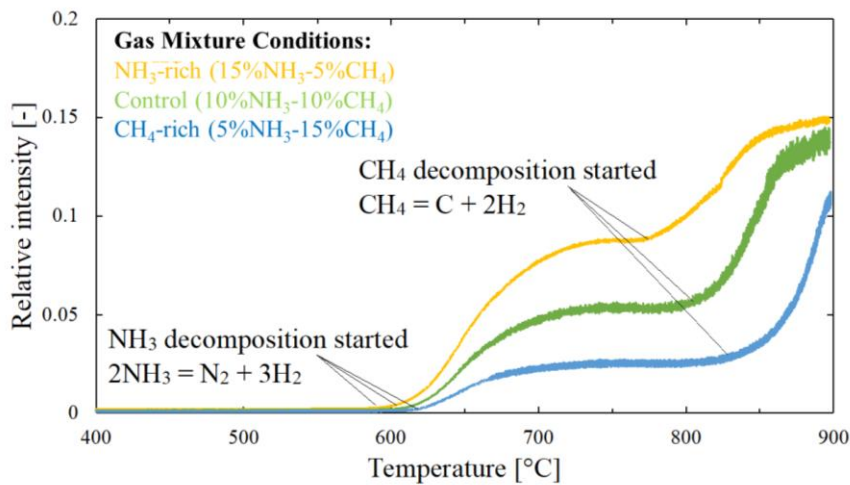


Figure 10. Changes in the relative intensities of H_2 ion under different reducing gas mixture conditions: NH_3 -rich, control, and CH_4 -rich, holding at various temperatures.

According to previous research [32], NH_3 decomposition occurs after the direct reduction process. When a substantial amount of NH_3 is supplied, the duration during which only direct reduction takes place is reduced. Consequently, NH_3 decomposition commences at lower temperatures with higher NH_3 ratios. Furthermore, the reduction process in this experiment was predominantly driven by NH_3 . Therefore, an increased NH_3 ratio not only accelerates the reduction process but also hastens the onset of CH_4 decomposition. This behavior underscores the significant role of NH_3 concentration in influencing the kinetics of both reduction and decomposition reactions. The higher NH_3 concentration leads to a faster reduction rate and an earlier start of CH_4 decomposition, as evidenced by the shifts in the H_2 concentration profiles.

Figure 11 depicts the changes in reduction degrees and carbon contents of samples subjected to reduction at temperatures of 800°C , 850°C , and 900°C under different CH_4 - NH_3 mixtures. The data indicate that higher NH_3 concentrations expedite the reduction process. However, this trend is not mirrored in the carbon content measurements. At 800°C , the sample reduced with a gas mixture of 15% NH_3 and 5% CH_4 exhibited the highest carbon content. Conversely, at 850°C and 900°C , the sample reduced with a mixture of 10% NH_3 and 10% CH_4 showed the highest carbon content. Across all temperatures, the sample reduced with 5% NH_3 and 15% CH_4 consistently displayed the lowest carbon content. The elevated carbon content in the sample reduced at 800°C with 15% NH_3 and 5% CH_4 can be attributed to the rapid reduction process facilitated by the higher NH_3 concentration. However, a high NH_3 concentration concurrently means a lower CH_4 concentration and consequently a reduced supply of carbon. This suggests that post- 800°C , the sample reduced with 10% NH_3 and 10% CH_4 received more carbon than the sample reduced with 15% NH_3 and 5% CH_4 , leading to the former's higher carbon content at 850°C and 900°C . The sample reduced with 5% NH_3 and 15% CH_4 exhibited the slowest reduction rate due to the lower NH_3 concentration, resulting in the lowest carbon content

up to 900°C. Nevertheless, a significant increase in H₂ concentration was observed after 850°C for this sample. Therefore, it is plausible that with further reaction, the sample reduced with 5% NH₃ and 15% CH₄ could eventually surpass the carbon content of the sample reduced with 10% NH₃ and 10% CH₄.

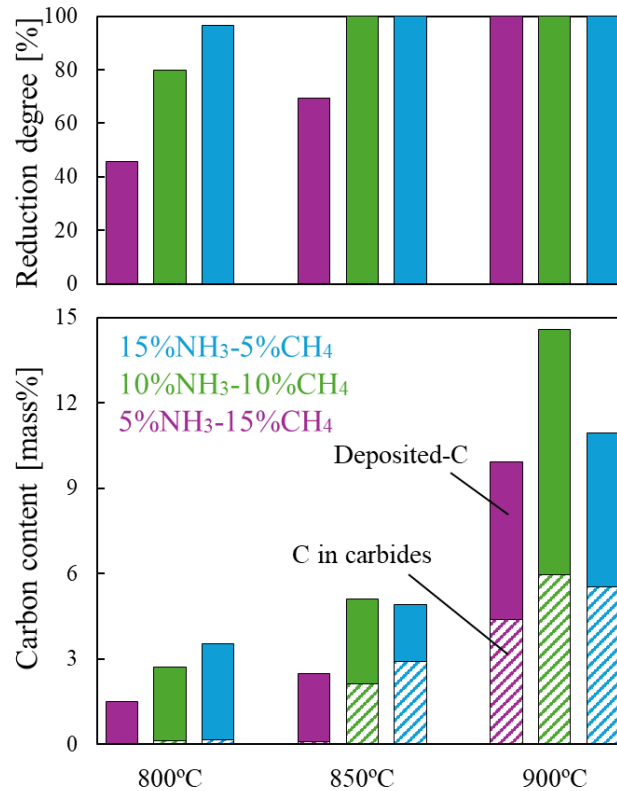


Figure 11. Changes in the reduction degree and carbon content in the reduced ore A under different CH₄-NH₃ mixtures and reduction temperatures.

CONCLUSION

In this study, carbon addition to reduced iron ore was successfully achieved by reducing dehydrated, high-CW-content iron ore using an ammonia-methane mixed reducing gas. The reduction temperature and composition of the reducing gas were varied to investigate their effects on the reaction and carbon content. From these experiments, the following conclusions were drawn:

1. When employing a reducing gas mixture of ammonia and methane, ammonia was initially consumed for iron reduction. The majority of the reduction was carried out by ammonia and the hydrogen generated from its decomposition, while most of the methane decomposed into carbon and hydrogen.
2. In the case of iron ore reduced under the ammonia-methane mixture, methane decomposition commenced around 800°C, resulting in a significant increase in the carbon content of the ore.
3. The holding temperature significantly influences the carbon content. Higher temperatures accelerated both the reduction process and the increase in carbon content.
4. The ammonia-methane mixing ratio also affects the reduction degree and carbon content of the reduced ore. A higher ammonia ratio expedited the reduction and methane decomposition. Consequently, the most substantial carbon content was observed when the sample was reduced at 800°C. However, a lower methane ratio resulted in less carbon being supplied. At 850°C, a 1:1 mixture of ammonia and methane yielded a more significant carbon content than mixtures with a higher ammonia ratio.

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