56) L. S. Darken, R. W. Gurry, "Physical Chemistry of Metals" p.437 (1953), McGraw Hill, N.Y.

57) W. Jost, "Diffusion in Solids, Liquids and Gases" p.436 (1960), Academic Press, N.Y.

Studies on Nitrides Formation by Means of Nitrogen Plasma Jet (Part 2)

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Received Jan. 23 1970

Nitrides formation by the reaction between the nitrogen plasma jet and tablets made of metal oxides such as Al_2O_3 , TiO_2 and ZrO_2 , and graphite powder were studied. AlN , TiN and ZrN were formed. The mixing ratio of graphite to oxides affected the yield of nitrides formation. Intermediates as nonstoichiometric oxides and oxycarbides were identified. The overall reaction may be carried out by the reaction

The nitriding of zirconium silicate in the same way as nitridation of oxides was studied and ZrN was formed.

1. Introduction

In the previous paper,¹⁾ the apparatus and experimental procedures for this study and nitrides formations by the reaction between respective metals and the nitrogen plasma jet with use of a transferred type plasma torch were described.

In this paper, nitrides formation by the reaction between respective oxides and the nitrogen plasma jet in the same way as the previous paper¹⁾ were reviewed.

2. Nitrides Formation by Nitridation of Oxides

Various nitrides such as AlN ^{2),3)}, TiN ⁴⁾ and

ZrN ⁵⁾ were formed by the reaction between respective oxide-graphite tablet acting as an anode and the nitrogen plasma jet with use of the reaction apparatus as shown previously¹⁾.

The nitriding of Al_2O_3 by nitrogen was carried out as in the following equation.

This process was previously planned to fix nitrogen⁶⁾ and was known as Haglund process. If this process could be carried out effectively, the hopeful application of a plasma jet will be expected. The direct nitridings of oxides by the nitrogen plasma jet were also examined.

In this chapter, experimental procedures,

Fig. 1 Reaction apparatus for nitriding of oxide-graphite tablet

results and the discussion of the reaction of nitrides formation by nitriding various oxides with the nitrogen plasma jet and by nitriding zirconium silicate with the nitrogen plasma jet were reviewed.

2.1 Experimental procedures

2.1.1 Apparatus The apparatus for the reaction was described previously. The specimen tablet was set on the graphite block placed on the copper anode as shown in Fig. 1. The arc was formed between the tungsten cathode in the torch and the graphite block. The apparatus for a measurement of temperature and conformations of products were described previously¹⁾.

2.1.2 Experimental methods The formation of nitrides was carried out in the same way as described previously¹⁾. The products were confirmed by an X-ray diffraction, chemical analysis, infrared absorption and electron diffraction.

2.2 Formation of Aluminum Nitride by Nitriding Aluminum Oxide^{2),3)}

2.2.1 Temperature measurement: The surface temperature of the tablet and the graphite block under the nitrogen plasma jet were measured with a micro-pyrometer. The relation between the surface temperature and the current intensity at various nitrogen flow

Fig. 2 Relation between surface temperature of tablet and the current intensity

rates is shown in Fig. 2. The surface temperature of the tablet raised with increasing current intensity and was higher than the melting point of Al_2O_3 .

2.2.2 Confirmation of products When the nitrogen plasma jet reacted with the tablet, greyish powder was deposited on the graphite, on the coil and the wall of the chamber. The greyish cake was also formed on the graphite block.

Each product was confirmed by an X-ray diffraction and chemical analysis. Typical X-ray diffraction patterns are shown in Fig. 3. The product deposited on the graphite block was confirmed to be AlN , while the cake formed on the graphite was AlN containing an unreacted Al_2O_3 and graphite. The product deposited on the coil and the wall of the chamber were amorphous.

2.2.3 Influence of the mixing ratio of carbon to Al_2O_3 ($\text{C}/\text{Al}_2\text{O}_3$) The influence of $\text{C}/\text{Al}_2\text{O}_3$ to the reaction is shown in Fig. 4^{*1}.

*1 In Fig. 4, Al conversion rate (Al C.R.) is defined as follows, Al C.R. = $[(\text{Al as AlN in product (g)} - (\text{Al as Al}_2\text{O}_3 \text{ in original tablet (g)}))] \times 100(\%)$

Fig. 3 X-ray diffraction patterns of deposited materials

Fig. 4 Relation between Al C.R. and C/ Al_2O_3

The Al C.R. of the product on the coil and of the cake formed on the graphite block increased gradually with increasing a C/ Al_2O_3 , while that of the product deposited on the graphite block

Fig. 5 X-ray diffraction patterns obtained for various C/ Al_2O_3

Fig. 6 Relation between Al C.R. and the current intensity

increased with increasing C/ Al_2O_3 up to C/ Al_2O_3 =3.

X-ray diffraction patterns of products deposited on the graphite. block at different ratio of C/ Al_2O_3 are shown in Fig. 5. When C/ Al_2O_3 exceeded 3, main product was

AlN. AlN contents obtained by a chemical analysis are also shown in Fig. 5. From these results the reaction seemed to proceed rapidly at C/Al_2O_3 larger than 3.

2.2.4 Influence factors on the formation of AlN Influences of various conditions such as the current intensity, the nitrogen flow rate and the reaction time to the formation of AlN were also examined.

The relation between Al C.R. and the current intensity is shown in Fig. 6. Al C.R. of the cake on the graphite block decreased with increasing current intensity, while that of products deposited on other parts kept nearly constant even if the current intensity was varied.

The relation between Al C.R. and the nitrogen flow-rate is shown in Fig. 7. Al C.R. of the cake on the graphite block linearly decreased with increasing the nitrogen flow rate, while that of products deposited on other parts gradually increased with increasing the nitrogen flow rate.

The relation between Al C.R. and the reaction time is shown in Fig. 8. Al C.R. of the cake on the graphite block was kept nearly constant regardless the reaction time. On the

Fig. 7 Relation between Al C.R. and the nitrogen flow rate

Fig. 8 Relation between Al C.R. and the reaction time

Fig. 9 X-ray diffraction patterns of products sampled from the surface of the cake at various reaction times

other hand, that of the product deposited on the coil increased with increasing reaction time and that of the product deposited on the coil increased with increasing reaction time and that of the product deposited on the graphite block increased with increasing reaction time up to 60

Table 1 Relation between the reaction time and AlN formation on the tablet surface

Reaction time (sec)	Sample weight (g)	AlN content (%)
15	0.110	19.0
30	0.125	25.3
60	0.134	24.3
120	0.141	21.2

Reaction condition: C/Al₂O₃ = 6, 80A, 3 l/min

sec.

Substances on the surface of the cake formed on the graphite block were examined by an X-ray diffraction and chemical analysis. Results obtained are shown in Fig. 9 and Table 1, which indicate that the crystallization of AlN proceeds, with the reaction time.

2.2.5 Discussion of AlN formation As mentioned previously¹⁾, the nitrogen plasma jet is supposed to consist in mainly atomic nitrogen. Heavy heating by the plasma jet will cause the melting of Al₂O₃. In the melt, Al₂O₃ reacted with carbon and might be reduced to a lower oxidation state (such as AlO, Al₂O or oxycarbide)⁸⁾. AlN formation will proceed through the reaction between atomic nitrogen and these intermediates.

Since AlN begins to sublime above

Fig. 10 Relation between ΔG° of the reaction of AlN formation and temperature

2,000°C⁹⁾, AlN formed on the surface of the tablet would sublime a deposit on the copper coil, on the wall of the chamber and on the graphite block. The product on the copper coil and on the wall of the chamber may be cooled suddenly and thus deposited as an amorphous state, while that deposited on the graphite block may be cooled gradually and crystal was formed.

The mixing ratio of carbon to Al₂O₃ (C/Al₂O₃) was very effective to AlN formation. The temperature dependence of the free energy change was calculated for the probable reaction of AlN formation¹⁰⁾ and are shown in Fig. 10. From Fig. 10 and experimental results, the formation of AlN at 3,000°K may be carried out by the following reaction,

2.3 Formation of Zirconium Nitride Nitriding Oxide⁵⁾

2.3.1 Temperature measurement The surface temperature of TiO₂-graphite mixture tablet and the graphite block under the nitrogen plasma jet was measured with a micro-pyrometer. The relation between the surface temperature and the current intensity at various nitrogen flow rates is shown in Fig. 11.

Conditions: C/TiO₂=2, N₂ flow rate 1.5~4 l/minFig. 11 Relation between the surface temperature of TiO₂-graphite tablet and current intensity

The surface temperature of the tablet raised with increasing current intensity and was higher than the melting point of TiO_2 .

2.3.2 Confirmation of product When nitrogen plasma jet reacted with the tablet, a black powder was deposited on the copper coil and on the wall of the chamber. The metallic cake was formed on the graphite block. Typical X-ray diffraction patterns are shown in Fig. 12. In the powder deposited on the copper coil and the wall of the chamber, only graphite was observed. The cake formed on the graphite block was confirmed to be almost TiN .

Fig. 12 X-ray diffraction patterns of deposited material by nitriding of TiO_2

2.3.3 Influence of the mixing ratio of carbon to TiO_2 (C/TiO_2) The influence of C/TiO_2 to the reaction is shown in Fig. 13*. The Ti C.R. increased with increasing C/TiO_2 up to 2 or 2.5. When C/TiO_2 exceeded 2 or 2.5, Ti C.R. decreased with increasing C/TiO_2 and was maximum at $\text{C}/\text{TiO}_2 = 2$ or 2.5 under various current intensities.

X-ray diffraction patterns of the cake formed on the graphite block at $\text{C}/\text{TiO}_2 = 0.5 \sim 5$ are shown in Fig. 14. In the case of $\text{C}/\text{TiO}_2 \leq 2$

Fig. 13 Relation between Ti C.R. and C/TiO_2

Fig. 14 X-ray diffraction patterns of cake obtained by various C/TiO_2

main product was TiN , and C/TiO_2 exceeded 3 main product was TiC . In the case of $\text{C}/\text{TiO}_2 = 2.5$ TiN and TiN-TiC solid solution were formed. Nitrogen and carbon contents in the product obtained by chemical analysis are listed in Table 2. Nitrogen content was maximum at $\text{C}/\text{TiO}_2 = 2$ or 2.5. From these results, the reaction seems to

* In Fig. 13, Ticonversion rate (Ti C.R.) is defined as follows, $\text{Ti C.R.} = [(\text{Ti as TiN in product (g)})/(\text{Ti as TiO}_2 \text{ in original tablet (g)})] \times 100(\%)$

Table 2 Chemical analysis results of products by nitriding of TiO_2 for various C/TiO_2

C/TiO_2	N (%)	Combined C (%)	Free C (%)
0.5	9.76	4.91	3.34
1.0	11.8	3.91	3.82
2.0	16.7	0.58	2.25
2.5	10.8	5.58	0.58
3.0	7.94	8.08	1.78
5.0	0.33	14.6	22.0

Reaction condition: 80A, N_2 3 l/min, 2 min

proceed rapidly at $\text{C/TiO}_2 = 2$ or 2.5.

2.3.4 Influence factors on the formation of TiN Influences of various conditions such as the current intensity, nitrogen flow rate and reaction time to the formation of TiN were examined.

The relation between Ti C.R. and the current intensity is shown in Fig. 15. In the case of $\text{C/TiO}_2 = 2$ Ti C.R. was almost constant even if the current intensity was varied, and in the case of $\text{C/TiO}_2 = 2.5$ Ti C.R. decreased with increasing the current intensity up to 70 amp. Ti C.R. gradually increased with the current intensity. In the case of $\text{C/TiO}_2 = 2$ the main product was almost TiN even if the current

Fig. 15 Relation between Ti C.R. and current intensity

intensity was changed. At the current intensity of 50 amp., Ti_2O_3 was formed.

The relation between Ti C.R. and the nitrogen flow rate is shown in Fig. 16, and Ti C.R. decreased with increasing the nitrogen flow

Fig. 16 Relation between Ti C.R. and N_2 flow rate

Fig. 17 Relation between Ti C.R. and the reaction time

Table 3 Free energy change of carbon reduction and nitriding reaction of titanium oxides

Reaction	ΔG° (kcal/mole)							
	500	1000	1500	2000	2500	3000	3500	4000
$\text{TiO}_2 + 1/2 \text{C} \rightarrow 1/2 \text{Ti}_2\text{O}_3 + 1/2 \text{CO}$	+20.7	+9.9	-0.3	-12.3	-24.2	-36.0	-47.9	-60.0
$1/2 \text{Ti}_2\text{O}_3 + 1/2 \text{C} \rightarrow \text{TiO} + 1/2 \text{CO}$	+32.1	+21.7	+12.0	+0.7	-10.1	-20.1	-31.9	-43.2
$\text{TiO}_2 + \text{C} \rightarrow \text{TiO} + \text{CO}$	+52.8	+31.7	+11.7	-11.6	-34.4	-56.1	-79.8	-103.2
$\text{TiO} + \text{C} \rightarrow \text{Ti} + \text{CO}$	+76.6	+55.1	+34.7	+15.3	-2.0	-16.8	-32.3	-60.5
$\text{TiO}_2 + 2\text{C} \rightarrow \text{Ti} + 2\text{CO}$	+129.5	+86.7	+44.9	+3.7	-36.0	-72.9	-110.0	-163.7
$1/2 \text{Ti}_2\text{O}_3 + \text{N} \rightarrow \text{TiN} + 3/4 \text{O}_2$	-10.7	-8.0	-4.3	+0.2	+7.6	+16.2	+23.7	+30.1
$\text{TiO} + 1/2 \text{N}_2 \rightarrow \text{TiN} + 1/2 \text{O}_2$	+42.1	+40.9	+39.1	+33.6	+28.0	+23.7	+20.6	+18.5
$\text{TiO} + \text{N} \rightarrow \text{TiN} + 1/2 \text{O}_2$	-61.4	-53.7	-45.7	-34.9	-21.4	-7.8	+4.7	+16.0

rate.

The relation between *Ti* C.R. and the reaction time is shown in Fig. 17. When $\text{C}/\text{TiO}_2 = 2$ *Ti* C.R. was maximum at 60 sec, and when $\text{C}/\text{TiO}_2 = 2.5$ *Ti* C.R. gradually increased with increasing the reaction time. In both cases, when the reaction time was shorter than 30 sec., TiO was observed in the products.

2.3.5 Discussion of TiN formation The surface temperature of the tablet under the nitrogen plasma jet was higher than the melting point of TiO_2 , and TiO_2 was a liquid state. In the melt, TiO_2 reacted with carbon and should be reduced to a lower oxidation state. Intermediates such as Ti_2O_3 and TiO were identified in the product. The reaction might be carried out through these intermediate states.

In case of the nitriding TiO_2 with NH_3 ¹¹⁾, the reaction was carried out through the reduction of TiO_2 to TiO and TiN formed by nitriding TiO with NH_3 .

The temperature dependency of the free energy change of the reduction of TiO_2 with carbon and the nitriding of titanium oxides with atomic nitrogen¹⁰⁾ are listed in Table 3. TiO_2 should be reduced with carbon to TiO thermodynamically. The nitriding TiO with atomic nitrogen might be more probable than the reduction of TiO to Ti with carbon.

The nitridings of TiO^* and Ti_2O_3^* by the nitrogen plasma jet were examined and results obtained are shown in Fig. 18, TiN was formed by the reaction between TiO and the nitrogen plasma jet.

From these results mentioned above, the nitriding of TiO_2 by nitrogen plasma jet should

Reaction conditions: 100A, N_2
3 ℓ /min, 2min

Fig. 18 X-ray diffraction patterns of products by the nitriding of TiO and Ti_2O_3

* TiO and Ti_2O_3 were made by oxidation of titanium with argon-oxygen plasma jet¹²⁾

be carried out through the following steps : i) the reduction of TiO_2 to TiO with carbon, and ii) the nitriding of TiO with atomic nitrogen.

The temperature dependency of the free energy change for probable overall reaction of TiN formation are shown in Fig. 19. From Fig. 19 and the experimental results, the formation of TiN was carried out at about $3,000^\circ\text{K}$ by the reaction,

Fig. 19 Relation between ΔG° of the reaction of TiN formation and temperature

2.4 Formation of Zirconium Nitride by Nitriding Oxide⁵⁾

2.4.1 Temperature measurement The surface temperature of the ZrO_2 –graphite mixture tablet and a graphite block under the nitrogen plasma jet was measured with a micro-pyrometer. The relation between the surface temperature and the current intensity at various nitrogen flow rate is shown in Fig. 20. The surface temperature of the tablet raised with increasing current intensity and was higher than the melting point of ZrO_2 .

2.4.2 Confirmation of product When the nitrogen plasma jet reacted with the tablet, the

Fig. 20 Relation between the surface temperature of ZrO_2 -graphite tablet and current intensity

metallic cake was only formed on the graphite block. It was confirmed to be almost ZrN from X-ray diffraction data.

2.4.3 Influence of the mixing ratio of carbon to ZrO_2 (C/ZrO_2) The influence of

Fig. 21 Relation between Zr C.R. and C/ZrO_2

Fig. 22 X-ray diffraction patterns of products obtained by various C/ZrO_2

C/ZrO_2 to the reaction is shown in Fig. 21*. The Zr C.R. decreased with increasing C/ZrO_2 up to 2. When C/ZrO_2 exceeded 2, Zr C.R. decreased with increasing C/ZrO_2 , and Zr C.R. was maximum at $C/ZrO_2 = 2$.

X-ray diffraction patterns of the cake formed on the graphite block at $C/ZrO_2 = 0.5 \sim 5$ are shown in Fig. 22. When $C/ZrO_2 \leq 2$ main product was ZrN , and when it exceeded 3 main product was ZrC . The solid solution of ZrN and ZrC was formed at $C/ZrO_2 = 2.5$. Nitrogen and

Table 4 Chemical analysis results of products by nitriding of ZrO_2 for various C/ZrO_2

C/ZrO_2	N (%)	Combined C (%)	Free C (%)
0.5	3.26	0.40	0.76
1.0	4.24	0.69	0.46
2.0	7.05	1.31	0.45
2.5	3.95	4.69	1.21
3.0	0.96	9.85	1.45
5.0	0.24	11.3	12.2

Reaction condition: 100A, N_2 3 l/min, 2 min

* In Fig. 21, Zr conversion rate (Zr C.R.) is defined as follows, Zr C.R. = $[(Zr \text{ as } ZrN \text{ in product (g)}) / (Zr \text{ as } ZrO_2 \text{ in original tablet (g)})] \times 100 (\%)$

carbon contents in the product obtained by chemical analysis are listed in Table 4. Nitrogen content was maximum at $C/ZrO_2 = 2$. From these results, the reaction seems to proceed rapidly at $C/ZrO_2 = 2$.

2.4.4 Influence factors on the formation of ZrN Influences of various conditions such as the current intensity, the nitrogen flow rate and the reaction time to the formation of ZrN were examined.

The relation between Zr C.R. and the current intensity at $C/ZrO_2 = 2$ is shown in Fig. 23. Zr C.R. increased with increasing the current intensity. When the current intensity exceeded 80 amp., Zr C.R. was independent of the change of the current intensity. When the current intensity was lower than 60 amp., identified compounds in the products were ZrN , cubic ZrO_2 ^{13),14)} and monoclinic ZrO_2 which was a starting material. When the current intensity exceeded 70 amp. the product was almost ZrN .

The relation between Zr C.R. and the nitrogen flow rate is shown in Fig. 24. Zr C.R. was almost constant even if the nitrogen flow rate was varied. When the nitrogen flow rate was smaller than 2 l/min, ZrN and cubic ZrO_2 were found in the products. However, the product was

Fig. 23 Relation between Zr C.R. and current intensity

Fig. 24 Relation between Zr C.R. and N₂ flow rate

Fig. 25 Relation between Zr C.R. and the reaction time

almost ZrN when the nitrogen flow rate was more than 3 l/min.

The relation between Zr C.R. and the reaction time is shown in Fig. 25. Zr C.R. increased with the increasing reaction time. X-ray

Fig. 26 X-ray diffraction patterns of products obtained by various reaction time

diffraction patterns of the product by different reaction time are shown in Fig. 26. ZrN was already formed at 15 sec. from the beginning of reaction and when the reaction time was shorter than 30 sec. the cubic ZrO₂ and the monoclinic ZrO₂ which was the starting material were contained. Diffraction lines based on an fcc crystal, 2θ of which were lower than those of ZrN were found in the products. It was identified as zirconium oxycarbide in the form of ZrO_xCy¹⁵⁾.

2.4.5 Discussion of ZrN formation The surface temperature of the tablet under the nitrogen plasma jet was higher than the melting point of ZrO₂, and ZrO₂ was a liquid state. In the melt, ZrO₂ reacted with carbon and should be a more reactive state than ZrO₂. At the beginning of the reaction intermediates such as ZrO₂ and oxycarbides, ZrO_xCy, were identified in the product. The reaction should be carried out through these intermediate states. Combined carbon contents were relatively high in the product that contained cubic ZrO₂ and ZrO_xCy. Cubic ZrO₂ was considered as zirconium oxynitride¹⁶⁾. It is considered that molten ZrO₂ reacted with carbon or atomic nitrogen and these intermediates were formed. Then atomic nitrogen would react with these intermediates

Fig. 27 Relation between ΔG° of the reaction of ZrN formation and the temperature and ZrN was formed.

The temperature dependence of the free energy change for probable overall reaction of ZrN formation⁹⁾ are shown in Fig. 27. From Fig. 27 and the experimental results, the formation of ZrN at about 3,000°K was carried out through the reaction,

Fig. 28 Relation between surface temperature of ZrSiO₄-graphite tablet and current intensity

2.5 Formation of Zirconium Nitride by Nitriding Zirconium Silicate⁷⁾

2.5.1 Temperature measurement The surface temperature of the ZrSiO₄-graphite mixture tablet under the nitrogen plasma jet was measured with a micro-pyrometer. The relation between the temperature of the surface of the tablet and the current intensity is shown in Fig. 28. The surface temperature was higher than the decomposition temperature of ZrSiO₄ at the current intensity of 50 amp. The temperature raised with increasing current intensity, and when the current intensity came up to higher than 80 amp. the surface temperature was higher than the melting point of ZrO₂.

2.5.2 Confirmation of products As nitrogen plasma jet reacted with the tablet, the metallic cake was formed on the graphite block and a yellow powder deposited on the copper coil.

By an X-ray diffraction, the cake was of ZrN, ZrC and SiC in several cases. The powder deposited on the copper coil was not identified by an X-ray diffraction, and the powder may be amorphous or of very fine crystal. The powder was identified by means of an infrared absorption spectrum measurement and an electron diffraction. The infrared absorption spectra of the powder deposited on the coil are shown in Fig. 29. The band at 1,080 cm⁻¹ was identified as an Si-O stretching vibration and that at 450 cm⁻¹ was identified as an O-Si-O deformation vibration. The infrared band at 900 cm⁻¹ was identified as an Si-N stretching vibration¹⁷⁾. In Fig. 29, the infrared absorption spectra of

Fig. 29 Infrared absorption spectra of the powder deposited on the coil and α -quartz

α -quartz was shown as an comparison. The powder obtained was different from α -quartz. From an electron diffraction, the powder is identified as silicon, β -quartz or α -SiC. It was considered that the powder was the mixture of fine crystals of various silicon oxides including Si_3N_4 and SiC.

2.5.3. Influence of the mixing ratio of carbon to ZrSiO_4 (C/ZrSiO_4) The influence of C/ZrSiO_4 to the reaction is shown in Fig. 30* Zr C.R. was maximum at $\text{C}/\text{ZrSiO}_4 = 3$. In Fig. 30, the relation between Zr C.R. and C/ZrO_2 by nitriding ZrO_2 is shown as a comparison. Both show a similar tendency.

Identified compounds in the cake are listed in Table 5. When C/ZrSiO_4 was smaller than 3, monoclinic ZrO_2 was found with ZrN , but when C/ZrSiO_4 was 3 the product was almost ZrN . A solid solution of ZrN and ZrC was formed at $\text{C}/\text{ZrSiO}_4 = 4$, and when C/ZrSiO_4 exceeded 5 the product was ZrC containing SiC. The infrared absorption spectra of the powder obtained by different C/ZrSiO_4 are shown in Fig.

Fig. 30 Relation between Zr C.R. and C/ZrSiO_4

* In Fig. 30, Zr conversion rate (Zr C.R.) is defined as follows.
 $\text{Zr C.R.} = [(\text{Zr as ZrN in product (g)})/(\text{Zr as ZrSiO}_4 \text{ in original tablet (g)})] \times 100(\%)$

Table 5 Identified compounds in the cake obtained for various C/ZrSiO_4

C/ZrSiO ₄	Identified compounds
0	ZrO ₂ (m)*
1	ZrO ₂ (m), ZrN
2	ZrO ₂ (m), ZrN
3	ZrN
4	ZrN-ZrC
5	ZrC, β -SiC
6	ZrC, β -SiC

* $\text{ZrO}_2(\text{m})$: monoclinic ZrO_2
Reaction condition: 80A, N₂ 3 l/min, 1 min

31. In every case, infrared bands were observed at $1,080\text{ cm}^{-1}$. When C/ZrSiO_4 was 3 the band at 900 cm^{-1} was observed. When C/ZrSiO_4 exceeded 5 the band at 850 cm^{-1} that was identified as an Si-C stretching vibration was observed.

Fig. 31 Infrared absorption spectra of the powder deposited on the coil by various C/ZrSiO_4

2.5.4. Influence factors on the formation of ZrN Influences of various conditions such as the current intensity, the nitrogen flow rate and the reaction time to the formation of ZrN were examined.

The relation between Zr C.R. and the current intensity is shown in Fig. 32, and Zr C.R. gradually increased with current intensity.

The relation between Zr C.R. and the nitrogen flow rate is shown in Fig. 33, and Zr C.R. gradually increased with increasing the

nitrogen flow rate, and then Zr C.R. was almost constant.

The relation between Zr C.R. and the reaction time is shown in Fig. 34. The reaction proceeded with increasing reaction time up to 60 sec.

In Figs. 32, 33 and 34, relations between Zr

Fig. 32 Relation between Zr C.R. and the current intensity

Fig. 33 Relation between Zr C.R. and the nitrogen flow rate

Fig. 34 Relation between Zr C.R. and the reaction time

C.R. and various nitriding factors of $ZrSiO_4$ showed a similar tendency to those of nitriding ZrO_2 .

2.5.5 Discussion of nitriding of $ZrSiO_4$ As mentioned previously¹⁾ 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 by the reaction between atomic nitrogen, ZrO_2 , SiO_2 and graphite.

The temperature dependence of the free energy change for probable reaction of ZrO_2 - SiO_2 -C system and atomic nitrogen¹⁰⁾ were calculated and are shown in Fig. 35. From Fig. 35, every reaction may proceed at above 2,500°K and $C/ZrSiO_4$ may affect to the reaction. When $C/ZrSiO_4$ is smaller than 3 main reaction may be $SiO_2 + C \rightarrow SiO + CO$, on the other hand when $C/ZrSiO_4 = 3$ reactions as $ZrO_2 + 2C + N \rightarrow ZrN + 2CO$ and $SiO_2 + 2C + 4/3N \rightarrow 1/3 Si_3N_4 + 2CO$ may also proceed. When $C/ZrSiO_4$ exceeds 4, $ZrO_2 + 3C \rightarrow ZrC + 2CO$ and $SiO_2 + 3C \rightarrow SiO + 2CO$ may also proceed.

From experimental results, when $C/ZrSiO_4$ was smaller than 2 the main product was SiO. ZrN , SiO and Si_3N_4 were formed at $C/ZrSiO_4 =$

Fig. 35 Relation between ΔG° of ZrSiO_4 nitriding reaction and temperature.

3, and when C/ZrSiO_4 exceeded 4 ZrC and SiC were formed. SiO and Si_3N_4 are gaseous state at above $2,500^\circ\text{K}$ and deposited on the copper coil by quenching. In this case, SiO changes to SiO_2 and silicon by a disproportionation reaction at a temperature below $2,000^\circ\text{K}$ and they might be amorphous with X-ray diffraction data.

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

The optimum nitriding condition of zirconium silicate was $\text{C}/\text{ZrSiO}_4 = 3$ and the overall reaction may proceed in the following way,

2.6 Consideration of Nitrides Formation by Nitriding Oxides

Various nitrides were formed by nitriding oxides and silicate by the nitrogen plasma jet. As nitriding of metal oxides and a silicate was difficult to carry out, it was necessary to add a

small amount of carbon as a reductant.

Nitrogen plasma jet is supposed to consist in mainly atomic nitrogen. Heavy heating by nitrogen plasma jet will cause melting of oxides-graphite mixtures. Nitrides formation will proceed through there reaction between atomic nitrogen and molten oxides.

The mixing ratio of graphite to oxide affected the nitride formation. Intermediates such as a nonstoichiometric oxides and an oxycarbides were identified. The reduction of oxide by carbon should be carried out at a beginning of reaction, then the nitriding by atomic nitrogen was occurred.

From experimental results and thermodynamical consideration, the overall reaction may be carried out by the reaction,

The yields of nitrides were affected by stability of nitrides likewise in case of nitriding metals.

The nitriding of zirconium silicate in the same way as the case of metal oxides was studied as an application. ZrN was formed through the following reaction,

In this case, ZrN was formed as a molten state and SiO was formed as a gaseous state. Therefore, SiO was separated from ZrN and pure ZrN was obtained. This method will be applied to nitriding other silicates.

3. Summary

Nitrides formation by the reaction between nitrogen plasma jet and tablets made by various oxides as Al_2O_3 , TiO_2 and ZrO_2 , and graphite powder were also examined, and AlN , TiN and ZrN were formed. The formation of nitrides will proceed by the reaction between the atomic nitrogen and the molten oxides. The mixing ratio of graphite to oxides affected the nitrides formation. Intermediates as nonstoichiometric oxides and oxycarbides were identified. The reduction of oxide by carbon should be carried out at a beginning of the reaction, then the

nitriding by atomic nitrogen be occurred. The overall reaction may be carried out through the reaction,

The nitriding of zirconium silicate by the same way as the case of metal oxides was studied. ZrN was formed by the reaction,

ZrN was formed.

Literatures:

- 1) O. Matsumoto, Y. Shirato, Y. Hayakawa, *This Journal* 37, (1969).
- 2) O. Matsumoto, Y. Shirato, M. Miyazaki, *ibid.* 36, 219 (1968).
- 3) O. Matsumoto, Y. Shirato, M. Miyazaki, *Denki Kagaku* 36, 41 (1968), (in Japanese).
- 4) O. Matsumoto, Y. Shirato, *Denki Kagaku* 36, 519 (1968), (in Japanese).
- 5) O. Matsumoto, *ibid.* 36, 877 (1968), (in Japanese).
- 6) I.E. Cambell, "High Temperature Technology" p. 175 (1956), The Electrochemical Society Inc., N.Y.
- 7) O. Matsumoto, Y. Shirato, *Denki Kagaku* 38, 168 (1970), (in English).
- 8) J. M. Hall, AD 431,797 (1963).
- 9) L. M. Dreger, V. V. Davota, J. L. Margrave, *J. Phys. Chem.* 66, 1556 (1962).
- 10) JANAF, "Thermochemical Table" (1965), Dow Chemical Corp., Midland, Michigan.
- 11) D. Douglas, *Met. Soc. Conf.* 8, 785 (1961).
- 12) O. Matsumoto, *This Journal* 37, 199 (1969).
- 13) R. Ruh, *J. Am. Ceram. Soc.* 50, 257 (1967).
- 14) C. F. Gravin, *ibid.* 50, 288 (1967).
- 15) J. P. Guerlet, P. Leur, *Compt. rend.* 260, 899 (1965).
- 16) J. G. Gilles, *Bull. Soc. Chim. France* 1962, 2118.
- 17) M. J. Grieco, F. L. Worthy, B. Schwartz, *J. Electrochem. Soc.* 115, 525 (1968).