



A study of carbon deposition on fuel cell power plants — morphology of deposited carbon and catalytic metal in carbon deposition reactions on stainless steel

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Abstract

Carbon deposited on SUS304 stainless steel (18Cr 8Ni) has been observed by two different methods. One method was Field Emission Transmission Electron Microscopy (FE-TEM), with developed preparation for in situ observation of a cross-section of the deposited carbon from the base (SUS) to the top. The other method was X-ray Photoelectron Spectroscopy (XPS), obtaining composition–depth profiles by argon ion sputtering. Carbon was deposited on SUS304, 550°C, 1 atm, H₂/CO/CO₂ = 75/15/10, after drained the steam-reformed natural gas composition. One result from FE-TEM identified the major form of deposited carbon was tubular in shape with a variety of diameters, ranging from approximately 7 to 100 nm. Some tubes contained metallic particles which were about 20 nm in size at their tips. Therefore, it can be established that the carbon deposition mechanism is similar to that reported for metals such as Fe, Ni, and that the deposited carbon can grow after the SUS surface is covered with deposits under the above conditions. Observations from EDX attached to FE-TEM also determined that most of the particles consisted of Fe and from XPS, that the content of Fe on the surface of the reaction plate was lower than on the unreacted sample. This indicates that carbon deposition on stainless steel was influenced by Fe rather than Ni and Cr. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In fuel cell power plants, reformed natural gas and coal gas can be used as fuel. However, such fuel gases include carbon monoxide (CO), which may cause carbon deposition in the fuel gas stream. Carbon deposition is a serious problem because it may cause gas channel plugging and the plant can eventually be put out of operation. Therefore, preventing carbon deposition is essential for stable operation of fuel cell power plants.

Furuya et al. [1] reported that large amounts of carbon from reformed natural gas were deposited in the gas flow channel of the heat exchanger (HEX) plate fin during long-term operation of a Phosphoric Acid Fuel Cell (PAFC) power plant, which periodically caused cessation of operation. Analysis was conducted on the carbon deposits and

all parts of the HEX, which consists of the SUS plate and the SUS fin joined by an Ni alloy. As a result, carbon deposition was assumed to be caused by Ni in the Ni alloy [1]. However, present experiments on SUS and the Ni alloy indicated that carbon deposition occurred not only with the Ni alloy but also with stainless steel. The origin of the carbon deposition could not be determined.

While the morphologies, mechanisms and conditions of carbon deposition on metals such as Fe and Ni [2–6] have already been reported, carbon deposition on the stainless steel of typical materials in fuel cell power plants has not been studied sufficiently.

Mechanisms of carbon deposition have been reported on metals such as Fe or Ni [3–5]. These are generalized as illustrated in Fig. 1. Gases adsorb on the carbides, carbon atoms are separated from gases, dissolve in the carbides and precipitate from the carbides. Carbon filaments grow as these processes are repeated. In other words, metal carbide particles created at the metal surface can be cat-

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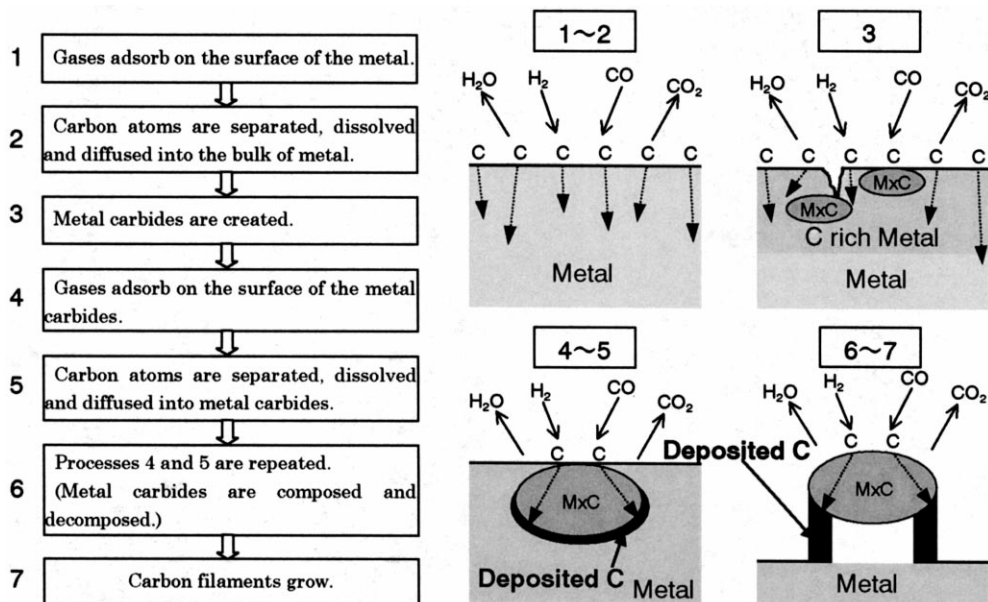


Fig. 1. Generalized carbon deposition mechanism.

alytic for filamentous carbon growth. This indicates that, if the carbon deposition mechanism on stainless steel is similar to such mechanisms, it may be observe under an electron microscope that carbon filaments include metal carbide particles at their tips. It may then be possible to identify the catalytic metal from carbon deposition by analyzing the metal in the metal carbide at those tips.

Initially, to compare the mechanism on Fe or Ni and that on stainless steel, SEM and Field Emission Transmission Electron Microscopy (FE-TEM) were used to observe deposited carbon morphology. Secondly, to determine major metal elements, metallic particles included in carbon filaments were analyzed for metal by EDX attached to FE-TEM. Furthermore, quantitative analysis of burned deposited carbon by ICP confirm the identity of the majority of metal in the deposited carbon and provided evidence that the result from EDX was correct. Finally, to confirm the most pernicious metal for carbon deposition and to predict the behaviour of metal elements in stainless steel, X-ray Photoelectron Spectroscopy (XPS) was used for obtaining composition–depth profiles by argon ion sputtering.

2. Experimental

2.1. Preparation of the deposited carbon sample

First, a commercial SUS304 plate was prepared as a substrate for carbon deposition by cutting to a size of

Table 1

Normal chemical composition of SUS304, wt.%

Fe	Ni	Cr	C	Si	Mn	P	S
Bal	8–11	18–20	≤ 0.08	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.030

4 × 200 × 0.1 mm. Second, oil was removed from the surface of the SUS304 with ethanol and by washing with purified water and drying. The elemental composition of SUS304 is listed in Table 1. Gas mixtures were supplied directly to the equipment illustrated in Fig. 2. The reaction zone in which the specimen was placed consisted of a quartz tube covered by an SUS tube outside, under isothermal conditions. The conditions of the reaction were as follows:

Temperature: 550°C,

Pressure: 1 atm,

Gas composition: H₂/CO/CO₂/H₂O = 75/15/10/0,

Reaction time: 24 h.

The Boudouard reaction for carbon deposition and the water–gas shift reaction proceed simultaneously when carbon deposition occurs because the rate of the water–gas

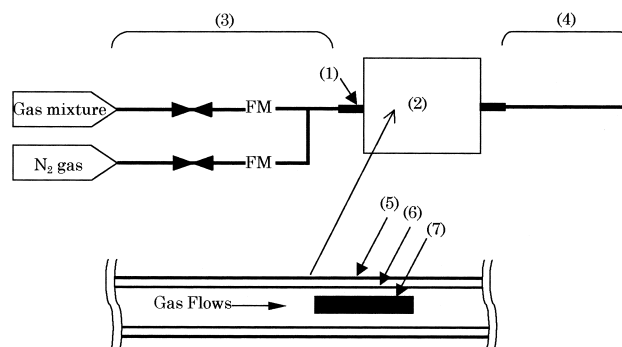


Fig. 2. Schematic diagram of experimental apparatus for carbon deposits: (1) sample holder, (2) electric heater, (3) gas inlet, (4) gas outlet, (5) SUS tube, (6) quartz tube, (7) specimen.

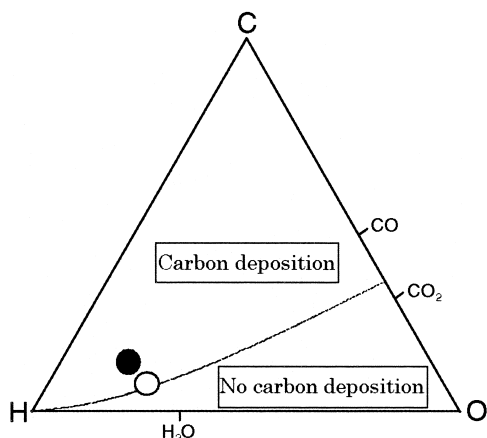
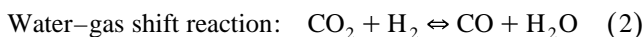
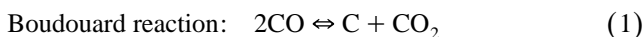


Fig. 3. C–H–O phase diagram containing the boundary of carbon deposition at 1 atm, 550°C. ○: Steam-reformed natural gas composition; ●: water removed composition from steam-reformed natural gas.

shift reaction is relatively fast compared with the Boudouard reaction.



The C–H–O equilibrium diagram and the curve for boundary conditions was calculated from equilibria in reactions (1) and (2) is shown in Fig. 3. Carbon may be deposited in equilibrium above the curved line indicated in the phase diagram. The open circle symbol (○) represents the steam-reformed natural gas composition. The solid circle symbol (●) signifies the gas composition supplied after H₂O was removed. This composition allows a shorter experimental time for carbon deposition. During the time that the temperature was varied, N₂ gas was supplied to the reaction part of the furnace.

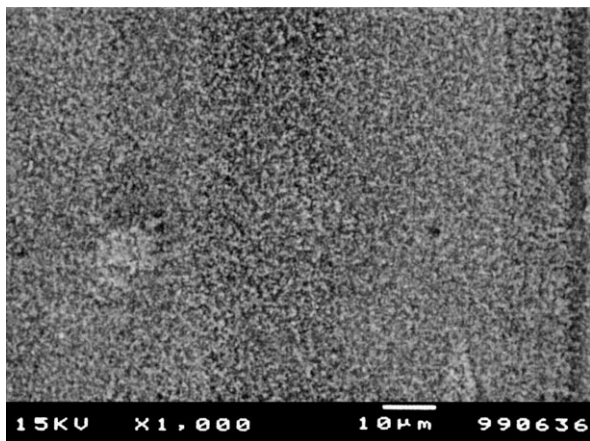


Fig. 4. SEM image of deposited carbon, coarse magnification, after carburization by exposure to H₂/CO/CO₂ at 550°C.

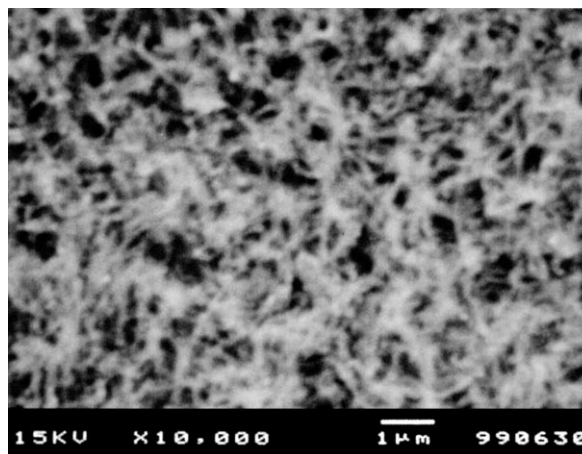


Fig. 5. SEM image of deposited carbon, high magnification, after carburization by exposure to H₂/CO/CO₂ at 550°C.

2.2. Carbon and stainless steel analysis method

The features of the carbon deposited were observed by SEM (JEOL JSM-T220) and FE-TEM (HITACHI HF-3000). Metallic particles included in carbon filaments were analyzed for metal by EDX attached to FE-TEM. The metal contained in all the deposited carbon was quantitatively analyzed by ICP. After stripping deposited carbon from the SUS304 plate with cotton wool, specimens were analyzed by XPS (JEOL JPS-90SX). Analysis of elements and their chemical states according to depth was success-

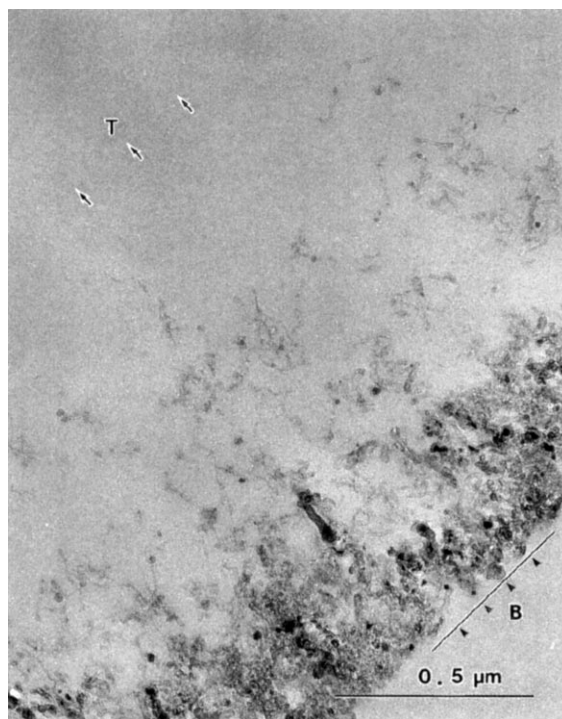


Fig. 6. TEM image of deposited carbon by a resin-embedded, thin-sectioning method, after carburization by exposure to H₂/CO/CO₂ at 550°C: B side, stainless steel; T side, exposed to gases.

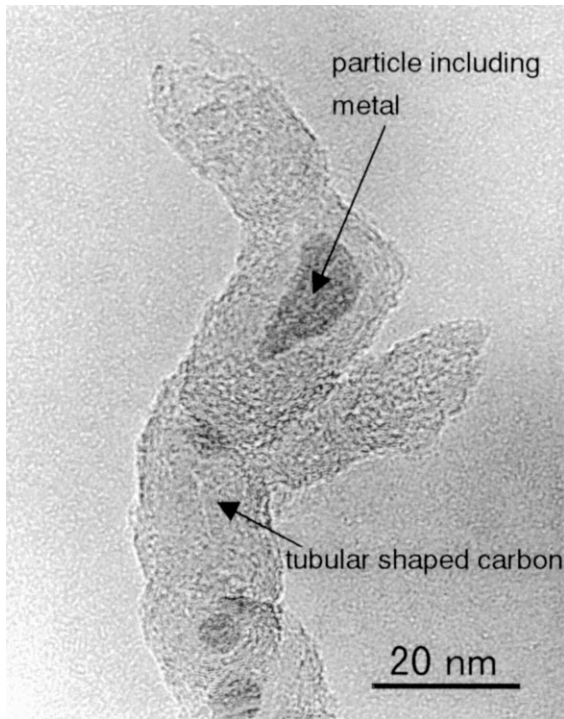


Fig. 7. TEM image of the tip of a carbon filament.

fully conducted by an accompanying argon ion sputtering method.

3. Results and discussion

3.1. Morphology of deposited carbon

The carbon deposited was a black powder and uniformly covered the stainless steel. This uniform carbon deposited is shown in Fig. 4, a low magnification SEM image. In Fig. 5, a high magnification SEM image, the shape of deposited carbon evidenced filaments of about 100 nm diameter.

It was confirmed that carbon deposition occurred on stainless steel using the method of resin embedded, 50 nm thick in cross-section, specimens for in situ FE-TEM ob-

servation of deposited carbon from the base to the top (Fig. 6). The black line, symbol “B” in the figure indicates the root of carbon growth, that is the surface of SUS304. Carbon was observed to grow toward symbol “T”, at which point the top of the deposited carbon is still in contact with the gas mixture. Carbon density near the SUS304 surface was higher than in other areas. While complete figures of filaments could not be observed because curved filaments grew across the resin section vertically and horizontally, it was determined that most of the deposited carbon had filamentous shapes with disordered curves, and various lengths.

When FE-TEM, which provides higher resolution than SEM, was performed, the diameter of carbon filaments was confirmed to vary from 7 to 100 nm. Though filaments of various diameters were observed near the SUS plate, many filaments of 20 nm diameter were observed especially at distances farther from the plate. This indicates that the rate of such filament growth is faster than others.

This observation also indicates that many of the deposits have filamentous shapes with particles, including metal, at their tips. To observe more closely and clearly, carbon filaments must be taken from the microgrid and suspended in space. Resin thicknesses greater than the diameters of carbon filaments were difficult to observe under higher magnification because the resin stripe image was impossible to distinguish from the carbon lattice image of carbon filaments. The tip of a filament image is apparent in Fig. 7. The sizes of most of the particles, including metal, were about 20 nm; carbon surrounded the particles and grew in a tubular shape. The carbon lattice image was observed clearly using FE-TEM with high interference. Carbon filaments were observed to grow vertically to the z -axis of the graphite lattice, and their structure was estimated to be similar to that of deposited carbon on Fe, Ni, as reported previously. On the other hand, some carbon filaments without metal particles at their tips were also observed (Fig. 8). Many of such filament type have thin diameters, comparable to those of carbon nanotubes. No filaments of such configuration have been reported before and the mechanism of such filament growth is unknown. It is thought that this type of carbon

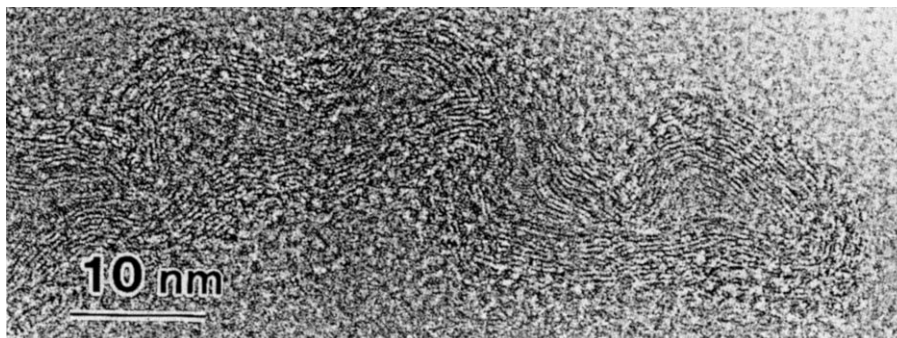


Fig. 8. TEM image of a carbon filament having no metallic particles.

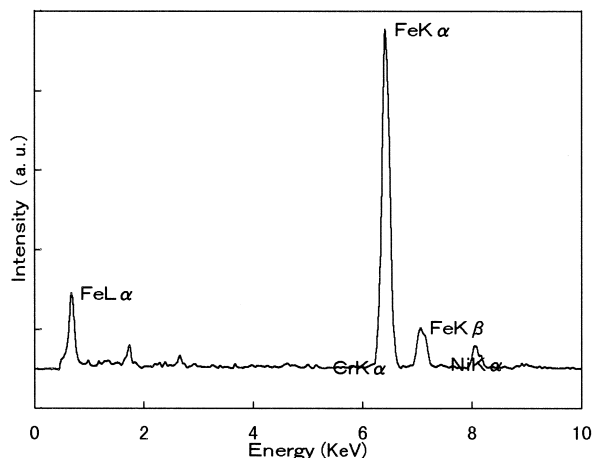


Fig. 9. Typical EDX spectra of particles included in the carbon filaments.

itself may be catalytic carbon growth because of the uneven filament surface. It will be necessary to discover the mechanism of such filament growth. As a result, the carbon growth mechanism on stainless steel is presented as basically similar to that on metals, that is, Fe and Ni.

3.2. Metals: reaction of carbon deposition

From the mechanism explained in Fig. 1, it was judged that particles, including metal at the tips of filaments, are the catalyst for carbon deposition. The particles were analyzed elementally by EDX attached to FE-TEM and typical spectra were obtained, such as in Fig. 9. Only Fe was detected: Cr and Ni were not detectable. It was also found that a few of the particles contained trace amounts of Cr or Ni in the presence of Fe. As a result, it was presented that the major element is Fe in all particles and that the Fe concentration of particles was higher than that of SUS304, the composition of which is listed in Table 1. Consequently, it is assumed that Fe mainly acts as the catalyst to grow carbon filaments.

In addition, to obtain correct data on the overall deposition carbon, ICP quantitative analysis of metals in all deposited carbon was performed; EDX attached to FE-TEM is only a spot analytical method. ICP analytical data is listed in Table 2.

It was established that the content of Fe in all deposited carbon was greater than that of SUS304. This indicates that Fe is the major metal included in the deposited carbon.

Considering both results obtained by EDX and ICP methods, it can be concluded that Fe mainly catalyzes carbon deposition on stainless steel.

Table 2

Chemical composition of metal in deposited carbon, wt. %

Fe	Ni	Cr
89	4	7

3.3. Analysis of chemical states and metal composition on stainless steel

The chemical state of stainless steel was analyzed as a function of depth from the surface by XPS with argon ion sputtering.

The spectrum taken before the carbon deposition reaction is illustrated in Fig. 10(a). It indicates that a mixture of Fe and Cr exists in an oxidized state and Ni does not exist in the oxidized state on the surface of SUS304 in the sample of this study (~ 50 s).

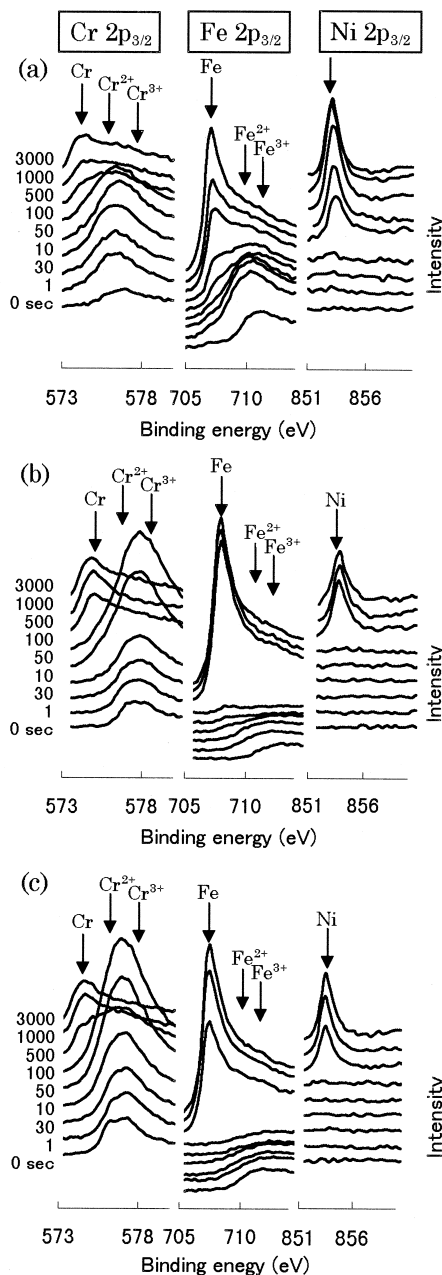


Fig. 10. Detail of the $2p_{2/3}$ photoelectron peaks of SUS304 for three different reaction times: (a) no reaction (b) after 24 h of reaction (c) after 300 h of reaction. Each peak was recorded after argon-ion sputtering of various times, from 0 to 3000 s.

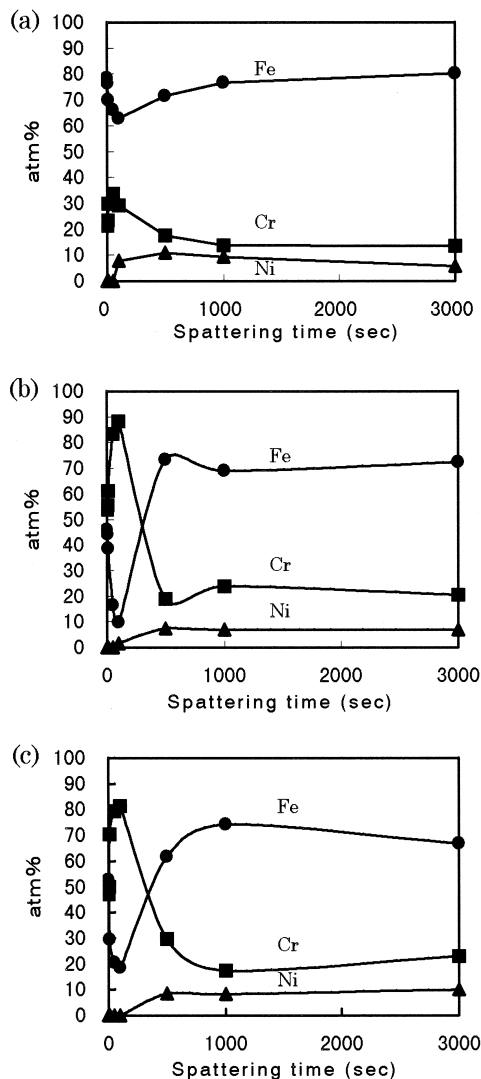


Fig. 11. Depth profiles through SUS304 for three different reaction times: (a) no reaction (b) after 24 h of reaction (c) after 300 h of reaction.

After 24 h of reaction, it was found that the metal state is not changed by the carbon deposition reaction, as shown in Fig. 10(b). In Fig. 10(c), the result from 300 h of reaction is similar to (b), though the reaction time of (c) is longer than (b). Apparently, the reaction time does not influence the chemical state of the stainless steel surface.

The 3000-s argon-ion sputtered depth was measured at about 1 μm and the stainless steel was checked for uniform sputtering by Scanning Laser Microscopy (SLM). Since the 3000-s sputtered specimens of (a)(b)(c) all have the same chemical states and metal composition, it was confirmed that carbon deposition proceeds within 1 μm depth in the oxidized layer of the stainless steel.

Fig. 11 shows quantitative analysis data, a depth profile based on Fig. 10. In Fig. 11(a),(b) and (c), each datum

point corresponds to Fig. 10, respectively. The concentration for each metal is calculated as if the total amount of Fe, Cr and Ni is 100.

The Fe content decreased drastically on the surface (~ 500 s), while to Cr concentration increased. This suggests that Fe particles were selectively expelled by deposited carbon from the surface. Ni could not be detected on the surface (~ 50 s) before the reaction; after the reaction, Ni content decreased at a greater depth (~ 100 s). Such Ni behavior can be explained by bulk Ni at most deeper position diffusing to the surface of the stainless steel, and then being expelled into the carbon deposit accompanied by Fe. On the other hand, the behaviour of Fe and Cr was established from comparison of (b) and (c). The change of concentration after 300 h of reaction was smaller than that after 24 h of reaction. It is suggested that the rate of diffusion may be faster than the rate of expulsion that Fe particles are expelled by deposited carbon from the surface on initial reaction, and that Fe existing in the bulk is also expelled up after diffusing to the surface.

4. Conclusions

The mechanism and effect of metals in carbon deposition on stainless steel was determined by analyzing the deposited carbon and stainless steel.

Deposited carbon tends to be tubular in shape, having particles including metal at its tip, and the carbon deposition mechanism on stainless steel is basically similar to that on metals, such as Fe and Ni.

The major element in the particles was Fe; this suggests that the Fe catalyzes carbon deposition. Carbon deposition on stainless steel was influenced by Fe rather than Ni and Cr, since Cr has little catalytic activity, and the content of Ni is low on the surface of stainless steel.

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