Research Paper

Nitritization of Zirconium Silicate by Means of Nitrogen Plasma Jet*

Osamu MATSUMOTO and Yoshiaki SHIRATO

(Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Megurisawa, Setagaya-ku, Tokyo)

(Received Nov. 21, 1969)

The nitritization of zirconium silicate by means of nitrogen plasma jet was studied. The plasma jet was produced by passing nitrogen at ordinary pressure through an electric arc discharged between a graphite anode and a tungsten rod cathode. The nitrogen plasma jet is supposed to consist mainly atomic nitrogen by the spectrum observation. The nitrogen plasma jet reacted rapidly with a pellet made of zirconium silicate and graphite powder that was placed on the anode. Metallic cake was formed on the graphite anode and yellow powder was deposited on the coil placed over the anode. X-ray diffraction patterns, chemical analysis, infrared absorption spectra and electron diffraction patterns showed that the cake was ZrN, ZrC and SiC and the powder was silicon oxide, silicon nitride and silicon carbide. From thermodynamic analysis and experimental results, the nitriding of zirconium silicate may be carried out as follows:

1 Introduction

The authors have studied nitridings of Al_2O_3 ¹⁾, TiO_2 ²⁾, and ZrO_2 ³⁾ by reactions between corresponding oxides pellets made by mixing with carbon and the nitrogen plasma jet by the use of a transferred type plasma torch.

This paper deals with the results on the nitriding of zirconium silicate by the reaction between a pellet of zirconium silicate-graphite mixture and the nitrogen plasma jet conducted in same way.

The formation of zirconium carbide by a carbonization of zirconium silicate was studied by Kroll⁴⁾. It was carried out by the reaction as follows:

2 Experimentals

Materials: The pellet of 15 mm in diameter and 3 mm thickness was made by the following way. ZrSiO_4 (calcined at 1100°C, ZrO_2 67.2% and SiO_2 32.9%) and graphite powder were mixed in estimated ratio. 1 g of mixed powder was pressed using propylene glycol as binder and was baked at 1100°C, in a reducing atmosphere provided by a graphite powder packing.

Nitrogen and argon of high purity were used.

Apparatus: The apparatus used for the reaction was described previously¹⁾. Spectrum of the nitrogen plasma jet was taken by the use of a grating

spectrograph made by Mizojiri Kogaku Co.. An intensity of the spectrum was measured by Type 7 microphotometer made by Shimazu Seisakusho Ltd.

Methods: The method of the nitriding of zirconium silicate was carried out in the same way as that reported previously¹⁾.

The identification of the products was made by means of chemical analysis, X-ray diffraction method, electron diffraction method and infrared absorption method.

3 Results and Discussion

3.1 Consideration of the nitrogen plasma jet

The spectrum of the nitrogen plasma jet that bombarding the pellet of ZrSiO_4 -graphite mixture was taken. The intensity of the spectrum was measured by means of the microphotometer. Spectrogram obtained are shown in Fig. 1.

The spectrum lines based on N and N^+ are observed in the range of wave length between 4000 Å and 5000 Å. The spectrum line based on O is also observed in the range of wave length between 7500 Å and 8500 Å.

N and N^+ may be formed by the decomposition and the ionization of nitrogen in the nitrogen plasma jet. The temperature of the nitrogen plasma jet was determined by the two lines radiance ratio method. The intensities of two lines of atomic nitrogen at 4100 Å and 4935 Å were measured and

* Studies of Chemical Reaction at High Temperature (Part 11)

Reported on 3rd Symposium of Fused Salt Chemistry (held on Nov. 14, 1969 at Osaka)

Scherrer pattern and Photo. 2 is a Laue pattern. From Photo. 1, the powder is identified as silicon. From Photo. 2, its crystal structure is a hexagonal and is identified as β -quartz or α -SiC.

From the infrared absorption spectra and the electron diffraction patterns, the powder deposited on the coil may be fine crystals that have Si-O, Si-N and Si-C bonds.

3.3 Reaction temperature measurement

A surface temperature of ZrSiO_4 -graphite mixture pellet reacting with the nitrogen plasma jet was measured with a micropyrometer. The relation between the temperature of the surface of the pellet and the current intensity is shown in Fig. 4. The surface temperature was higher than a decomposition point of ZrSiO_4 at the current intensity of 50 A. The temperature elevated with increasing current intensity. When the current intensity came up to higher than 80 A, the surface temperature was higher than the melting point of ZrO_2 .

Fig. 4 Surface temperature of the pellet vs. current intensity

3.4 Influences of various conditions on the reaction

The influences of the mixing molar ratio of carbon to ZrSiO_4 , the current intensity, N_2 flow rate and the reaction time on the reaction were studied. As a degree of the reaction, a zirconium conversion rate (Zr C.R.) that is defined as follows is used.

$$\text{Zr C.R.} = \frac{\text{Zr as ZrN in product (g)}}{\text{Zr as ZrSiO}_4 \text{ in original pellet (g)}} \times 100 (\%)$$

(a) Influence of the mixing molar ratio of carbon to ZrSiO_4 (C/ZrSiO_4): The chemical analysis data of the products on the graphite anode are listed in Table 1. Nitrogen contents increased with increasing C/ZrSiO_4 and was maximum at $\text{C}/\text{ZrSiO}_4 = 3$. When C/ZrSiO_4 exceeded 3, nitrogen content decreased with increasing C/ZrSiO_4 . The carbon content increased with increasing C/ZrSiO_4 .

Table 1 Chemical analysis data of products on the graphite anode by various C/ZrSiO_4

C/ZrSiO_4	N content (%)	C content as ZrC (%)	C content as SiC (%)	Free C content (%)
0	0.17	—	—	—
1	1.03	0.41	0.05	0.52
2	1.66	0.73	0.01	0.52
3	6.72	1.51	0.53	0.56
4	4.41	3.34	0.64	0.60
5	1.90	5.95	3.88	1.77
6	1.20	7.46	4.80	6.90

Reaction conditions: 80 A, N_2 flow rate 3 l/min, 1 min.

Table 2 X-ray diffraction data of products on the graphite anode by various C/ZrSiO_4

C/ZrSiO_4	Identified compounds	a_0 of fcc (Å)
0	$\text{ZrO}_2(m)^*$	—
1	$\text{ZrO}_2(m)$, ZrN	—
2	$\text{ZrO}_2(m)$, ZrN	4.566
3	ZrN	4.587
4	ZrN-ZrC	4.643
5	ZrC, β -SiC	4.674
6	ZrC, β -SiC	4.704

* $\text{ZrO}_2(m)$: monoclinic ZrO_2

X-ray diffraction data of the products on the graphite anode are listed in Table 2. When C/ZrSiO_4 was smaller than 3, ZrO_2 was also formed with ZrN. When C/ZrSiO_4 was 3, the product was almost ZrN. A solid solution of ZrN and ZrC was formed at $\text{C}/\text{ZrSiO}_4 = 4$. When C/ZrSiO_4 exceeded 5, the product was ZrC including SiC.

The chemical analysis data of the powder deposited on the coil are listed in Table 3. Nitrogen content was maximum at $\text{C}/\text{ZrSiO}_4 = 3$. Carbon content was increased with increasing C/ZrSiO_4 . It was amorphous by X-ray diffraction.

The infrared absorption spectra of the powder obtained by various C/ZrSiO_4 are shown in Fig. 5. In every case, the infrared bands at 1080 cm^{-1} and 450 cm^{-1} were observed. When C/ZrSiO_4 was 3, the infrared band at 900 cm^{-1} was also observed. It may be identified as a Si-N stretching vibration. When C/ZrSiO_4 exceeded 5, the band at 850 cm^{-1}

Table 3 Chemical analysis data of products on the coil by various C/ZrSiO_4

C/ZrSiO_4	N content (%)	Combined C content (%)	Free C content (%)
0	0.15	—	—
1	0.72	0.10	10.70
2	2.63	2.04	9.18
3	4.64	2.70	5.54
4	2.62	2.87	5.88
5	2.33	7.60	7.27
6	1.36	7.20	7.60

Fig. 5 Infrared absorption spectra of powders deposited on the coil by various C/ZrSiO₄

was also observed. It may be identified as a Si-C stretching vibration.

It was considered that the powder deposited on the coil was mixture of fine crystals of various silicon oxides. In some cases, silicon nitride and silicon carbide may be also formed in the powder.

Assuming nitrogen was almost fixed as ZrN in the product obtained on the graphite anode, the relation between Zr C.R. and C/ZrSiO₄ is shown in Fig. 6. Zr C.R. was maximum at C/ZrSiO₄=3. In this figure, the relation between Zr C.R. and C/ZrO₂ by the nitriding of ZrO₂ is also shown. Both shows similar tendency.

Fig. 6 Zr C.R. vs. C/ZrSiO₄ and C/ZrO₂

(b) Influence of the current intensity: The chemical analysis and X-ray diffraction data of the products obtained on the graphite anode by various current intensities are listed in Tables 4 and 5. The relation between Zr C.R. and the current intensity is shown in Fig. 7. The nitrogen content and Zr C.R. were gradually increased with increasing current intensity.

(c) Influence of the nitrogen flow rate: The chemical analysis and X-ray diffraction data of the products on the graphite anode by various N₂ flow rate are listed in Tables 6 and 7. The relation

Table 4 Chemical analysis data of products on the graphite anode by various current intensities

Current (A)	N content (%)	C content as ZrC (%)	C content as SiC (%)	Free C content (%)
60	5.79	0.12	0.43	1.06
70	6.40	0.78	0.11	1.04
80	6.72	1.51	0.52	0.56
90	7.25	1.55	0.47	0.42
100	7.13	1.06	0.72	0.38

Reaction conditions: C/ZrSiO₄=3, N₂ flow rate 3 l/min, 1 min

Table 5 X-ray diffraction data of products on the graphite anode by various current intensities

Current (A)	Identified compounds	a ₀ of fcc (Å)
60	ZrN, ZrO ₂ (m)	4.582
70	ZrN	4.582
80	ZrN	4.587
90	ZrN	4.599
100	ZrN	4.599

Fig. 7 Zr C.R. vs. current intensity
○: C/ZrSiO₄=3, ●: C/ZrO₂=2

Table 6 Chemical analysis data of products on the graphite anode by various N₂ flow rates

N ₂ flow rate (l/min)	N content (%)	C content as ZrC (%)	C content as SiC (%)	Free C content (%)
1.5	5.30	0.87	1.31	1.48
2	5.46	0.90	1.32	3.10
3	6.72	1.51	0.52	0.56
4	7.29	1.59	0.36	0.40

Reaction conditions: C/ZrSiO₄=3, 80 A, 1 min

between Zr C.R. and N₂ flow rate is shown in Fig. 8. The nitrogen content and Zr C.R. were gradually increased with increasing N₂ flow rate.

(d) Influence of the reaction time: The chemical analysis and X-ray diffraction data of the pro-

Table 7 X-ray diffraction data of products on the graphite anode by various N_2 flow rates

N_2 flow rate (l/min)	Identified compounds	a_0 of fcc (Å)
1.5	$ZrO_2(m)$, $ZrO_2(c)^*$, ZrN	4.603
2	$ZrO_2(m)$, $ZrO_2(c)$, ZrN	4.592
3	ZrN	4.587
4	ZrN	4.586

* $ZrO_2(c)$: cubic ZrO_2

Fig. 8 Zr C.R. vs. N_2 flow rate

ducts on the graphite anode by various reaction time are listed in Tables 8 and 9. The relation between Zr C.R. and the reaction time is shown in Fig. 9. The reaction proceeded with increasing reaction time up to 60 sec. In the beginning of the reaction time, $ZrSiO_4$ and ZrO_2 were also observed in the product. They decreased with increasing reaction time. When the reaction time exceeded 60 sec., the product was almost ZrN.

In (a)~(d), relations between Zr C.R. and various factors of $ZrSiO_4$ nitriding showed similar tendency to these of ZrO_2 nitriding.

3.5 Discussion of the nitriding reaction of $ZrSiO_4$ by the nitrogen plasma jet

As mentioned above, the nitrogen plasma jet is supposed to consist in mainly atomic nitrogen. Heavy heating by the plasma jet will cause the decomposition of $ZrSiO_4$ to ZrO_2 and SiO_2 . The nitriding of $ZrSiO_4$ will proceed through the reaction between N and ZrO_2 , SiO_2 and graphite.

The temperature dependencies of the free energy change were calculated for probable reaction of ZrO_2 - SiO_2 -C system and atomic nitrogen from the thermochemical properties for each material in JANAF table⁷⁾ and are shown in Fig. 10. From

Table 8 Chemical analysis data of products on the graphite anode by various reaction times

Reaction time (sec)	N content (%)	C content as ZrC (%)	C content as SiC (%)	Free C content (%)
15	2.11	1.51	0.33	5.91
30	4.05	0.44	0.15	5.56
60	6.72	1.51	0.52	0.56
90	7.87	1.53	0.53	0.58
120	7.65	1.52	0.68	0.60

Reaction conditions: C/ $ZrSiO_4$ =3, 80 A, N_2 flow rate 3 l/min

Table 9 X-ray diffraction data of products on the graphite anode by various reaction times

Reaction time (sec)	Identified products	a_0 of fcc (Å)
15	$ZrSiO_4$, $ZrO_2(m)$, $ZrO_2(c)$, ZrN	—
30	$ZrO_2(m)$, $ZrO_2(c)$, ZrN	4.613
60	ZrN	4.587
90	ZrN	4.591
120	ZrN	4.582

Fig. 9 Zr C.R. vs. reaction time

Fig. 10, every reaction may proceed at 2500°K and C/ $ZrSiO_4$ may affect largely to the reaction. When C/ $ZrSiO_4$ is smaller than 3, a main reaction may be $SiO_2 + C \rightarrow SiO + CO$. Then SiO may be formed mainly. When C/ $ZrSiO_4$ is 3, the reaction as $ZrO_2 + 2C + N \rightarrow ZrN + 2CO$ and $SiO_2 + 2C + 4/3 N \rightarrow 1/3 Si_3N_4 + 2CO$ may also proceed. When C/ $ZrSiO_4$ exceeds 4, $ZrO_2 + 3C \rightarrow ZrC + 2CO$ and $SiO_2 + 3C \rightarrow SiC + 2CO$ may also proceed.

In experimental results, when C/ $ZrSiO_4$ was smaller than 2, the main product was SiO. ZrN, SiO and Si_3N_4 were formed at C/ $ZrSiO_4$ =3. When C/ $ZrSiO_4$ exceeded 4, ZrC and SiC were also for-

- 1 : $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$, 2 : $\text{ZrO}_2 + 3\text{C} \rightarrow \text{ZrC} + 2\text{CO}$
 3 : $\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$, 4 : $\text{ZrO}_2 + 2\text{C} + \text{N} \rightarrow \text{ZrN} + 2\text{CO}$
 5 : $\text{SiO}_2 + 2\text{C} + 4/3\text{N} \rightarrow 1/3\text{Si}_3\text{N}_4 + 2\text{CO}$

Fig. 10 Free energy change of reactions among ZrO_2 , SiO_2 , carbon and nitrogen vs. temperature

med. SiO and Si_3N_4 are gaseous state at 2500°K and deposited on the the cooling coil by quenching.

In this case, SiO changes to SiO_2 and Si by a disproportionation below 2000°K . So they are amorphous by X-ray diffraction.

The behaviour of zirconium in the reaction at $\text{C}/\text{ZrSiO}_4=3$ was similar that in the nitriding of ZrO_2 at $\text{C}/\text{ZrO}_2=2$. It is considered that ZrO_2 and SiO_2 react with carbon and nitrogen independently.

Then, the optimum nitriding condition of the zirconium silicate was $\text{C}/\text{ZrSiO}_4=3$ and the overall reaction may proceed as follows :

Acknowledgement : The authors wish to thank Professor Y. Hayakawa for many helpful discussions and suggestions during this work.

Literature

- 1) O. Matsumoto, Y. Shirato, M. Miyazaki, *J. Electrochem. Soc. Japan* **38**, 219 (1968).
- 2) O. Matsumoto, Y. Shirato, *Denki-Kagaku* **36**, 519 (1968), (In Japanese).
- 3) O. Matsumoto, *ibid.* **36**, 877 (1968), (In Japanese).
- 4) W.J. Kroll, C.T. Anderson, H.P. Holmes, L.A. Yerkes, H. L. Gilbert, *Trans. Electrochem. Soc.* **94**, 1 (1948).
- 5) J. Irmer, M. Worm, *Z. Physik. Chem.* **231**, 215 (1966).
- 6) M.J. Grillo, F.L. Worthing, B. Schwartz, *J. Electrochem. Soc.* **115**, (1968).
- 7) JANAF, "Thermochemical Table" (1965), Dow Chemical Co., Midland, Michigan.

Research Paper

The Solubility of TiCl_4 in KCl-LiCl Eutectic Melt

Katsumi NIKI, Masamitsu YAMAUCHI*, Tadao TOMONARI

(Department of Electrochemistry Yokohama National University, Ohoka, Minami-ku, Yokohama)

(Received Dec. 19, 1969)

The vapor pressure of TiCl_4 from the crystalline K_2TiCl_6 and over the KCl-LiCl eutectic melt was investigated. The thermodynamic functions were calculated from the values of the vapor pressure of TiCl_4 . At a constant temperature, Henry's law was applicable to these systems. The dependence of the solubility of TiCl_4 (in mole fraction) in the KCl-LiCl eutectic melt on a pressure P (in atm) of gaseous TiCl_4 and a temperature $T(^{\circ}\text{K})$ is given by $\log N = \log P - 5.07 + 2529/T$. Solubilities of TiCl_4 at various temperatures were given by $\log N = 4.66 - 3477/T$, by using the results obtained in the present work and by Mui and Flengas. The heat of dissolution of TiCl_4 into the KCl-LiCl eutectic melt is $H_d = -11.57 \pm 0.67$ kcal/mol. The relatively large values (negative) of the heat of solution of TiCl_4 in the melt and the large equilibrium constant suggest that the strong interaction of TiCl_4 with the solvent and the formation of the complex anions of TiCl_4 are quite probable.

1 Introduction

Fused salt electrolysis of titanium tetrachloride as a means of producing metallic titanium has always

been considered as the most attractive process. However, very little is known about the stability and the electrochemical behavior of titanium tetrachloride in fused salts.

* Present Address : Semiconductor Division, Nippon Electric Co. Ltd., Shimonumabe, Kawasaki