Decomposition of Trichloroethylene by Microwave-Induced Ar Plasma Generated from SiC Ceramics under Atmospheric Pressure

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Behavior of microwave-induced Ar plasma generated from SiC ceramics under atmospheric pressure in different flowing gas mixtures and decomposition behavior of trichloroethylene by the microwave-induced Ar plasma have been investigated systematically. Although the behavior of the microwave-induced Ar plasma was varied with the composition of the flowing gas mixture, the plasma could be generated even in the flowing Ar containing 0.64% trichloroethylene and 9.0% O₂. In addition, 0.64% trichloroethylene balanced with Ar at a flow rate of 500 cm³ min⁻¹ could be completely decomposed by the addition of 9.0% O₂ by means of the microwave-induced Ar plasma of a power above 90 W, without producing any partial decomposition products as well as CO. In contrast, a large amount of CO was formed by thermal decomposition of trichloroethylene even at a temperature as high as 900°C. Therefore, the decomposition by the Ar plasma is confirmed to offer several advantages, compared with the thermal decomposition, with respect to complete oxidation, concentration of partial decomposition products and energy efficiency.

1 INTRODUCTION

Much attention has been denoted to effective decomposition of gaseous pollutants, such as chlorofluorocarbons, carbon tetrachloride and trichloroethylene, by plasma chemical processing from the viewpoint of global environmental issues.¹⁻⁶⁾ To decompose these pollutants in large quantities, stable plasma should be generated under an atmospheric environment, but this requires relatively high power of several tens kV. Under a reduced environment, such stable plasma can be generated with relatively low power. However, a large vacuum facility is indispensable, and such process limits decomposition

efficiency. To realize further expansion of this plasma chemical processing in decomposing these pollutants, therefore, improvement of the energy efficiency for the plasma generation under an atmospheric environment is of importance.

We found that white and woolly β -SiC whiskers fabricated by thermal decomposition of sulfur-containing silicon oils exhibited amazingly high electrical conductivity in the range of 10²-10³ S cm⁻¹ at room temperature.⁷⁾ These whiskers were red heated and then emitted N₂ plasma discharge in flowing air under atmospheric pressure upon irradiation of 2.45 GHz microwave. Then, fluorocarbons and trichloroethylene could be decomposed by such microwave-induced (MI) N₂ plasma under atmospheric pressure.^{7,8)} However, the contribution of the thermal decomposition over the heated whiskers was suggested to be significant under MI N₂ plasma in air. In contrast, a strong bluish Ar plasma streak was generated from the whiskers upon irradiation of microwave under flowing Ar under atmospheric pressure without being red heated. Our additional

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study has revealed that the MI Ar plasma was more advantageous in decomposing trichloroethylene with less partial decomposition products than the MI N₂ plasma.⁹⁾ However, no systematic study was carried out with respect to the effects of the trichloroethylene, oxygen and water vapor contents in the Ar flowing on the decomposition behavior.

The present study explores first the ability of SiC ceramics for generating MI Ar plasma under atmospheric pressure. Then, the performance of the MI Ar plasma for the decomposition of trichloroethylene was evaluated under different concentrations of trichloroethylene, oxygen and water vapor.

2 EXPERIMENTAL

2.1 Generation and characterization of MI Ar plasma

A microwave power generator (MR-200, Unidux), capable of modulating the output power from 15 to 200 W at 2.45 GHz, equipped with a box cavity was used as a microwave source. SiC ceramic pieces prepared by crushing a siliconit heating element (Siliconit Konetsu Kogyo Co., Ltd) were used as a trigger of the MI Ar plasma. Several pieces of the SiC ceramics of 2-3 mm in size were set in a quartz glass tube (12 mm in diameter) in an atmospheric flow apparatus located in the cavity. The emission spectrum of the MI Ar plasma in the flowing Ar containing 0.11% trichloroethylene at a flow rate of 500 cm³ min⁻¹ was analyzed by Multi Channel Photo Detector (MCPD-1000, Otsuka Electronics). The effect of the addition of oxygen and water vapor on the MI Ar plasma behavior was also examined at a total flow rate of 500 cm³ min⁻¹.

2.2 Decomposition of trichloroethylene by MI Ar plasma

Decomposition behavior of trichloroethylene was measured under atmospheric pressure by employing the same flow apparatus as above. A gaseous mixture of trichloroethylene, oxygen and water vapor balanced with Ar was fed at a flow rate of 500 cm³ min⁻¹ to the quartz glass tube located in the cavity. The composition of the feed gas was 0.11-0.64% trichloroethylene, 0-9.0% O₂ and 0-0.77% H₂O. Variations in conversion of trichloroethylene and in concentration of partial decomposition products with the microwave power consumed were analyzed by gas chromatography (GC-14B, Shimadzu) and gas chromatography-mass spectroscopy (QP-5000, Shimadzu).

Fig. 1 Photographs of MI Ar plasma generated from SiC ceramics in (a) flowing Ar containing 0.11% trichloroethylene (basic flowing), (b) basic flowing plus 3.0% O₂, and (c) basic flowing plus 0.38% water vapor (microwave power: 100 W).

2.3 Thermal decomposition of trichloroethylene

For comparative purpose, thermal decomposition of trichloroethylene was conducted by employing the same flow apparatus and under the same flow condition. The gas composition after the thermal decomposition over the SiC ceramics heated by an electric furnace was analyzed. The effect of the oxygen and water vapor addition was also tested.

3 RESULTS AND DISCUSSION

3.1 Characterization of MI Ar plasma generated from SiC ceramics

A streak of a strong, long and narrow bluish white light, like phosphorescence, was observed in the downstream from the SiC ceramics upon irradiation of microwave in flowing pure Ar, as reported for the case using SiC whiskers as the trigger.^{8,9)} A streak of light

could also be generated from the SiC ceramics even in the flowing Ar containing 0.11% trichloroethylene, as shown in Fig. 1(a). Hereafter this flowing will be referred as the basic flowing. The streak was generated when the microwave power absorbed by the SiC ceramics was beyond a threshold value, which was dependent on the surrounding atmosphere. Length of the streak was about 8 cm under the condition of the present study, but the color was rather greenish compared with that in the pure flowing Ar. The emission spectrum measured in the basic flowing is shown in Fig. 2(a). A lot of sharp peaks observed in the range of 700–850 nm were all assigned to the emission peaks of Ar atoms based on the 4s–4p electron transition. Thus, the streak of light is confirmed to be the MI Ar plasma. This fact confirms again our previous finding⁹⁾ that materials exhibiting high electrical conductivity generate MI Ar plasma, and that the MI Ar plasma can be maintained even in an atmosphere containing gases which have a tendency to produce negative ions upon decomposition. Additional peaks were observed in the range of 300–550 nm and were assigned to emission peaks of C atoms, as shown in Fig. 2(a). This fact suggests that trichloroethylene can be decomposed to constituent atoms in the MI Ar plasma. Since O₂ was not involved in the basic flowing, formation of soot was observed in the downstream of the MI Ar plasma after the decomposition of trichloroethylene in the flowing Ar.

Color of the MI Ar plasma streak became reddish and length of the streak was shortened by the addition of 3.0% O₂ to the basic flowing, as shown in Fig. 1(b). Besides the emission peaks of Ar atoms, a sharp peak around 777 nm was newly observed in the spectrum of the plasma, as shown in Fig. 2(b), and was assigned to an emission peak of O atoms. Furthermore, emission peaks of C atoms were disappeared, suggesting the oxidation of C atoms in the presence of O₂.

Addition of 0.38% water vapor, instead of 3.0% O₂, to the basic flowing highlighted bluish color of the MI Ar plasma. In contrast to the case of O₂, the length of the MI plasma streak remained almost unchanged by the addition of 0.38% water vapor, as shown in Fig. 1(c). Under this condition, intensity of emission peaks of C atoms became lower than those in Fig. 2(a), but the emission peak of O atoms could not be observed, as shown in Fig. 2(c). These results imply that water vapor in the MI Ar plasma acts as a source

Fig. 2 Spectra of MI Ar plasma generated from SiC ceramics in (a) flowing Ar containing 0.11% trichloroethylene (basic flowing), (b) basic flowing plus 3.0% O₂, and (c) basic flowing plus 0.38% water vapor (microwave power: 100 W).

of O atoms to oxidize C atoms, but as a weak oxidizing agent.

The length of the MI Ar plasma streak decreased to about 4 cm with the addition of 9.0% O₂ to the basic flowing. Similar behavior was observed with increasing the concentration of trichloroethylene in the basic flowing. Such a phenomenon is undoubtedly caused by shorter lifetime of the MI Ar plasma under higher concentration of negative ions. Nevertheless, a MI Ar plasma streak of about 3 cm in length could be generated even in the flowing Ar containing 0.64% trichloroethylene and 9.0% O₂.

Fig. 3 Variations in (a) conversion of trichloroethylene and in (b) and (c) concentration of partial decomposition products in the MI Ar plasma decomposition with the microwave power absorbed (feed gas: flowing Ar containing 0.11% trichloroethylene and 3.0% O₂).

3.2 Decomposition of trichloroethylene by MI Ar plasma

3.2.1 Decomposition behavior of trichloroethylene under an atmosphere containing O₂

Flowing Ar containing 0.11% trichloroethylene and 3.0% O₂ was first used as a feed gas. Figure 3 shows variations in conversion of trichloroethylene and in concentration of partial decomposition products with the microwave power absorbed. Although the MI Ar plasma streak could not be generated in the microwave power range of 20–40 W, the conversion increased gradually with an increase in the microwave power, as shown in Fig. 3. Under this feed gas flowing, the MI Ar plasma streak started to generate at a microwave power of 50 W, and then the conversion abruptly attained 100%. The plasma streak and the 100% conversion level held at the powers higher than above 50 W. The concentration of partial oxidation and decomposition products, such as CO, COCl₂, CCl₄ and C₂Cl₄, reached their maxima at 50 W, and then

Fig. 4 Variations in (a) conversion of trichloroethylene and in (b) and (c) concentration of partial decomposition products in the MI Ar plasma decomposition with the microwave power absorbed (feed gas: flowing Ar containing 0.11% trichloroethylene and 9.0% O₂).

decreased with increasing the microwave power, as shown in Figs. 3(b) and 3(c). On the other hand, the concentration of CO₂ increased with an increase in the microwave power above 40 W, and then reached an almost steady-state value above 90 W. The concentration of CCl₄, C₂Cl₄, and COCl₂ became negligibly small above 80 W, but a small amount of CO was detected even at a power as high as 90 W. Thus, it is revealed that the 3.0% O₂ addition is not enough to achieve complete oxidation of trichloroethylene under the present experimental conditions.

Addition of 9.0% O₂ led to an improvement in decomposition behavior of trichloroethylene, as shown in Fig. 4. The MI Ar plasma could be generated above 50 W, irrespective of the higher O₂ concentration. The concentration of CO₂ reached a steady-state value and CO was rarely detected above 60 W, while the concentration of CO reached its maximum at 40 W, as shown in Fig. 4(b). In addition, other partial decomposition products were not detected above 70 W,

Fig. 5 Variations in (a) conversion of trichloroethylene and in (b) and (c) concentration of partial decomposition products in the MI Ar plasma decomposition with the microwave power absorbed (feed gas: flowing Ar containing 0.11% trichloroethylene and 0.38% H_2O).

as shown in Fig. 4(c). Thus, it is confirmed that trichloroethylene can be decomposed completely by the MI Ar plasma of a microwave power higher than 70 W under the flowing Ar containing 0.11% trichloroethylene and 9.0% O_2 .

3.2.2 Decomposition behavior of trichloroethylene under an atmosphere containing water vapor

In contrast to the above two cases, the MI Ar plasma streak could be generated upon irradiation of a microwave power as low as 20 W under the flowing Ar containing 0.11% trichloroethylene and 0.38% water vapor. However, the conversion was very low at 20 W, as shown in Fig. 5(a). The conversion increased gradually with increasing the microwave power, and then reached almost 100% at 60 W. A large amount of CO was produced and formation of CO_2 was rarely found even at the 100% conversion level, as shown in Fig. 5(b). These results confirm again that water vapor acts as a weak oxidizing agent in the MI Ar plasma. However, it was found that the concentration of partial decomposition products was lower than that shown in Fig. 3 or 4. Especially, formation of C_2Cl_4 was rarely observed in the whole range of the microwave power tested, as shown in Fig. 5(c). Water vapor might accelerate the oxidation of the partial decomposition products or promote a different decomposition route of trichloroethylene. Another possibility is that partial decomposition

Table 1 Decomposition behavior of trichloroethylene (TCE).

Method	No.	Concentration(%)			MW power for 100% conversion of TCE (W)	Complete oxidation (no CO)	Maximum concentration of COCl_2 (ppm)	MW power for 5 ppm decomposition products (W)
		TCE	O_2	H_2O				
Plasma	1	0.11	3.0	0	50	No	65 (50 W)	> 80
	2	0.11	9.0	0	50	Yes (> 60 W)	50 (50 W)	> 70
	3	0.11	0	0.38	62	No	25 (50 W)	63
	4	0.11	0	0.77	70	No	12 (50 W)	> 75
	5	0.11	3.0	0.38	50	Yes (> 80 W)	80 (60 W)	> 80
	6	0.23	9.0	0	60	Yes (> 100 W)	210 (50 W)	80
	7	0.64	9.0	0	60	Yes (> 90 W)	245 (60 W)	80
Thermal	8	0.11	3.0	0	50 ¹⁾ (680°C)	No	200 (60 W)	100
	9	0.11	0	0.38	93 ¹⁾ (930°C)	No	4 (70 W)	102

1) Electric power consumed by electric furnace.

Fig. 6 Variations in (a) conversion of trichloroethylene and in (b) and (c) concentration of partial decomposition products in the MI Ar plasma decomposition with the microwave power absorbed (feed gas: flowing Ar containing 0.11% trichloroethylene, 3.0% O₂ and 0.38% H₂O).

products likely dissolve in water condensed at some parts in the flow apparatus, though the details are not clear at present.

Almost the same results as above were obtained when the concentration of water vapor was increased to 0.77%. Typical features of the decomposition behavior of trichloroethylene under this condition are summarized in Table 1. Results obtained under other decomposition conditions are also summarized for easy comparison. The conversion reached 100% at a high microwave power of 70 W, but a large amount of CO (about 0.18%) was detected. The concentration of partial decomposition products became lower at a microwave power of 50 W than other conditions: the maximum COCl₂ concentration was 12 ppm at 50 W. Therefore, the addition of water vapor alone is found not to be enough for achieving the complete oxidation of trichloroethylene.

3.2.3 Decomposition behavior of trichloroethylene under an atmosphere containing O₂ and

Fig. 7 Variations in (a) conversion of trichloroethylene and in (b) and (c) concentration of partial decomposition products in the MI Ar plasma decomposition with the microwave power absorbed (feed gas: flowing Ar containing 0.64% trichloroethylene and 9.0% O₂).

water vapor

Figure 6 shows decomposition behavior of trichloroethylene under the flowing Ar containing both 3.0% O₂ and 0.38% water vapor. The simultaneous addition of water vapor and oxygen did not effect significantly on the decomposition behavior, as compared with Fig. 3, the concentration of partial decomposition products being at a high level. Thus, the decomposition behavior could not be improved by the simultaneous addition of oxygen and water vapor.

3.2.4 Decomposition behavior at a high trichloroethylene concentration level

As summarized in Table 1, 0.23% and 0.64% trichloroethylene could be decomposed completely above 100 W, provided that the flowing Ar contained 9.0% O₂. No CO and partial decomposition products were observed above 90 W, in spite of the high trichloroethylene concentration, as typically shown in Fig. 7. A common feature observed with the high trichloroethylene concentration is the formation of

Fig. 8 Thermal decomposition behavior of trichloroethylene over SiC ceramics. (a) Conversion of trichloroethylene and in (b) and (c) concentration of partial decomposition products of trichloroethylene (feed gas: flowing Ar containing 0.11% trichloroethylene and 3.0% O₂).

partial decomposition products in large quantities around a microwave power of 50-60 W. This tendency was further pronounced when only 3.0% O₂ was added to the flowing Ar, though the data were not cited in Table 1. If the microwave power is high and enough oxygen is added to the flowing Ar, however, it is confirmed that the high trichloroethylene concentration can be completely decomposed by the MI Ar plasma.

3.2.5 Thermal decomposition of trichloroethylene

Conversion of trichloroethylene and concentration of partial decomposition products after thermal decomposition over SiC ceramics are plotted against the power consumed by the electric furnace used for heating the ceramics, as shown in Fig. 8. Since the temperature of the decomposition zone is a function of several factors, such as the size of the furnace, the flow rate of gases and so on, it is difficult to directly

compare the power consumption between the thermal decomposition and the MI Ar plasma decomposition. However, the power consumed by the furnace and the temperature of the furnace attained are indicated in the lower and upper abscissa, respectively, for reference. In this case, the conversion reached almost 100% at a power consumption of 50 W, i.e. around 700°C. In contrast to the case of the MI Ar plasma decomposition shown in Fig. 3, a large amount of CO was produced by the thermal decomposition, and only a small amount of CO₂ was produced. It was also revealed that considerable amounts of partial decomposition products were formed by the thermal decomposition. When 0.38% water vapor was added, instead of 3.0% O₂, much higher electric power (about 90 W) was necessary to achieve 100% conversion, as summarized in Table 1. Even at a 100% conversion level, about 0.2% CO was produced and no CO₂ was observed, whereas the concentration of partial decomposition products was less than 1 ppm. These results confirm the potential advantage of the MI Ar plasma generated from SiC ceramics for decomposing trichloroethylene under atmospheric pressure with relatively low energy consumption.

4 CONCLUSION

It was confirmed that MI Ar plasma could be generated from SiC ceramics in flowing Ar containing trichloroethylene, oxygen and/or water vapor under atmospheric pressure. The analysis of decomposition behavior has revealed that trichloroethylene could be completely decomposed by the MI Ar plasma in the flowing Ar containing an appropriate amount of oxygen. In addition, 0.64% trichloroethylene balanced with Ar at a flow rate of 500 cm³ min⁻¹ could be completely decomposed by the addition of 9.0% O₂ upon irradiation of microwave higher than 90 W, without producing any partial decomposition products as well as CO. In contrast, a large amount of CO was formed by the thermal decomposition of trichloroethylene even at a temperature as high as 900°C. Thus, the decomposition by the MI Ar plasma is confirmed to offer several advantages, compared with the thermal decomposition, with respect to complete oxidation, concentration of partial decomposition products and energy efficiency. Since the MI Ar plasmas generated in this study was a streak like and was not spread out in the quartz glass tube, it is anticipated that the gaseous molecules of trichloro-

ethylene are not enough in contact with the MI Ar plasma. Therefore, further improvement in decomposition efficiency is possible by controlling the MI Ar plasma condition in future.

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