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Nano-structure of Carbons Deposited from CH_4 Blowing to and Injecting into Molten Slag

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How to produce the green hydrogen is important problem for reducing the CO_2 emission. Among many processes on the production of hydrogen, a thermal decomposition reaction of CH_4 can produce the pure hydrogen without CO and CO_2 gases. When the reaction proceeds by using a waste heat, the obtained hydrogen will be approached to the green hydrogen.

The thermal decomposition reaction of CH_4 is mainly studied kinetically from several decades ago.

$CH_4(g) = C(s)+ 2H_2(g)$

However, the decomposition reaction on the surface of molten slag was not studied. Authors have studied the kinetics of decomposition reaction of CH_4 on the surface of the molten slag in the previous study. The rate constant at 1 700 K for the surface of the molten slag was about four times larger than that of graphite surface. In addition to the kinetics of the reaction, the carbon properties precipitated are quite interesting, because the structures of carbon are changed by the conditions such as the temperature and kind of solid/liquid surface which provided the reaction sites. In this study, it was found that two kinds of carbon were precipitated during the decomposition of CH_4, when a molten slag existed in the system. The micro- and nano-structures of carbons precipitated were examined using SEM and TEM. The onion type carbon sphere were clarified, which were formed in the gas phase, furthermore, the high oriented graphite film was formed on the surface of molten slag.

KEY WORDS: onion carbon; hard carbon film; decomposition of CH_4; molten slag.

1. Introduction

How to produce the green hydrogen is an important problem for reducing the CO_2 emission. Among many processes on the production of hydrogen, a thermal decomposition reaction of CH_4 can produce the pure hydrogen without CO and CO_2 gases. When the reaction proceeds by using a waste heat, the obtained hydrogen will be approached to the green hydrogen. However, the reaction produces a solid carbon which will have a variety of morphologies depending on the deposition conditions. When the properties of carbons precipitated could be elucidated, the effective utilization of carbons would be developed more and more.

In the previous study,[1)] kinetic analyses on the decomposition reaction of CH_4 during blowing to the surface of slag and injecting into the molten slag were performed. It was found that the rate constant of decomposition reaction of CH_4 on the surface of molten slag was higher than that of graphite. The mechanism of CH_4 decomposition relating to the molten slag was presented and the phenomena during CH_4 injection into the molten slag were elucidated.

The thermal decomposition reaction of CH_4 is expressed by Eq. (1).

$$CH_4(g) = C + 2H_2(g) \quad (1)$$

The morphology of carbon formed shows many varieties depending on the experimental conditions. The carbon deposition reaction is complex phenomennon. Hüttinger and co-workers have shown the mechanism and kinetics of chemical vapor infiltration of pyrocarbon[2,3)] in an alumina pore. Kashiwaya, *et al*.[4)] has presented a mechanism of carbon infiltration phenomenon cooperated with a reduction reaction of iron ore.

A filamentous carbon grows under an existence of metallic catalyst.[5)] Similarly, the carbon deposition reaction from CO gas,

$$2CO(g) = C + CO_2(g) \quad (2)$$

which is an opposite reaction of the gasification reaction, also produced a filamentous carbon on the surface of metallic iron.[6)] Generally, the filamentous carbon has a catalyst (iron carbide) on the tip of the fiber and grown from the catalyst.

In this study, the morphologies of carbon formed during the decomposition reaction of CH_4 were studied using SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscope). The nanostructures of carbons were clarified.

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2. Experimental

The details of experiment were shown in the previous paper.[1] Graphite crucible was heated by an induction furnace. The reaction gas, Ar+CH_4 mixture was blown to an empty graphite crucible or a slag surface in the graphite crucible. In addition, the reaction gas was injected into a molten slag.

The slag was blast furnace (BF) slag and the chemical composition was shown in the previous paper.[1] The basicity of slag is 1.28, the contents of Al_2O_3 and MgO are 13.8 mass% and 6.28 mass%, respectively.

After experiment, the deposited carbons were sampled and examined using XRD, SEM and TEM.

3. Results and Discussion

3.1. Kinds of Carbon Deposited

Figure 1 shows the locations of carbon deposition during the CH_4 blowing to the slag surface in the graphite crucible. The kinds of carbon formed are classified into two types, one is a soot type carbon (a), the other is a film type carbon (b).

(a) Soot type carbon

The soot type carbon was sampled from the downstream position of graphite crucible, but a little soot was found in the crucible. The most of soot was trapped in the filter after the outlet of gas. The nucleation and growth of the soot type carbon will occur in the gas phase. Then, the precipitated carbon moved with the gas flow toward the downstream. The reaction mechanism of the decomposition reaction of CH was considered in the previous study.[1]

$$CH_4 \leftrightarrows CH_3^* + H^* \quad (3)$$

$$CH_3^* \leftrightarrows CH_2^* + H^* \quad (4)$$

$$CH_2^* \leftrightarrows CH^* + H^* \quad (5)$$

$$CH^* \leftrightarrows C^* + H^* \quad (6)$$

Where the superscript '*' means a radical state of species. Finally, solid carbon and hydrogen are produced in the system, The reaction between radical hydrogen 'H^*' and CH_4 become important. Then, the elementary reactions are expressed by Eqs. (3) to (11):

$$CH_4 + H^* \leftrightarrows CH_3^* + H_2 \quad (7)$$

$$CH_3^* + H^* \leftrightarrows CH_2^* + H_2 \quad (8)$$

$$CH_2^* + H^* \leftrightarrows CH^* + H_2 \quad (9)$$

$$CH^* + H^* \leftrightarrows C^* + H_2 \quad (10)$$

The formation of carbon was occurred by gathering of radical carbon C^*. The morphology of carbon would be decided by a circumstance.

$$nC^* \leftrightarrows C_n \text{ (soot)} \quad (11)$$

The soot type carbon is conveyed by the gas stream and falls on the surface of reaction tube and the gas tubing system, finally, most of soot is trapped in the filter.

(b) Film type carbon

On the other hand, a film type carbon, which was very hard, was found in the surface of slag, when the reaction gas was blown to. In the case of injection into the molten slag, the carbon deposited inside the bubble as shown in **Fig. 2**,

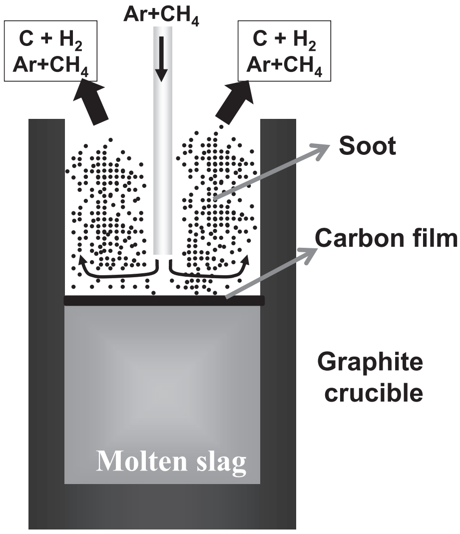

Fig. 1. Types of carbons formed during the blowing to the slag surface.

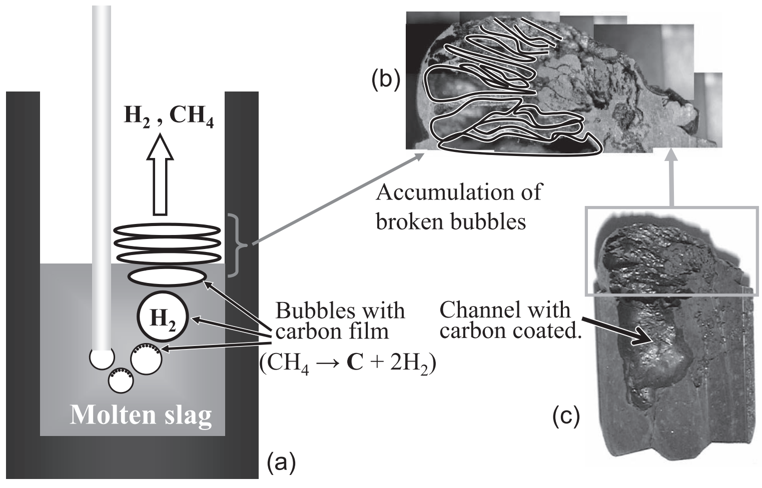

Fig. 2. Phenomena during CH_4 injection into molten slag.

which is the film type carbon as well as the carbon formed on the top surface of slag melt. Since the decomposition reaction of CH_4 is an endothermic reaction, the slag around the bubbles will solidify and the bubbles with solidified slag layer rise up to the top of slag melt. Finally, the bubbles are accumulated on the top of slag melt (Fig. 2(a)). The cross section of slag and bubbles accumulated is shown in Figs. 2(b) and 2(c). The place where the bubbles were accumulating had a lamella structure with slag and carbon films as shown in Fig. 2(b).

The accumulating bubbles were analyzed by XRD. The result is shown in **Fig. 3**. Kashiwaya, *et al.*[7] has shown the crystal phases of same slag (BF slag) in TTT diagram. Generally, Gehlenite (C_2AS: $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) and Merwinite ($C_3MS_2$: $3CaO{\cdot}MgO{\cdot}2SiO_2$) precipitate during a solidification under relatively slow cooling rate. When the cooling rate become higher around 100 K/s, the slag solidifies as an amorphous (glass) phase. The crystal phase of slag in the accumulating bubbles was Gehlenite mixed with carbon having graphite structure. However, Merwinite was not found in the sample. From this result, the condition of slag solidification accompanied with CH_4 decomposition is different from the ordinary solidification of slag. It is considered that the cooling rate of slag at the periphery of bubble is higher than that of bulk slag. The difference of cooling rate of slag around the bubble may result in the precipitation of Gehlenite only.

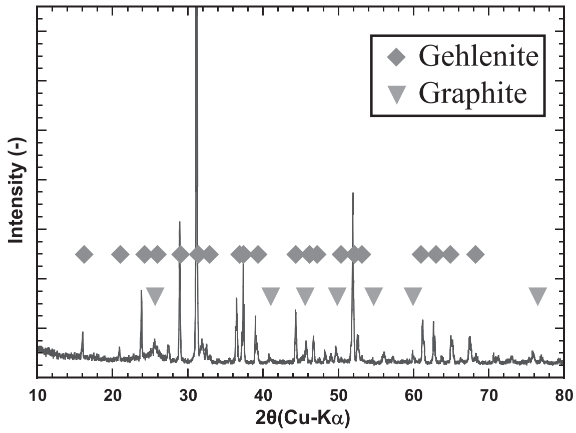

Fig. 3. Result of XRD of bubbles accumulating.

Figure 4 shows the result of EDS analysis of the part of bubbles accumulated. The film type carbon is intervolving in the slag layer. The Gehlenite contains Al_2O_3 and Merwinite contains MgO in the calcium silicate. From the result of XRD, only the Gehlenite was crystallized. However, Al_2O_3 and MgO are equally existed in the sample without segregation (Fig. 4), which meant that the Merwinite did not crystallize. As mentioned above, a slag around the bubble will be quenched by the endothermic reaction of CH_4 decomposition. However, the slag apart from reaction interface will be cooled slowly. In the TTT diagram,[7] as the Merwinite precipitates earlier than the Gehlenite, only Merwinite around a bubble became an amorphous state because of rapid cooling rate by endothermic reaction. Moreover, the existence of carbon might be a nucleation site of slag solidification. However, the detail of mechanism for the dominant precipitation of Gehlenite is not yet clear, further investigation will be necessary to clarify the phenomenon.

3.2. Nanostructures of Carbons

(a) Soot type carbon

Figure 5 shows the variety of carbon particles in the soot type carbon which precipitated in the different temperatures. Originally, the carbon particles have a spherical shape. However, the particles are sticking each other depending on the experimental conditions. In the case of lower temperature less than 1 473 K, the carbon particles show the irregular shape and agglomerate. The surface of carbon is not smooth at 1 273 K. In the higher temperatures at 1 673 K and 1 773 K, the each carbon particles show the clear outlines, although the particles are adhered each other. However, it was found that some of particle were separated and showed a complete spherical shape, especially in high temperature as shown below.

Figure 6 shows the results of TEM observation of the spherical carbon particles. The largest particle is 383 nm in

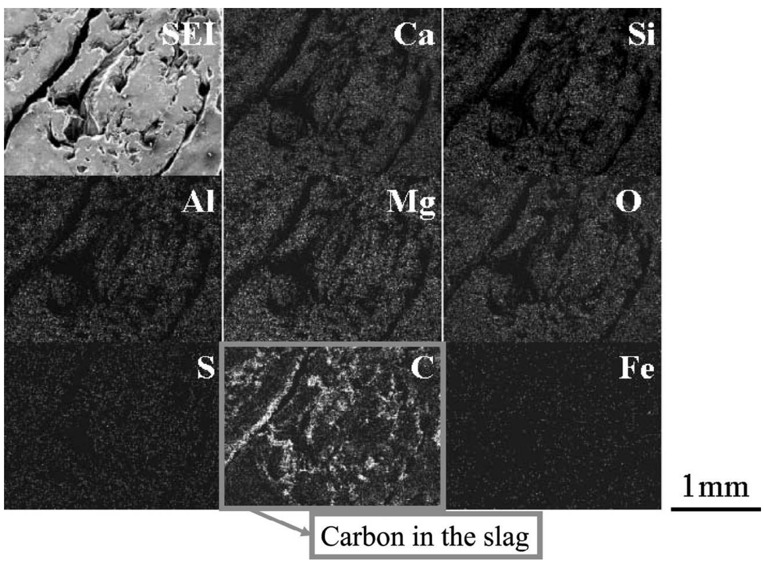

Fig. 4. Result of EDS analysis for the foamed slag.

diameter and shows almost complete sphere. The SAD (selected area diffraction) pattern shows the amorphous structure totally, however, the <002> of graphite hexagonal plane in the selected area aligns roughly to the same direction, which means that the carbon particle has an onion type structure. The high resolution TEM observation was performed and the result was shown in **Fig. 7**. The fringe of (002) can be seen clearly in the edge of the spherical particle. The lattice spacing of (002) of the stable graphite crystal is 0.336 nm, while the spacing of fringe in Fig. 7 is about 0.38 nm. Although these values are close, the spherical carbon particle is relatively in a low graphitization degree. On the other hand, the crystal structure at the center of particle cannot make clear, because the electron beam cannot transfer and the graphite (002) are normal to the electron beam.

The onion-like carbon was firstly reported by Iijima[8] under vacuum deposition of carbon vapor. Ugarte[9] reported a larger and spherical carbon onions around a few tens of nanometers. Mostly, the diameter of onion is less than 100 nm,[10] while the spherical onion with 383 nm in diameter was found in this study.

(b) Film type carbon

Figure 8 shows the mechanism of carbon deposition through the decomposition reaction of CH_4 in cooperation with slag melt.[1] The soot type carbon mainly formed in the gas phase, so that the soot was flowed to the downstream of gas. On the other hand, the film type carbon formed on the slag surface.

The carbon film was very hard and the thickness was from 50 μm to 70 μm. When it was taken from the slag surface, it looked like a metal foil in view point of the hardness and shiningness. As the purpose of this paper is to clarify the nanostructure of carbon, the hardness of carbon film was not measured, unfortunately. Most of hard carbon film are produced by the arc deposition process.[11,12] The hardness is around 40 GPa to 60 GPa in maximum. It is interesting to measure the properties of the carbon film in future.

Figure 9 shows the SEM image of fragment of carbon film. The fragment was sampled from a larger carbon foil which was taken from the surface of slag using pincette. Figure 9(b) shows the surface of carbon film in high magnification. The white small particles on the surface are the carbon spheres which are the same as the soot type carbon mentioned above. It was considered that those carbon spheres fell from the gas phase because the mechanisms of formation of the carbons were different. Except those carbon particles, the microstructure of this carbon film shows a lumpy surface where a round domain about 100 nm in diameter existed.

Figure 10 shows the TEM image of carbon film and SAD

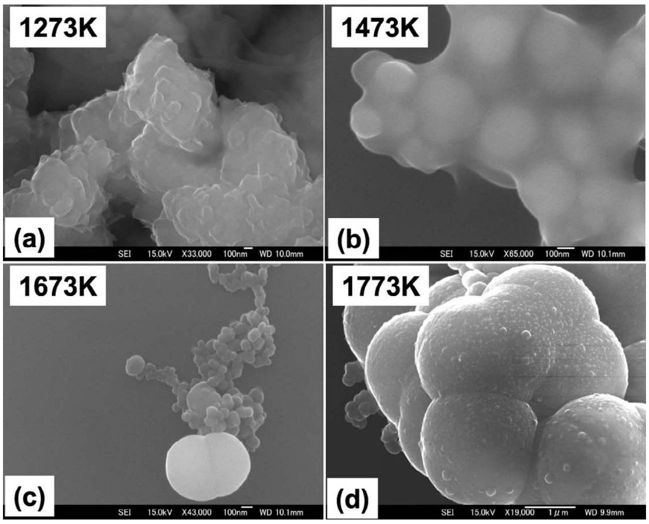

Fig. 5. Results of SEM observation of the soot type carbon particles precipitated at different temperatures.

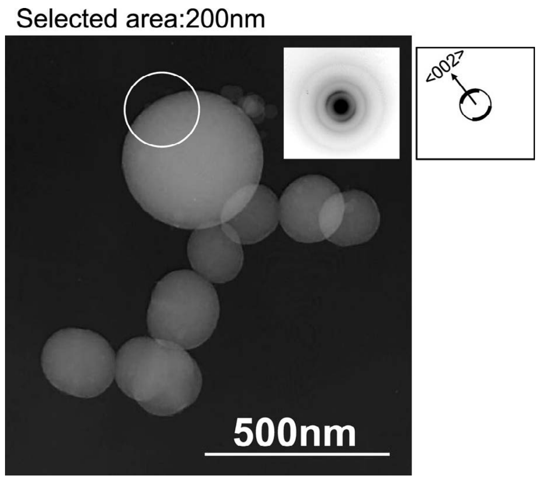

Fig. 6. TEM image and SAD pattern of the spherical carbon particle precipitated at 1 773 K.

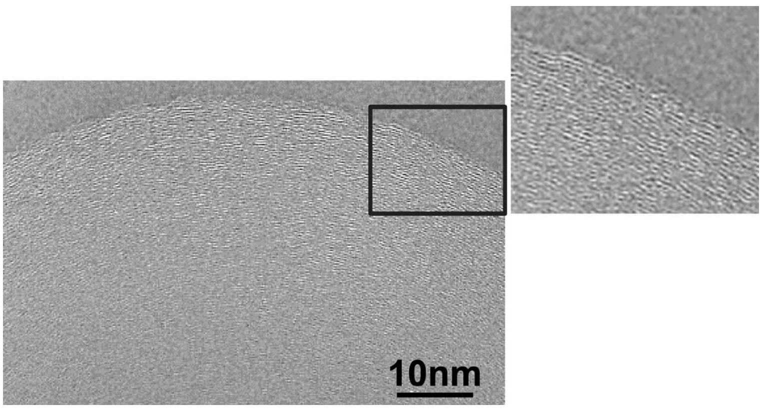

Fig. 7. High resolution TEM observation of onion type carbon particle.

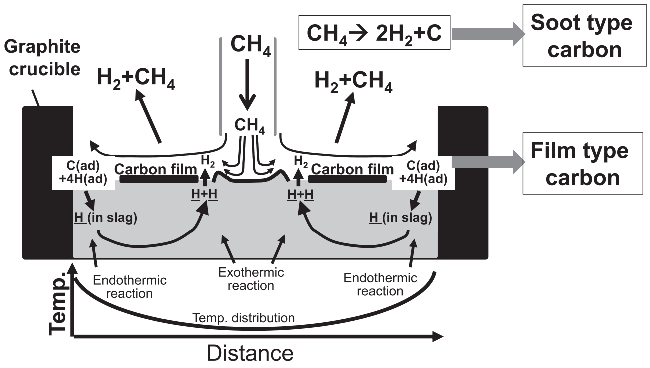

Fig. 8. Reaction mechanism for forming of the carbon film in cooperation with slag melt and soot type carbon formation in gas phase.

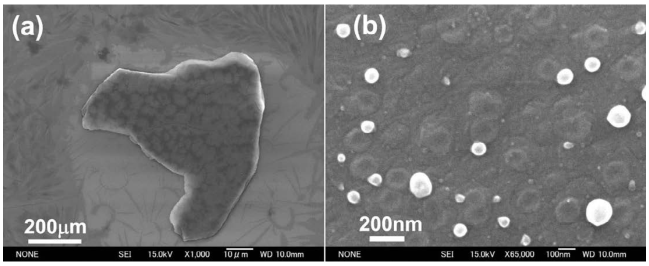

Fig. 9. SEM observation of carbon film. (a) Fragment of carbon film, (b) High magnification of surface of carbon film with carbon particles.

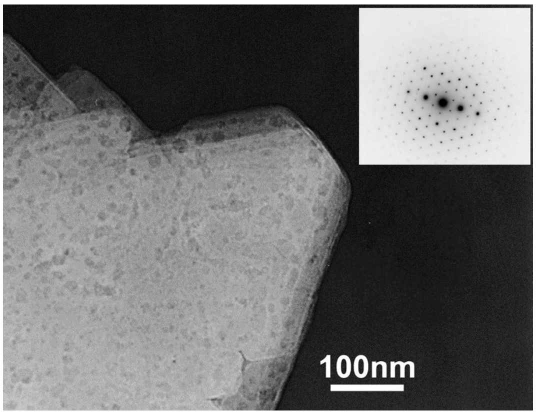

Fig. 10. TEM image and SAD pattern of carbon film.

pattern of the carbon film. From the SAD pattern, the carbon film had a high oriented graphite structure. However, many small defects around 10 nm existed on the plane of (002). Although the carbon film has many defects, the graphite crystal itself was close to a perfect crystal of graphite in the area observed.

4. Conclusion

Two kinds of carbon, which were obtained from the decomposition reaction of CH_4 in the graphite crucible having a molten slag, were examined using SEM and TEM. The nanostructures of the two carbons were clarified. The obtained results are as follows.

(1) Soot type carbon was formed in the gas phase and moved with gas stream.

(2) Film type carbon was formed on the surface of molten slag.

(3) The soot type carbon consisted of spherical carbon, however, the carbon particles stuck and agglomerated each other and the surface of carbon particles showed an irregular shape especially in the lower temperature. In the case of high temperature, the surface of carbon particle became smooth and closed to a perfect spherical.

(4) The nanostructure of spherical carbon in the soot was an onion type.

(5) On the other hand, the nanostructure of film type carbon was a high oriented graphite structure.

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