2638 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2638—2642 (1983) [Vol. 56, No. 9

Reaction Process of Zirconium Tetrachloride with Ammonia in the Vapor Phase and Properties of the Zirconium Nitride Formed

Akimasa Yajima, Yutaka Segawa, Ryoko Matsuzaki, and Yuzo Saeki*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259, Nagatsuta-cho, Midori-ku, Yokohama 227

(Received March 24, 1983)

The reaction products of gaseous $ZrCl_4$ with ammonia were $ZrCl_4\cdot 2NH_3$ at 300 °C; $ZrCl_4\cdot 2NH_3$, ZrClN, and NH_4Cl at 350—700 °C; $ZrCl_4\cdot 2NH_3$, ZrClN, ZrN_x, Zr_3N_4, and NH_4Cl at 750 °C; ZrClN, ZrN_x, Zr_3N_4, and NH_4Cl at 800—950 °C; ZrN_x, Zr_3N_4, and NH_4Cl at 1000—1050 °C; and ZrN_x, NH_4Cl, and HCl at 1100—1400 °C. The N/Zr atomic ratios, x, of the ZrN_x formed was 1.28 at 1100 °C, 1.24 at 1200 °C, 1.18 at 1300 °C, and 1.12 at 1400 °C. The lattice constants of the ZrN_x formed were shown. The reaction process of gaseous $ZrCl_4$ with ammonia can be represented as follows: The reaction of gaseous $ZrCl_4$ with ammonia to form $ZrCl_4\cdot 2NH_3$ occurs first. Above *ca.* 330 °C, the $ZrCl_4\cdot 2NH_3$ reacts with ammonia to form ZrClN. Above *ca.* 750 °C, the ZrClN reacts with ammonia to form ZrN_x and Zr_3N_4. Above *ca.* 1000 °C, ZrN_x was also formed by the thermal decomposition of the Zr_3N_4. On heating the $ZrN_{x(x=1.28)}$, formed by the vapor-phase reaction, at temperatures higher than 700 °C in an argon atmosphere, the value of x decreased and became close to that of the stoichiometric nitride, being 1.03 at 1100—1300 °C.

The vapor-phase reaction of transition metal chlorides with ammonia has recently become important for the preparation of fine powders of transition metal nitrides, which are aquiring importance as new industrial materials. Concerning the formation of zirconium nitride from zirconium tetrachloride ($ZrCl_4$) by the vapor-phase reaction, Okabe *et al.*[1] have reported the preparation of zirconium nitride powders by a vapor-phase reaction of the $ZrCl_4$–NH_3–N_2–H_2 system at 1000—1500 °C with emphasis on the effect of reaction conditions on the conversion of the $ZrCl_4$ to zirconium nitride. However, no information is at present available on the reaction process of $ZrCl_4$ with ammonia in the vapor phase.

In this paper, the reaction products of gaseous $ZrCl_4$ with ammonia at 300—1400 °C were examined in detail. The possible reactions which were considered to occur during the reaction process on the basis of the above experiments were examined. The N/Zr atomic ratios, lattice constants, and thermal stability of the zirconium nitrides formed were also examined. The zirconium nitrides which formed were also examined by electron microscopy.

Experimental

Materials. The $ZrCl_4$ used was prepared by the reaction of zirconium sponge (Reactor grade, Nippon Mining Co., Ltd.) with chlorine at 330 °C and purified by fractional sublimation. The chemical analysis gave Zr, 39.1; Cl, 60.8% (calcd for $ZrCl_4$: Zr, 39.14; Cl, 60.86%). The ammonia was dried by passing it over sodium hydroxide granules and barium oxide powders.

Experimental Procedures. A transparent quartz or alumina tube (1000 mm length) was used for examining the reaction products of gaseous $ZrCl_4$ with ammonia. Gaseous $ZrCl_4$ was formed by heating solid $ZrCl_4$ (14 g) at 280 °C and was carried by a stream of argon (50 cm^3/min) into the reaction zone (28 mm i.d., 250 mm length) held at a specified temperature. The $ZrCl_4$ inlet tube consisted of two concentric tubes. Gaseous $ZrCl_4$ carried by argon was introduced through the inner tube and the outer tube was utilized for introducing argon (50 cm^3/min) as a sheath gas to prevent formation of the product deposits at the chloride inlet tube. Ammonia was simultaneously introduced at a flow-rate of 100 cm^3/min into the reaction zone through a separate tube. The mean flow-rate of gaseous $ZrCl_4$ was 6.0 cm^3/min. A quartz or alumina tube was inserted inside the reaction tube to make the removal of the reaction product easier. The reaction was allowed to proceed for 2 h.

The by-product ammonium chloride (NH_4Cl) which deposited outside the reaction zone together with the zirconium nitride formed was separated by heating the mixture *in vacuo* at 400 °C.

Analytical. Chemical analyses of the reaction products were performed as follows: The zirconium content of the $ZrCl_4$–NH_3 adduct was gravimetrically determined as ZrO_2 using mandelic acid as a precipitating agent, after dissolving the sample in water. The chlorine and ammonia contents were determined by a gravimetric method as AgCl and by the Kjeldahl method from the aqueous solution. The zirconium content of zirconium chloride nitride (ZrClN) was gravimetrically determined as ZrO_2 after hydrolyzing the sample in water. The chlorine and nitrogen contents were determined by the gravimetric method and by the Kjeldahl method, respectively, from the filtrate.

X-Ray analysis of the product was performed with an X-ray powder diffractometer equipped with a proportional counter using Ni filtered Cu radiation. The sample chamber of the diffractometer was maintained under a dry nitrogen atmosphere, if necessary, to prevent any contamination of the sample with atmospheric moisture during the irradiation.

The sensitivity of the quartz helix used for thermogravimetry (TG) was approximately 113 mm/g. The sample (0.2 g) was heated at a rate of 2.5 °C/min and the flow-rate of ammonia was maintained at 50 cm^3/min.

The N/Zr atomic ratio of the zirconium nitride formed was evaluated as follows: The sample zirconium nitride was oxidized to ZrO_2 by heating in an oxygen atmosphere to 700 °C, using a Shimadzu high-sensitive thermal balance, Model TGA31. The zirconium content of the sample was calculated from the amount of ZrO_2 formed. The amount of nitrogen was determined as the difference between the amount of the initial sample and that of the zirconium. The value of the N/Zr atomic ratio was evaluated with an accuracy within ±0.01.

The lattice constant of the zirconium nitride was calculated based on the X-ray diffraction data obtained by using silicon powders as an internal standard and under the scanning speed of 1/2—1/4° min^{-1}.

Throughout this work, the $ZrCl_4$ and the reaction products were handled in an argon atmosphere or *in vacuo* to prevent contamination by atmospheric moisture.

Results and Discussion

Reaction Products of Gaseous Zirconium Tetrachloride with Ammonia. The products formed by heating gaseous $ZrCl_4$ in an ammonia stream at various temperatures were examined by both X-ray analysis[2–5] and chemical analysis. Reaction temperatures above 300 °C were employed, because gaseous $ZrCl_4$ was generated at 280 °C.

The product formed at 300 °C showed a hitherto unknown X-ray diffraction pattern which was clearly different from those of known zirconium compounds. The chemical analysis of the product gave Zr, 34.1; Cl, 53.0; NH_3, 12.8%. The ratio of Zr : Cl : NH_3 was calculated to be 1:4.00:2.01. This was considered to indicate that the product formed at 300 °C had a composition of $ZrCl_4 \cdot 2NH_3$ (calcd for $ZrCl_4 \cdot 2NH_3$: Zr, 34.15; Cl, 53.10; NH_3, 12.75%). The X-ray diffraction data of the $ZrCl_4 \cdot 2NH_3$ formed are shown in Table 1. Based on these data, $ZrCl_4 \cdot 2NH_3$ could be indexed on cubic lattice with $a_0 = 10.13$ Å, as shown in Table 1.

TABLE 1. X-RAY DIFFRACTION DATA OF $ZrCl_4 \cdot 2NH_3$

d/Å	I/I_0	$h\ k\ l$	d_{calcd}/Å
5.83	100	1 1 1	5.849
5.07	80	2 0 0	5.065
3.58	10	2 2 0	3.581
3.06	50	3 1 1	3.054
2.92	60	2 2 2	2.924
2.53	90	4 0 0	2.532
2.33	15	3 3 1	2.324
2.27	45	4 2 0	2.265
1.949	20	3 3 3	1.950
1.791	45	4 4 0	1.791
1.713	12	5 3 1	1.712
1.689	20	6 0 0, 4 4 2	1.688
1.461	12	4 4 4	1.462

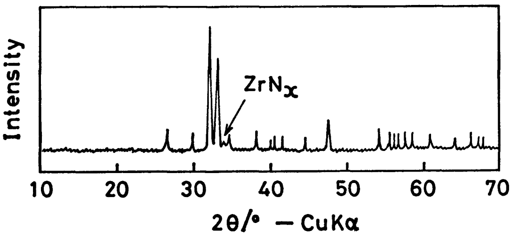


Fig. 1. X-Ray diffraction pattern of the product obtained inside the reaction zone at 950 °C.

X-Ray analysis of the product formed at 750—1050 °C showed a hitherto unknown X-ray diffraction pattern in addition to those of the known α-ZrClN,[2] β-ZrClN,[3] ZrN_x,[4] NH_4Cl,[5] and the above $ZrCl_4 \cdot 2NH_3$. As shown in Fig. 1, the product obtained at 950 °C inside the reaction zone showed an X-ray diffraction pattern consisting of the unknown pattern and a very weak diffraction line corresponding to the strongest line of ZrN_x ($2\theta = 34.0°$). The product was thus examined by chemical analysis. The chlorine content of the product was first checked after heating the sample in molten sodium carbonate. The result showed that the product contained no chlorine. This indicated that the product was zirconium nitride. The N/Zr atomic ratio of the product was found to be 1.33. As described above, this product contained a slight amount of ZrN_x. As seen from the results shown in Table 5 described later, the N/Zr atomic ratio of ZrN_x formed by the vapor-phase reaction increased with the decrease in the reaction temperature, the N/Zr atomic ratio of ZrN_x formed at 1100 °C being 1.28. Considering these facts and the accuracy of the measurement of the N/Zr atomic ratio (±0.01), the presence of a slight amount of ZrN_x caused no significant error in the measurement of the N/Zr atomic ratio of the product showing the unknown X-ray diffraction pattern. From these results and the fact that the presence of Zr_3N_4 in addition to ZrN_x had been reported[6–8] as zirconium nitride, the product showing the unknown X-ray pattern, formed at 750—1050 °C, was found to be Zr_3N_4.

TABLE 2. REACTION PRODUCTS OF GASEOUS $ZrCl_4$ WITH AMMONIA AT VARIOUS TEMPERATURES

Temp/°C	Products	
	In the reaction zone	Outside the reaction zone
300	$ZrCl_4 \cdot 2NH_3$	$ZrCl_4 \cdot 2NH_3$
350—400	$ZrCl_4 \cdot 2NH_3 \gg ZrClN[\alpha]$	$ZrCl_4 \cdot 2NH_3$; NH_4Cl
500—550	$ZrClN[\alpha]$	$ZrCl_4 \cdot 2NH_3$; NH_4Cl
600	$ZrClN[\alpha \gg \beta]$	$ZrCl_4 \cdot 2NH_3 \gg ZrClN[\alpha]$; NH_4Cl
650	$ZrClN[\alpha > \beta]$	$ZrCl_4 \cdot 2NH_3 \gg ZrClN[\alpha]$; NH_4Cl
700	$ZrClN[\beta > \alpha]$	$ZrCl_4 \cdot 2NH_3 \gg ZrClN[\alpha]$; NH_4Cl
750	$ZrClN[\beta > \alpha] \gg ZrN_x$, Zr_3N_4	$ZrCl_4 \cdot 2NH_3 > ZrClN[\alpha]$; NH_4Cl
800	$ZrClN[\beta > \alpha] \gg ZrN_x$, Zr_3N_4	$ZrClN[\alpha > \beta]$; NH_4Cl
850	$ZrClN[\beta > \alpha] \gg ZrN_x$, Zr_3N_4	$ZrClN[\alpha, \beta]$; NH_4Cl
900	$ZrClN[\beta] > Zr_3N_4 \gg ZrN_x$	$ZrClN[\alpha, \beta]$; NH_4Cl
950	$Zr_3N_4 \gg ZrN_x$	$ZrClN[\alpha, \beta] \gg ZrN_x$, Zr_3N_4; NH_4Cl
1000—1050	$Zr_3N_4 > ZrN_x$	$ZrN_x \gg Zr_3N_4$; NH_4Cl
1100—1400	—	ZrN_x; NH_4Cl, HCl

Table 3. Experimental results for $ZrCl_4 \cdot 2NH_3$ on heating in an ammonia stream

Heating temp/°C	Products		Unreacted $ZrCl_4 \cdot 2NH_3$/%
	In the boat	Outside the boat	
350	ZrClN[α](25)	ZrClN(3), $ZrCl_4 \cdot 2NH_3$(6), NH_4Cl	66
400	ZrClN[α](60)	ZrClN(25), $ZrCl_4 \cdot 2NH_3$(15), NH_4Cl	—

The value in parentheses is mole percentage of $ZrCl_4 \cdot 2NH_3$ converted to the product.

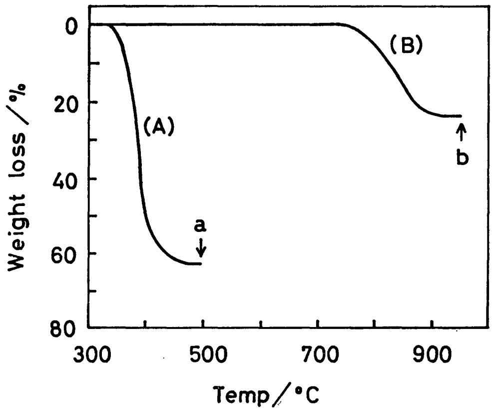


Fig. 2. TG curves of $ZrCl_4 \cdot 2NH_3$ and ZrClN in an ammonia stream.
(A): $ZrCl_4 \cdot 2NH_3$, (B): ZrClN.

The reaction products of gaseous $ZrCl_4$ with ammonia at various temperatures above 300 °C are summarized in Table 2. The symbols α and β in the parentheses represent the modifications of ZrClN.

Unreacted $ZrCl_4$ was not observed throughout the temperature range of this work. The products which formed below 750 °C were obtained inside and outside the reaction zone. Above 800 °C, a large portion of the products were obtained outside the reaction zone, and above 1100 °C, all the products were obtained outside the reaction zone. Above 1100 °C, HCl was formed in addition to by-product NH_4Cl. The percentage of HCl formed to the total amount of chlorine introduced as $ZrCl_4$ was $<1\%$ at 1100 °C, 10% at 1200 °C, 25% at 1300 °C, and 60% at 1400 °C. The value is nearly the same as that of the HCl formed by the thermal decomposition of NH_4Cl at each temperature under the experimental conditions in this work.[9] This was considered to indicate that the HCl formed was due to the decomposition of the by-product NH_4Cl.

Reaction Process of Gaseous Zirconium Tetrachloride with Ammonia. To elucidate the reaction process of gaseous $ZrCl_4$ with ammonia, the behavior of the $ZrCl_4 \cdot 2NH_3$, the ZrClN, and the Zr_3N_4, which had been formed during the reaction process, on heating in an ammonia stream were examined.

Behavior of $ZrCl_4 \cdot 2NH_3$ on Heating in an Ammonia Stream: The TG curve of $ZrCl_4 \cdot 2NH_3$ in an ammonia stream is shown in Fig. 2 (A).

$ZrCl_4 \cdot 2NH_3$ lost weight above 330 °C. It was observed that NH_4Cl and a small amount of $ZrCl_4 \cdot 2NH_3$ deposited outside the heating zone during the weight loss. The sample after the heating to point a was found to be α-ZrClN by X-ray analysis. The final weight loss was 62.8%. This value was considerably larger than the calculated value, 47.33%, based on the reaction, $ZrCl_4 \cdot 2NH_3 + 2NH_3 \rightarrow ZrClN + 3NH_4Cl$. This was considered to be due to the vaporization of a part of the $ZrCl_4 \cdot 2NH_3$.

In order to obtain more detailed information on the behavior of $ZrCl_4 \cdot 2NH_3$ on heating in an ammonia stream, $ZrCl_4 \cdot 2NH_3$ (1.0 g) in a quartz boat (70 mm length, 15 mm width, 7 mm depth) was placed in a straight reaction tube (28 mm i.d., 1000 mm length). Ammonia was introduced into the reaction tube at a flow-rate of 100 cm^3/min. The sample part was then placed in the centre of an electric furnace (300 mm heating length) maintained at a specified temperature for 1 h. The products obtained inside and outside the boat were examined by X-ray analysis and chemical analysis. The results are shown in Table 3.

From these results, it was found that on heating $ZrCl_4 \cdot 2NH_3$ in an ammonia stream, $ZrCl_4 \cdot 2NH_3$ reacted with ammonia above about 330 °C to form ZrClN and NH_4Cl and that the reaction was accompanied by the vaporization of a part of $ZrCl_4 \cdot 2NH_3$. The formation of ZrClN outside the boat was considered to indicate that the reaction of gaseous $ZrCl_4 \cdot 2NH_3$ with ammonia to form ZrClN also occurred.

Behavior of ZrClN on Heating in an Ammonia Stream: The TG curve of ZrClN in an ammonia stream is shown in Fig. 2(B). α-ZrClN obtained inside the reaction zone by the reaction of gaseous $ZrCl_4$ with ammonia at 500 °C was used. ZrClN lost weight above 750 °C. The sample after the heating to point b was found to be a mixture of ZrN_x and a small amount of Zr_3N_4 by X-ray analysis. It was observed that NH_4Cl alone was deposited outside the heating zone during the weight loss.

In order to obtain more detailed information on the behavior of ZrClN on heating in an ammonia stream, the products obtained by heating ZrClN(α) (0.5 g) in a quartz boat in an ammonia stream (100 cm^3/min) for 1 h at a specified temperature were examined by X-ray analysis and chemical analysis. The results are shown in Table 4.

These results showed that, on heating ZrClN(α) in an ammonia stream, the transition of α-ZrClN to β-ZrClN occurred above about 600 °C and that the reaction of ZrClN with ammonia occurred above about 750 °C to form ZrN_x, Zr_3N_4, and NH_4Cl at 750—1000 °C and ZrN_x and NH_4Cl at 1100 °C.

Behavior of Zr_3N_4 on Heating in an Ammonia Stream: The products obtained by heating Zr_3N_4 (0.2 g) in an ammonia stream (100 cm^3/min) for 1 h at various temperatures were examined. The sample Zr_3N_4 used was the Zr_3N_4 containing a slight amount of ZrN_x,

TABLE 4. EXPERIMENTAL RESULTS FOR ZrClN ON HEATING IN AN AMMONIA STREAM

Heating temp/°C	Products		Unreacted ZrClN/%
	In the boat	Outside the boat	
550	ZrClN[α]	—	100
600—700	ZrClN[α>β]	—	100
750	ZrClN[α>β], $ZrN_x>Zr_3N_4$	NH_4Cl	64
800	$ZrN_x>$ZrClN[β], Zr_3N_4	NH_4Cl	25
850	$ZrN_x>Zr_3N_4>$ZrClN[β]	NH_4Cl	10
900	$ZrN_x>Zr_3N_4$	NH_4Cl	—
1000	$ZrN_x\gg Zr_3N_4$	NH_4Cl	—
1100	ZrN_x	NH_4Cl	—

TABLE 5. N/Zr ATOMIC RATIOS AND LATTICE CONSTANTS OF THE ZrN_x FORMED

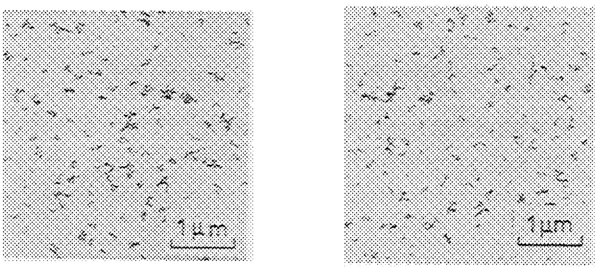
Formation temp/°C	x in ZrN_x	a_0/Å
1100	1.28	4.560
1200	1.24	4.564
1300	1.18	4.568
1400	1.12	4.571

which was formed by the reaction of qaseous $ZrCl_4$ with ammonia at 950 °C, because Zr_3N_4 alone was not obtained throughout the experiments in this work. X-Ray analysis of the sample after the heating at each temperature showed it to be $Zr_3N_4\gg ZrN_x$ (unchanged) at 900 °C, Zr_3N_4, ZrN_x at 1000 °C, and $ZrN_x>Zr_3N_4$ at 1100 °C. The results showed that Zr_3N_4 decomposed to ZrN_x above about 1000 °C in an ammonia stream.

From the results, it was considered that ZrN_x formed by heating ZrClN in an ammonia stream at temperatures lower than 1000 °C (Table 4) was formed without passing through Zr_3N_4. Consequently, it may be concluded that on heating ZrClN in an ammonia stream, it reacts with ammonia above about 750 °C to from ZrN_x and Zr_3N_4. Above about 1000 °C, ZrN_x was also formed by the thermal decomposition of the Zr_3N_4 formed.

Based on the above experimental results, the reaction process of gaseous $ZrCl_4$ with ammonia was discussed. As shown in Table 2, $ZrCl_4\cdot 2NH_3$ alone was formed at 300 °C. This fact indicates that the reaction of gaseous $ZrCl_4$ with ammonia to form $ZrCl_4\cdot 2NH_3$ occurs first. The ZrClN formed at 350—950 °C is considered to be due to the reaction of $ZrCl_4\cdot 2NH_3$ with ammonia, because the $ZrCl_4\cdot 2NH_3$ reacts with ammonia above about 330 °C to form ZrClN, as described above. The ZrN_x and Zr_3N_4 formed above 750 °C are considered to be due to the reaction of ZrClN with ammonia, because the ZrClN reacts with ammonia to form ZrN_x and Zr_3N_4 above about 750 °C. Above about 1000 °C, ZrN_x is considered to be formed also by the thermal decomposition of Zr_3N_4, because Zr_3N_4 decomposes to ZrN_x in an ammonia stream above about 1000 °C.

From the above-mentioned results, the reaction process of $ZrCl_4$ with ammonia in the vapor phase can be represented as follows: The reaction of gaseous $ZrCl_4$ with ammonia to form $ZrCl_4\cdot 2NH_3$ occurs first. Above about 330 °C, the $ZrCl_4\cdot 2NH_3$ reacts with ammonia to form ZrClN. Above about 750 °C, the ZrClN reacts with ammonia to form ZrN_x and Zr_3N_4. Above about 1000 °C, ZrN_x is also formed by the thermal decomposition of the Zr_3N_4.



(a) 1200 °C (b) 1400 °C

Fig. 3. Electron micrographs of the ZrN_x formed at various temperatures.

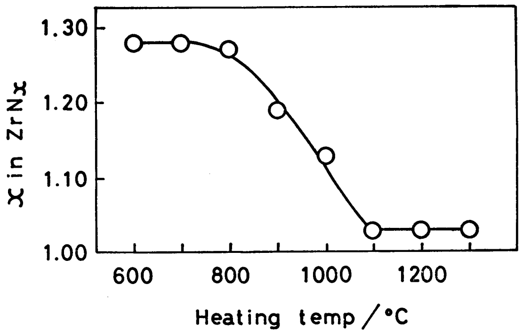


Fig. 4. N/Zr atomic ratios of ZrN_x obtained after heating $ZrN_{1.28}$ at various temperatures in an argon atmosphere.

Properties of the ZrN_x Formed. The N/Zr atomic ratios of ZrN_x formed outside the reaction zone by the reaction of geseous $ZrCl_4$ with ammonia at 1100—1400 °C are shown in Table 5. Prior to this examination, the presence of residual NH_4Cl in the ZrN_x, obtained after the removal of NH_4Cl at 400 °C *in vacuo*, was checked by chemical analysis,[10)] after the heating of the ZrN_x sample in molten sodium carbonate. The NH_4Cl content in the ZrN_x was 1.5% for the ZrN_x formed at 1100 °C, 0.9% at 1200 °C, 0.4% at 1300 °C, and <0.1% at 1400 °C. For the evaluation of the N/Zr atomic ratio of the ZrN_x formed, the initial weight of the sample was corrected by subtracting the amount of NH_4Cl contained, because the NH_4Cl was

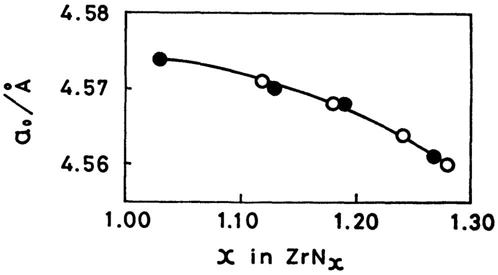


Fig. 5. Lattice constants of the ZrN_x with various x values.
○: From ZrN_x formed by the reaction of gaseous $ZrCl_4$ with ammonia, ●: From ZrN_x obtained after the heating of $ZrN_{1.28}$.

vaporized during the oxidation.[9]

It has been known that the ZrN_x phase has a NaCl structure.[4] The lattice constant of ZrN_x formed at each temperature is also shown in Table 5.

The ZrN_x formed by the reaction of gaseous $ZrCl_4$ with ammonia above 1100 °C were examined by electron microscopy. Typical micrographs of the ZrN_x are shown in Fig. 3.

As seen from Fig. 3, the ZrN_x formed is uniform, ultrafine powders with the particle diameters of the order of 1/100 μm.

Finally, to obtain knowledge of the thermal stablilty of the ZrN_x formed, the N/Zr atomic ratios of the samples obtained by heating $ZrN_{x(x=1.28)}$ at various temperatures in an argon atmosphere for 1 h were examined. The results are shown in Fig. 4. In addition, it was found that the residual NH_4Cl in the ZrN_x was completely removed by the heating above 900 °C.

The results indicated that when the ZrN_x formed was heated in an argon atmosphere at temperatures higher than 700 °C, the N/Zr atomic ratio decreased and became close to that of the stoichiometric nitride. The value of x was 1.03 at the heating temperatures of 1100—1300 °C.

The lattice constants of the ZrN_x with various x values, obtained in this work, are shown in Fig. 5.

The present work was partially supported by a Grant-in-Aid for Scientific Research No.56470058 from the Ministry of Education, Science and Culture.

References

1) Y. Okabe, J. Hojo, and A. Kato, *Yogyo Kyokai Shi*, **85**, 173 (1977).
2) R. Juza and J. Heners, *Z. Anorg. Allg. Chem.*, **332**, 159 (1964).
3) JCPDS, Powder Diffraction File 18-1493.
4) ASTM, X-Ray Powder Data File 2-956.
5) ASTM, Powder Diffraction File 7-7.
6) R. Juza, A. Gabel, H. Rabenau, and W. Klose, *Z. Anorg. Allg. Chem.*, **329**, 136 (1964).
7) R. Juza, A. Rabenau, and I. Nitschke, *Z. Anorg. Allg. Chem.*, **332**, 1 (1964).
8) V. P. Orlovskii, N. V. Rudenko, and B. V. Ivanov-Emin, *Russ. J. Inorg. Chem.*, **12**, 1217 (1967).
9) Y. Saeki, R. Matsuzaki, A. Yajima, and M. Akiyama, *Bull. Chem. Soc. Jpn.*, **55**, 3193 (1982).
10) JIS H 1615 (1973), p. 2.