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Deactivation of metal capillaries for gas chromatography

T. Takeichi*, K. Takahashi, T. Tanaka, Y. Takayama

School of Materials Science, Toyohashi University of Technology, Tampaku-cho, Toyohashi 441-8580, Japan

Abstract

A novel method to deactivate metal (stainless steel) capillaries for gas chromatography was developed using perhydropolysilazane (PSZ). A metal plate was used first to examine the nature of the pyrolyzed PSZ. The Auger analysis demonstrated that the PSZ layer pyrolyzed under a nitrogen atmosphere was composed of Si and N, but the layer pyrolyzed in air was composed of Si and O, indicating that the pyrolysis of the PSZ layer in air gives a silica layer. It was observed from scanning electron microscopy that the pyrolysis of PSZ on a metal plate gave a silica layer as a smooth film. Contact angle measurement revealed that the surface free energy and its components of the pyrolyzed PSZ in air were almost the same as those of silica. The interface between the stainless steel and coating silica layer was tough enough to endure the bending treatment. Deactivation of capillaries with PSZ was first examined using glass capillaries. A polarity test chromatogram showed tailing for the polar solutes, suggesting that the inner surface of capillaries is coated with silica layer rich in silanol groups after the pyrolysis of PSZ. Deactivation was accomplished by treating further with octamethyltetrasiloxane (D4), showing that PSZ treatment followed by D4 treatment is efficient as a deactivation method. Then, deactivation of metal capillaries was examined using the same procedure. It was found that deactivated metal capillaries were obtained successfully by the PSZ coating and pyrolysis followed by D4 treatment. It was also observed that pretreatment including acid washing and oxidation is recommended to obtain deactivated metal capillaries with high reproducibility.

Keywords: Capillary columns; Perhydropolysilazane; Metal capillary; Deactivation; Pyrolysis

1. Introduction

As a material of capillaries for gas chromatography (GC), fused silica is mainly used because of the easiness of deactivation. The fused silica capillaries, however, have some problems due to the brittleness of the silica and also due to the low thermal stability arising from the polyimide coating outside the capillaries that limits the use temperature to ca. 300°C. Metal capillaries have advantages in these points, and can be an ideal material as capillaries for GC. The problem for the metal capillaries is that they are very difficult to deactivate.

Takayama and Takeichi succeeded in deactivating the inner surface of metal capillaries by utilizing the pyrolysis of monosilane [1]. The deactivation was achieved by filling monosilane in oxidized metal capillaries, which was decomposed at above 500°C to give a silicon layer on the inner surface, thus shielding the active metal surface. The obtained metal capillaries are as deactivated as the fused silica capillaries, and can be continuously used at high temperatures above 400°C. The deactivated metal capillaries have been supplied commercially as capillaries for GC since 1986, and gained a high reputation for their high performance and reliability. The

*Corresponding author. Tel.: +81-53-247-0111; fax: +81-53-248-5833.

E-mail address: takeichi@tutms.tut.ac.jp (T. Takeichi)

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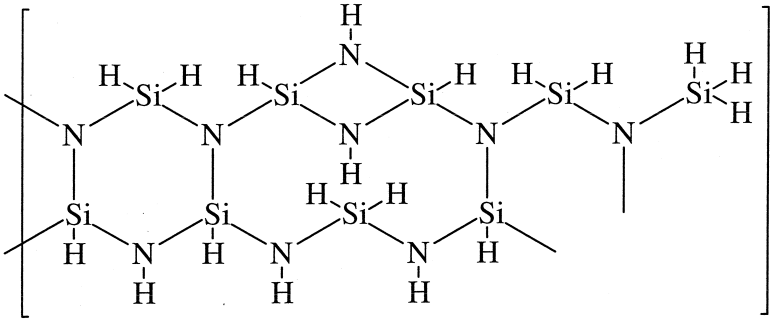

Fig. 1. Structure of perhydropolysilazane.

deactivation method, however, uses monosilane which is difficult to handle. This limits the extensive use of the deactivation method.

Perhydropolysilazane (PSZ) is an inorganic polymer composed of Si, N and H. The chemical structure of PSZ is shown in Fig. 1. PSZ has been extensively studied as a ceramic precursor. For example, amorphous silica is formed by pyrolyzing in air at ca. 400°C, and amorphous silicon nitride ceramic is obtained by pyrolyzing at ca. 600°C in an inert atmosphere [2–4]. Since PSZ is supplied as a solution, PSZ can be handled using syringe and is easy to coat on the capillaries. Thus, it is expected that deactivation of metal capillaries can be achieved by coating and pyrolyzing PSZ, shielding active metal surface by the silica layer. We intended here to develop a novel deactivation method using PSZ that is easier and safer than the deactivation method using monosilane.

2. Experimental

2.1. Materials

PSZ was obtained from Tonen, Japan, as a 20% *m*-xylene solution. The molecular mass of PSZ was 1000–1400. Octamethylcyclotetrasiloxane (D4) and reagents employed as Grob's sample mixtures were used as received. Stainless steel plates (SUS-316, 0.20×100×300 mm) were obtained from Nilaco, Japan. Commercial stainless steel capillaries of 0.25 mm I.D.×0.6 mm O.D. were used as metal capillaries. Glass capillaries of 0.25 mm I.D.×0.8 mm O.D. were used. For the deactivation experiment, glass or metal capillaries of 5 m long were used.

2.2. Surface treatment of stainless steel plate with PSZ

A stainless steel plate was cut into 50 mm×10 mm pieces, and washed with chloroform, methanol, water, methanol and chloroform for 5 min each using a supersonic bath. The SUS plate was then immersed in a *m*-xylene solution of PSZ, and after drying at room temperature, it was heated in air at 250°C or at 400°C for 2 h.

For the contact angle measurement, a stainless steel plate was cut into 30 mm×20 mm pieces, and washed with chloroform, methanol, water and additionally with 20% aq. HCl solution by immersing for 1 h, and then with water, methanol and chloroform. Oxidation of the stainless steel plate was performed by heating in an oven at 250°C for 1 h.

2.3. Pre-treatment of glass and metal capillaries

Before coating PSZ, glass capillaries were pretreated by washing with dichloromethane, methanol, water, 47% HF solution, water, methanol and dichloromethane (2 ml each)..

Metal capillaries were washed with acid and/or oxidized as pre-treatment before PSZ coating. Metal capillaries were washed with dichloromethane, methanol, water, concentrated HCl, water, methanol and dichloromethane (2 ml each). The metal capillaries were then oxidized by passing oxygen or air in an oven.

2.4. Coating of PSZ into capillaries

The capillaries were coated dynamically with 0.2–0.3 ml of PSZ, followed by heat treatment at various temperatures to pyrolyze PSZ.

2.5. Treatment with D4

After the treatment with PSZ, the capillaries were treated with D4 as follows. A plug of 100% D4 was inserted into the capillaries so that the length of the plug was ca. 10% of the capillaries, and dynamic coating was conducted. The rate of movement of the plug was ca. 2 cm/s. After passing the plug, the capillaries were dried with a nitrogen flow for 1 h. Both ends of the capillaries were sealed under vacuum. The capillaries were treated at 400°C for 10 h in an oven. After being cooled, the capillaries were opened and rinsed with dichloromethane.

2.6. Evaluation of deactivation of capillaries

To evaluate the degree of deactivation, a polarity test was performed following the Grob's polarity test [5,6]. As a pre-column, we employed a deactivated non-polar capillary column coated with OV-1, d_f= 0.2 μm, 15 m×0.25 mm I.D. [1]. The test mixture was a heptane solution of 0.5 mg/ml of each solute shown in Table 1. The test parameters were as follows: nitrogen flow-rate, 40 cm/s; initial temperature, 60°C; programming rate, 3°C/min; sample volume, 1 μl; and splitting ratio, 1:100.

Table 1
Grob's test mixture

Solute	Abbreviation
n-Decane	C_{10}
n-Undecane	C_{11}
n-Dodecane	C_{12}
Methyl decanoate	E_{10}
Methyl undecanoate	E_{11}
Methyl dodecanoate	E_{12}
2,3-Butanediol	D
1-Octanol	ol
2,6-Dimethylphenol	P
2,6-Dimethylaniline	A
Dicyclohexylamine	am
2-Ethylhexanoic acid	S

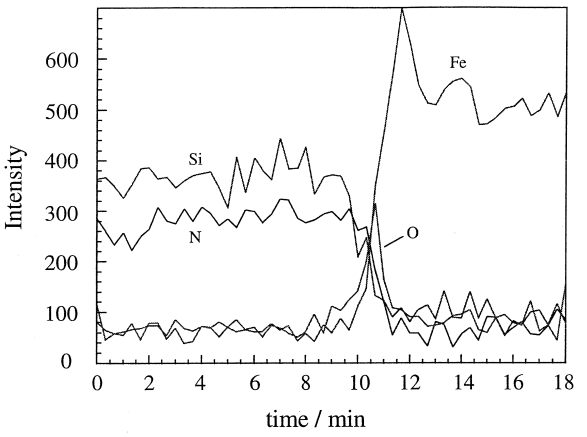

Fig. 2. Auger electron spectroscopy depth profile of SUS plate coated with PSZ and heated at 500°C for 2 h in N_2.

2.7. Measurements

The contact angle of the SUS plate was measured by the one-liquid method [7,8]. The receding contact angles of water and diiodomethane were measured at 20°C, using a Kyowa contact angle meter with a goniometer. The contact angle was determined from an average of 10 drops. Surface free energy and its components were calculated based on the Kaeble's equation [9,10]. Scanning electron microscopy (SEM) of the stainless steel plate was measured with JEOL JSM-5200. Auger electron spectroscopy on the

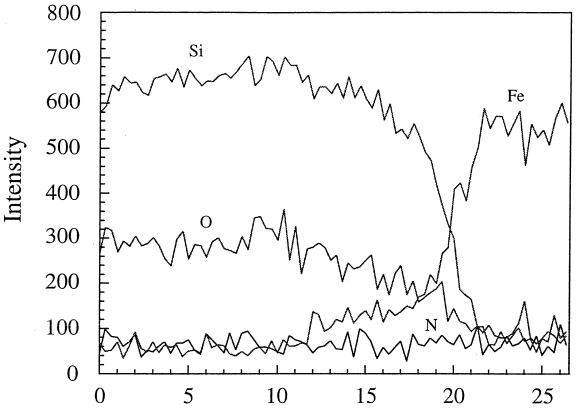

Fig. 3. Auger electron spectroscopy depth profile of SUS plate coated with PSZ and heated at 500°C for 2 h in air.

Table 2
Surface free energy of SUS and quarts plates

Substrate		Surface free energy (10^{-2} N m^{-1})		
		γ_S^D	γ_S^P	γ_S
SUS plate	Non-treated	36.5	9.0	45.5
	Oxidized (250°C/1 h, air)	33.0	22.2	55.2
	PSZ coated (250°C/1 h, air)	25.8	32.2	58.0
	PSZ coated (400°C/2 h, air)	25.6	40.6	66.2
Quartz plate	Non-treated	28.8	40.3	69.1

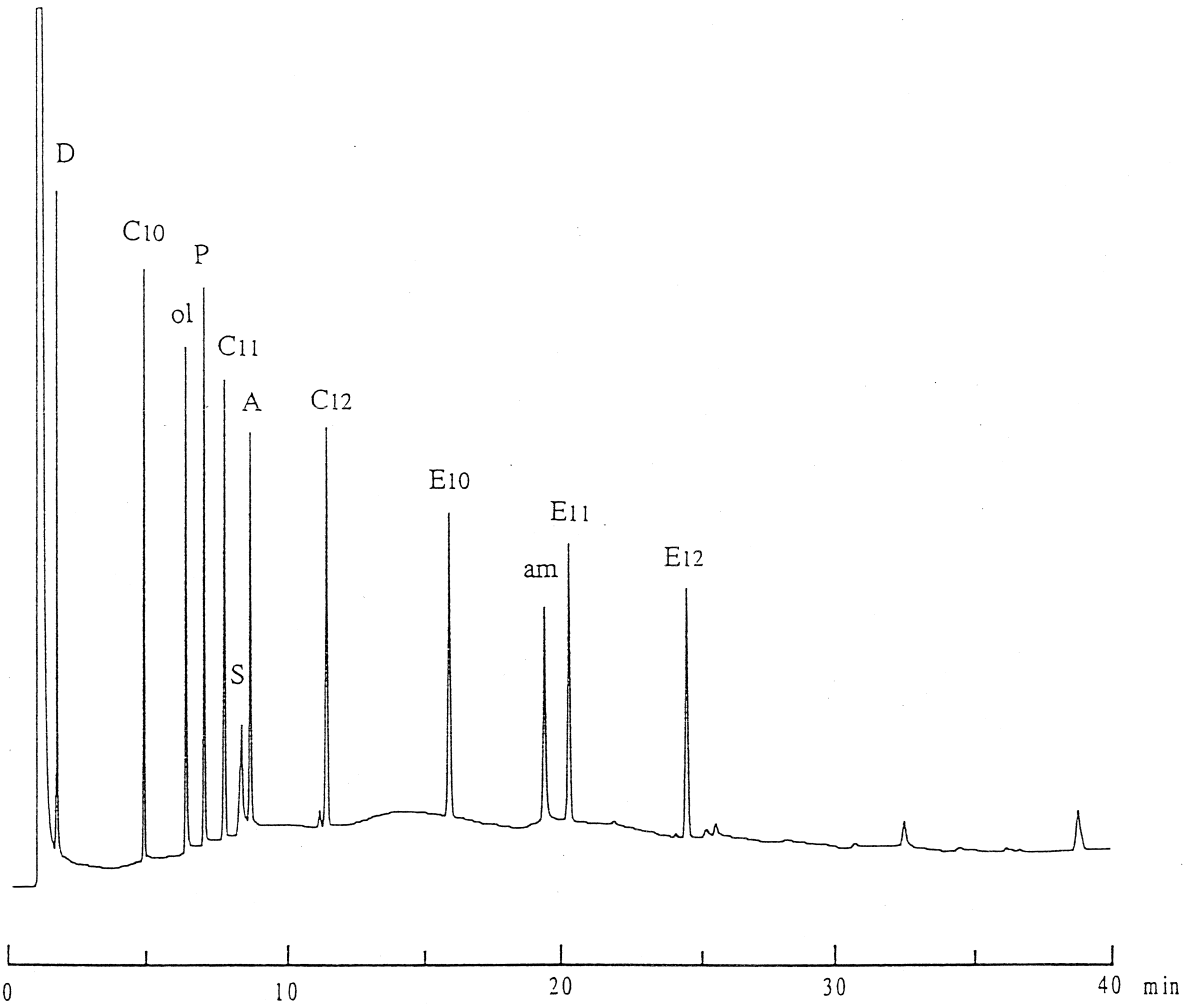

Fig. 4. Chromatogram of test mixture on a pre-column coated with OV-1. Test parameters: initial oven temperature, 60°C; programming rate, 3°C/min; nitrogen flow-rate, 40 cm/s; sample volume, 1 μl.

stainless steel plate was carried out as follows. The washed stainless steel plates were immersed in PSZ solution and dried at room temperature, followed by heating at 500°C for 2 h under a nitrogen atmosphere or in air. After the heat treatment, the SUS plate was cut into 5 mm×5 mm pieces, and washed with acetone to remove any organics attached on the surface using supersonic bath. The depth profile of the coating layer by Auger electron spectroscopy was measured with a JEOL JAMP-7800 with an etching speed of 20 nm/min.

3. Results and discussion

3.1. Characterization of pyrolyzed PSZ on SUS plates

PSZ is a class of inorganic polymer that forms silica on heating in air. The progress of the pyrolysis was studied by infrared spectroscopy (IR). With the increase of pyrolyzing temperature, the absorptions of Si–H, Si–N and N–H decreased, and the absorption of Si–O increased. Even the pyrolysis at 350°C

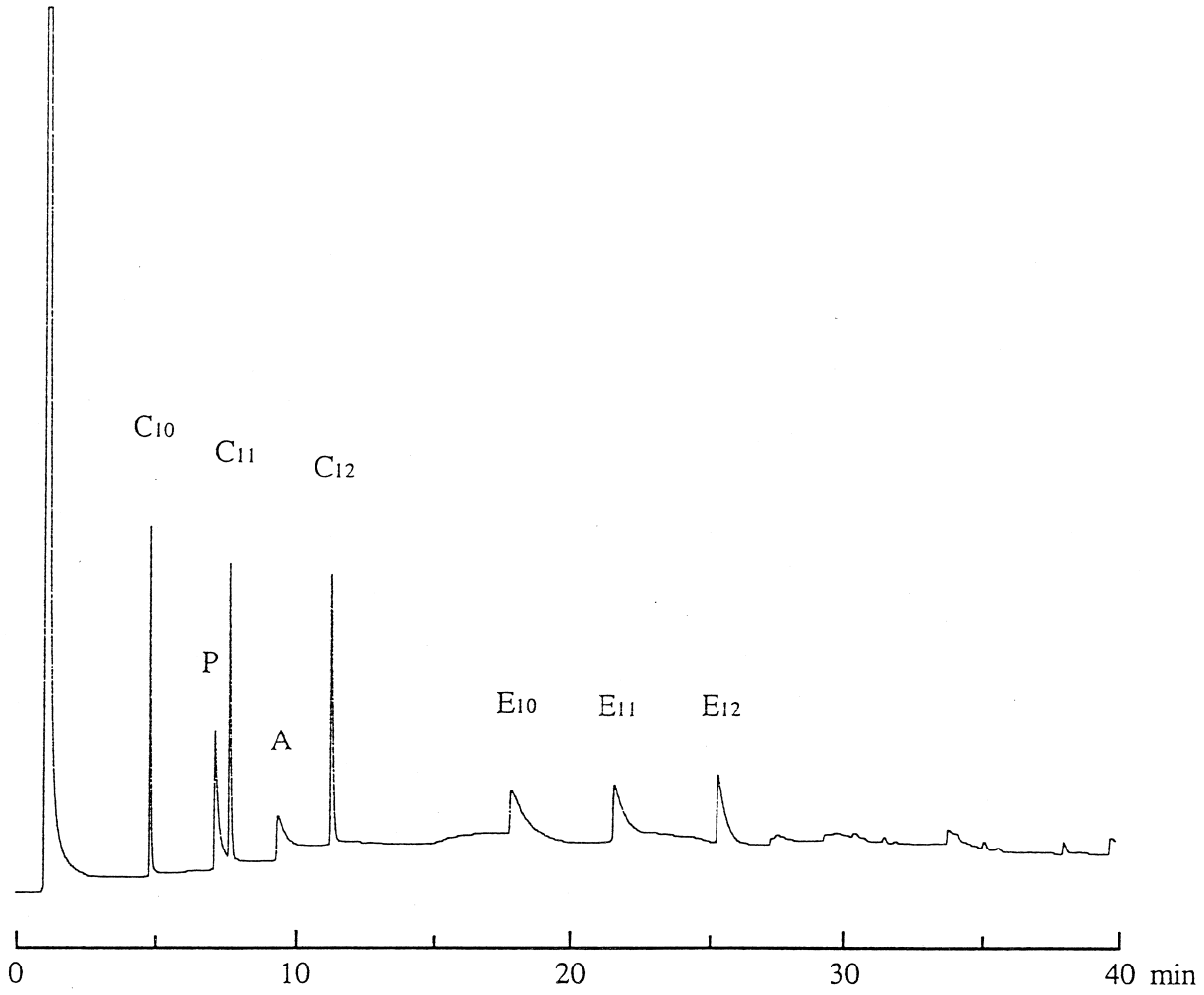

Fig. 5. Polarity test chromatogram of PSZ treated glass capillary with a pre-column of OV-1. Test parameters: see Fig. 4.

is not enough to completely pyrolyze PSZ, and heat treatment above 350°C is necessary. The pyrolysis at 450°C was enough to completely convert to silica.

If a dense silica layer is formed by the pyrolysis and if the silica layer is tightly adhered to a metal surface, deactivation of a metal capillary will be achieved. Characterization inside a capillary, however, is not easy. Therefore, before coating PSZ inside a metal capillary, PSZ was coated on a stainless steel (SUS) plate to examine the pyrolysis of PSZ on a metal surface, to characterize the pyrolyzed PSZ, and to evaluate how tightly the silica layer attaches to the metal surface.

A SUS plate was immersed in a *m*-xylene solution of PSZ and the dried plate was pyrolyzed at 250 and 400°C in air. To evaluate how tightly the silica layer attaches to the metal surface, the SUS plate was bent into circle of 2.5 cm in diameter. SEM observation before and after bending was performed. The surface of 250°C pyrolyzed film and also 400°C pyrolyzed film looked smooth, showing that the pyrolysis of coated PSZ gave flat and dense silica film. Formation of cracks, however, was observed for the 250°C pyrolyzed film after the bending, suggesting that the interface between the SUS and the pyrolyzed PSZ is not strong enough by the 250°C pyrolysis. After 400°C treatment for 2 h in air, cracks were not observed at all even after the bending, showing that the interface became strong enough.

To characterize the change of surface with the heat

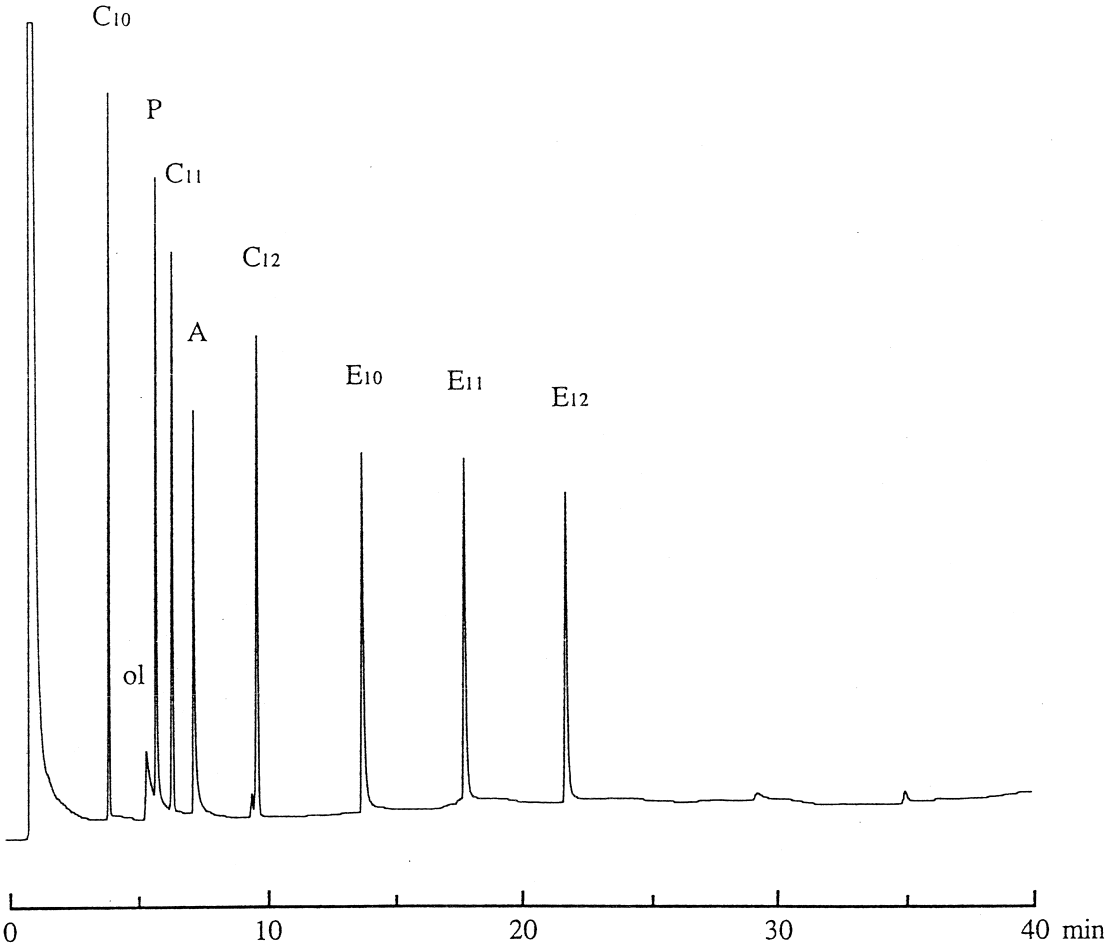

Fig. 6. Polarity test chromatogram of D4 treated glass capillary with a pre-column of OV-1. Test parameters: see Fig. 4.

treatment, contact angles of the metal surfaces were measured and surface free energy was calculated. The results are summarized in Table 2. The surface of the original SUS plate was non-polar and the polar component of the surface free energy, γ_S^P, was as low as $9.0 \cdot 10^2$ N m^{-1}. By oxidizing the SUS plate, the polar component increased to $22.2 \cdot 10^2$ N m^{-1}. The metal plate coated with PSZ followed by pyrolysis at 250°C had higher polar component. After the pyrolysis at 400°C, the surface free energy and its components were almost the same as those of a quartz plate. These changes in surface energy are in a good agreement with the IR analyses that showed 250°C treatment is not enough to make PSZ to silica, but 400°C treatment converted PSZ completely to silica.

Oxidation of the SUS plate gave higher polar components of surface free energy, which suggests that wettability of PSZ on oxidized SUS is better than on original SUS. This means that oxidation before coating the PSZ should be preferable to coat PSZ on the metal surface homogeneously.

The depth profile of the coated film was analyzed using Auger electron spectroscopy. As shown in Fig. 2, the pyrolysis in nitrogen at 500°C for 2 h gave films consisting of only Si and N. Oxygen was not observed in the pyrolyzed PSZ layer. However, oxygen was observed at the interface of Fe and coated film, showing that the oxidized Fe surface existed. From the etching speed of 20 nm/min, the depth of oxidized layer was calculated to be ca. 0.2 μm. On the other hand, when the 500°C treatment

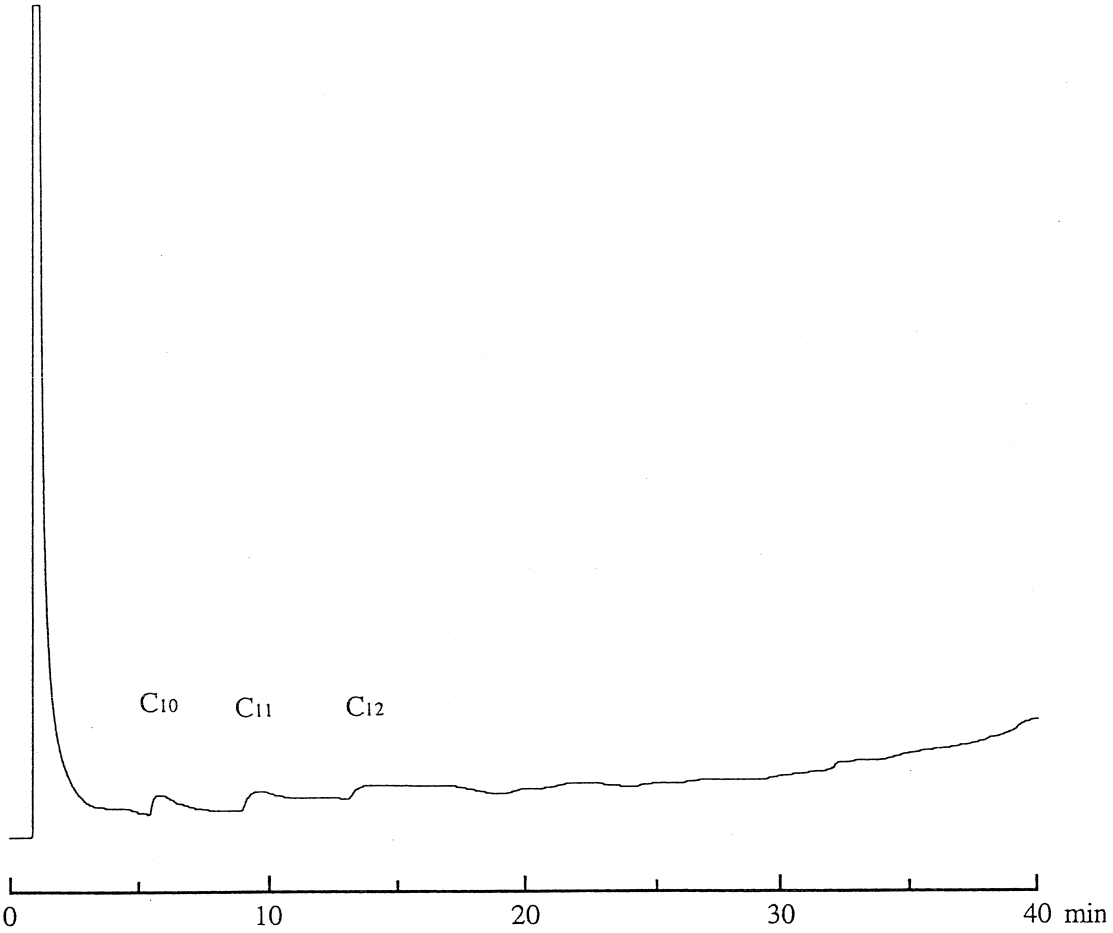

Fig. 7. Polarity test chromatogram of PSZ treated metal capillary with a pre-column of OV-1. Test parameters: see Fig. 4.

was performed in air for 2 h, as shown in Fig. 3, the main components of the coated layer are Si and O, suggesting that the coated layer changed to silica. No appreciable amount of N was observed, showing that nitrogen was completely removed from the film. The thickness of the layer was calculated to be ca. 0.4 μm from the etching speed.

3.2. Deactivation of glass capillaries with PSZ

To establish the condition to pyrolyze PSZ in capillaries, glass capillaries were employed first because they are easier to deactivate and easier to treat due to the visibility inside the capillaries. For each experiment, capillaries of 5 m long were used because a length of 5 m is enough to evaluate the degree of deactivation [1]. The degree of deactivation was examined using a pre-column coated with OV-1. The chromatogram of Grob's test samples for the pre-column is shown in Fig. 4.

The untreated glass capillaries were connected to the pre-column, and polarity test was performed. Only hydrocarbons eluted. When the glass capillaries were coated dynamically with PSZ followed by pyrolysis by passing oxygen, deactivation was accomplished to some extent as shown in Fig. 5, though the peaks other than hydrocarbons had tailing. This suggests that considerable amounts of silanol groups are present on the surface of pyrolyzed PSZ. The pyrolysis of PSZ under nitrogen atmosphere, however, gave a chromatogram similar to the untreated glass capillaries, suggesting that

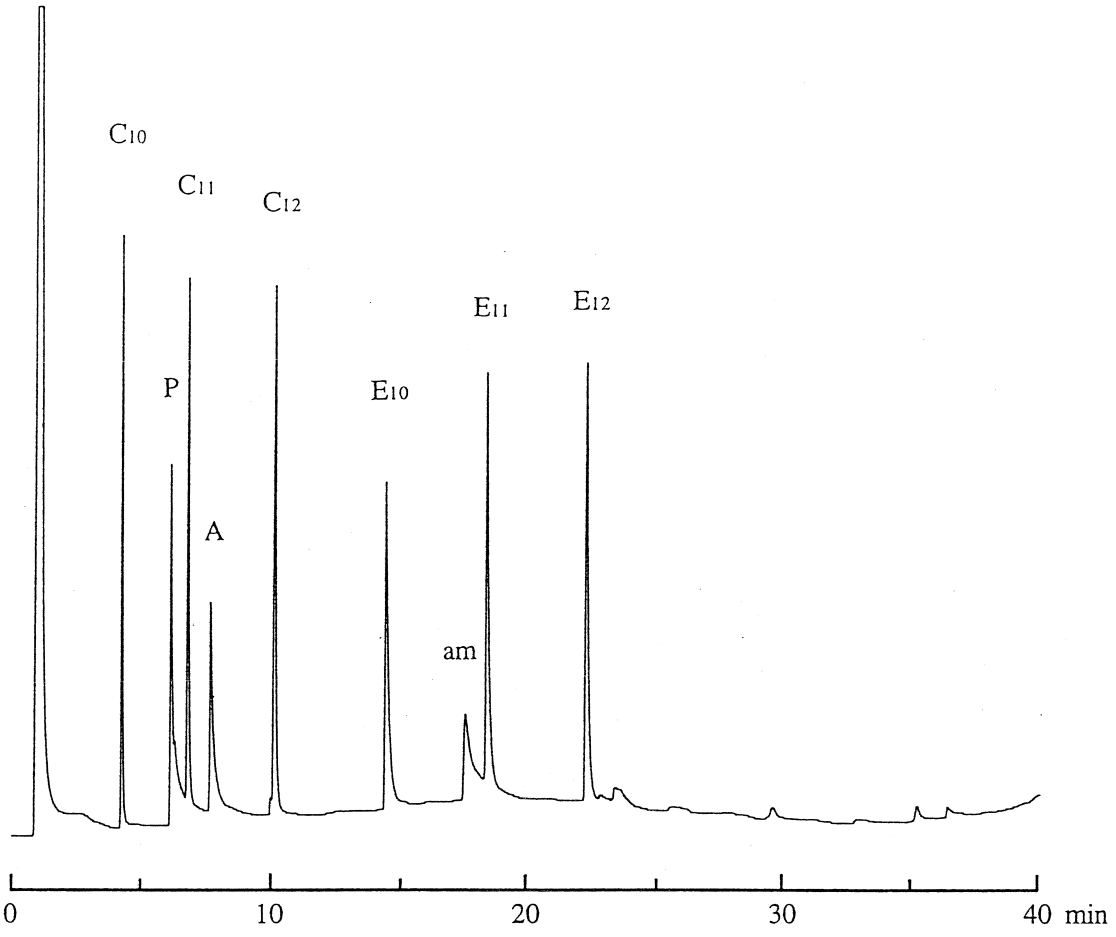

Fig. 8. Polarity test chromatogram of PSZ and D4 treated metal capillary with a pre-column of OV-1. Test parameters: see Fig. 4.

pyrolysis of PSZ under a nitrogen atmosphere gave an active ceramic surface for polar solutes.

D4 is known to deactivate glass surface by reacting with silanol groups on the glass surface. Thus, glass capillaries treated with PSZ in air were further treated with D4. As a result, the same chromatogram as that from head column (Fig. 4) was realized, which suggest that deactivation of glass capillaries was accomplished by treating with PSZ in air followed by treatment with D4. When D4 was directly coated on untreated glass capillaries, nine components out of 12 components eluted out (Fig. 6), showing that the deactivation was fairly good by the decrease of silanol groups on the untreated glass surface. However, elutions of ol and am are very poor with the direct D4 treatment, showing clearly the effect of PSZ treatment for those polar solutes.

3.3. Deactivation of metal capillaries with PSZ

Deactivation of glass capillaries being established using PSZ, deactivation of metal capillaries was examined. When the untreated metal capillaries were evaluated with polarity test, only broad peaks of hydrocarbons eluted with much delay, confirming the highly active surface of the metal. Even after the PSZ treatment on the metal capillaries, the chromatogram of polarity test only showed broad peaks of hydrocarbons, though the elution was in a normal time range (Fig. 7). After D4 treatment on the above

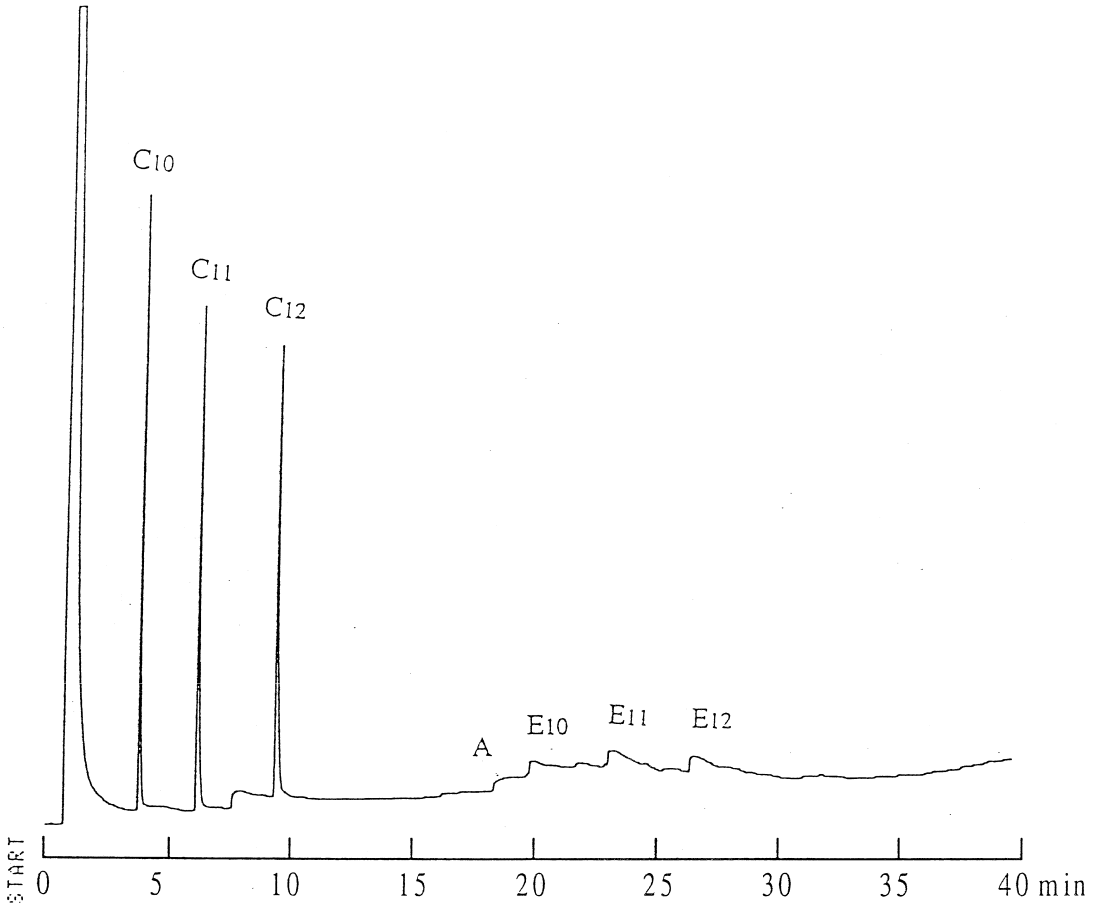

Fig. 9. Polarity test chromatogram of oxidized and PSZ treated (in air) metal capillary with a pre-column of OV-1. Test parameters: see Fig. 4.

PSZ treated metal capillaries, fairly good chromatogram was obtained as shown in Fig. 8. Still, ol did not elute and some polar solutes had tailing. D_4 treatment may not be sufficient.

The poor chromatogram of the metal capillaries that were treated with PSZ (Fig. 7) compared with the glass capillaries treated in the same way (Fig. 5) suggests the presence of pinholes in the metal capillaries due to the difference in wettability of the capillaries.

To establish a deactivation method using PSZ, pretreatment was examined. As pointed out from the surface free energy of the SUS plate, oxidation should have favorable effect on the wettability. Acid washing also is preferable to give deactivated metal capillaries having reproducible and constant quality. The criterion for the acid washing is that if dark green colored impurities were washed out or not from the provided metal capillaries. A chromatogram for metal capillaries treated with PSZ after acid washing and oxidation is shown in Fig. 9. The comparison of Fig. 9 (with oxidation) and Fig. 7 (without oxidation) clearly shows the effect of pretreatment. The chromatogram of Fig. 9 is almost the same as that obtained from glass capillaries treated with PSZ in air (Fig. 5). Thus, deactivation of metal capillaries will be accomplished using pyrolysis of PSZ, by combining pre-treatment and post-treatment for silanol elimination with D4 or others.

4. Conclusion

A hopeful and prospect novel deactivation method of metal capillaries was established. The key step for the deactivation is the pyrolysis of PSZ into amorphous silica. Pre-treatment including oxidation before PSZ coating was found to be important to give deactivated metal capillaries steadily having constant quality. Since the silica is highly thermally stable, the thermal stability of the deactivated metal capillaries should be very high.

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References

[1] Y. Takayama, T. Takeichi, J. Chromatogr. A 685 (1994) 61.
[2] O. Funayama, M. Arai, Y. Tashiro, H. Aoki, T. Suzuki, K. Tamura, H. Kaya, H. Nishii, T. Isoda, Nippon Seramikkusu Kyokai Gakujutu Ronbunshi 98 (1990) 104.
[3] Y. Yokoyama, T. Nanba, I. Yasui, H. Kaya, T. Maeshima, T. Isoda, J. Am. Ceram. Soc. 74 (1991) 654.
[4] O. Funayama, T. Isoda, H. Kaya, T. Suzuki, Y. Tashiro, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem. 32 (1991) 542.
[5] K. Grob, G. Grob, J. High Resolut. Chromatogr. Chromatogr. Commun. 2 (1979) 31.
[6] K. Grob, G. Grob, J. High Resolut. Chromatogr. Chromatogr. Commun. 1 (1978) 302.
[7] Y. Yamada, M. Yamada, T. Kimura, T. Izumi, M. Hirata, Nippon Kagaku Kaishi 1 (1989) 105.
[8] M. Zuo, T. Takeichi, A. Matsumoto, K. Tsutsumi, Colloid Polym. Sci. 276 (1998) 555.
[9] D.H. Kaelble, Physical Chemistry of Adhesion, Wiley-Interscience, New York, 1970, Ch. 5.
[10] K. Tsutsumi, S. Ishida, K. Shibata, Colloid Polym. Sci. 269 (1990) 31.