JOURNAL OF SOLID STATE CHEMISTRY 75, 99–104 (1988)

Novel Synthesis of the Layer Structured β-ZrNCl by the Direct Reactions of Zirconium Metal or Zirconium Hydride with Ammonium Chloride

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Received September 16, 1987; in revised form January 18, 1988

The layer structured β-ZrNCl can be synthesized in high yield by the direct reaction of zirconium metal or zirconium hydride with the vapor of ammonium chloride at temperatures ranging from 550 to 700°C. The as-prepared sample was contaminated with a small amount of oxide, and purified by chemical transport in a vacuum-sealed tube with a temperature gradient from 750 to 850°C. The sample transported to the higher temperature zone is highly crystalline and the structure is characterized by a rhombohedral stacking sequence of ZrNCl layers rather than a hexagonal random stacking sequence found in the as-prepared samples. © 1988 Academic Press, Inc.

Introduction

β-zirconium nitride chloride β-ZrNCl is a layer structured compound (*1*). Each stacking layer consists of a zirconium nitride layer sequenced Zr–N–N–Zr along the direction normal to the layer plane, which is in turn sandwiched between two close-packed chlorine layers. Such ZrNCl layers (Cl–Zr–N–N–Zr–Cl) are randomly stacked with each other by van der Waals interactions. In previous papers (*2, 3*), we showed that lithium can be intercalated into the interlayer spaces by breaking the weak interactions between the chloride layers. On intercalation of the lithium, the color of β-ZrNCl is changed from pale yellow-green to black. Since these color changes occur reversibly on redox intercalation and deintercalation of the lithium, β-ZrNCl can be a promising candidate for electrochromic electrode material. We also have proposed that β-ZrNCl can be used for solid lubricant (*4*). Recently, Ziebarth and Corbett (*5*) reported that ZrNCl was a useful nitrogen source in the synthesis of zirconium clusters containing nitrogen.

β-ZrNCl is generally prepared in two steps according to the method reported by Juza and Heners (*6*); in the first step, solid $ZrCl_4$ is subjected to reaction with gaseous ammonia at temperatures of 300 to 400°C, to form α-ZrNCl, which is a layered modification having the FeOCl structure. In the next step, the α form is heated at about 600°C to transform it into the β form. The problems encountered in these procedures are that the use of hydrolyzable $ZrCl_4$ is unavoidable, and in addition, that the yield for the total reaction is as low as about

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0022-4596/88 $3.00

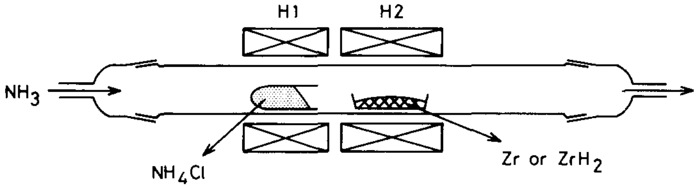

FIG. 1. Apparatus for the reaction of Zr or ZrH_2 with gaseous NH_4Cl.

20%. The low yield is probably due to the formation of a by-product $(NH_4)_2ZrCl_6$, which is removed from the system by vaporization during the second heating step (*7*).

Ohashi *et al.* (*8*) showed that the thermal decomposition of the amide $ZrCl_3(NH_2)$ in an ammonia atmosphere gave β-ZrNCl in high yield. In this procedure, however, the starting amide was also prepared by the ammonolysis of hydrolyzable $ZrCl_4$ with liquid ammonia. The operation is not so simple.

In the present study, a novel and simple synthesis route for β-ZrNCl has been developed; zirconium metal or zirconium hydride is subjected to reaction with ammonium chloride directly at elevated temperatures, which results in β-ZrNCl in high yield.

Experimental

Materials. Zirconium metal and zirconium hydride used were powder forms with the particle size of about 40 μm (Mitsuwa Pure Chemicals). The purity of gaseous ammonia was 99.999%. Ammonium chloride was dried by evacuation for 8 hr at 150°C prior to use.

Synthesis. Figure 1 shows the schematic diagram of a fused silica tube reactor with ground-glass joints at the ends for gas inlet and outlet. The dimensions of the tube is about 1 m in length and 35 mm in diameter. Two electric heaters, H1 and H2, were installed to surround the reactor. About 5 g of the dried ammonium chloride was loaded in a Pyrex glass tube with one end closed and placed in the reactor on the side of the heater H1; about 0.5 g of zirconium metal or zirconium hydride was weighed in a fused silica boat and placed in the reactor on the side of the heater H2. After evacuation, a stream of gaseous ammonia was passed through the reactor at a rate of about 50 ml/min during the reaction. The zirconium metal or zirconium hydride was heated by using the heater H2 to a desired preset temperature in the range of 400 to 900°C, and then ammonium chloride was vaporized at about 360°C by using the heater H1. The average vaporization rate of the ammonium chloride was measured to be about 100 mg/min. After standing for 30 min, the heater H1 was detached to stop the vaporization of ammonium chloride; the reactor was purged with dry nitrogen and cooled to room temperature. The resulting product in the boat was weighed and the phases present were identified by the measurement of the X-ray powder diffraction (XRD) patterns by using Ni filtered CuK_α radiation.

Chemical analyses. A weighed amount of the product (about 100 mg) was dissolved in 10 ml of 2 moles dm^{-3} sulfuric acid containing 2 ml of concentrated hydrofluoric acid. The zirconium and chlorine contents were determined gravimetrically as ZrO_2 and AgCl, respectively. Before filtration of the AgCl precipitate, 50 ml of 5% boric acid solution was added to the solution to prevent the glass filter from erosion by hydrofluoric acid. Nitrogen was analyzed by the Kjeldahl method. The oxygen content was determined by the chlorination method; the

TABLE I

REACTION PRODUCTS OF ZrH_2 WITH GASEOUS NH_4Cl AND THE YIELDS OF β-ZrNCl AT VARIOUS TEMPERATURES

Temp/°C	Products	Yield/%
400	$(NH_4)_2ZrCl_6$, α-ZrNCl	
500	β-ZrNCl	30
550	β-ZrNCl	76
600	β-ZrNCl	66
650	β-ZrNCl	74
700	β-ZrNCl	80
800	β-ZrNCl $\gg$ $ZrNH_{0.6}$	
900	β-ZrNCl > ZrN, $ZrNH_{0.6}$	

product was heated in a stream of chlorine gas at 600°C for 1 hr. The oxygen contained in the product remained in the boat as zirconium oxide.

Results

Formation region. The reactivities of zirconium metal and zirconium hydride were found to be very similar in the reactions with ammonium chloride. In most cases, the hydride was used as reactant. The phases identified in the reaction products of zirconium hydride at different temperatures are listed in Table I. As seen from the table, β-ZrNCl was obtained as a single phase at the temperatures ranging from 500 to 700°C. At higher temperatures, the phases without containing chlorine such as $ZrNH_{0.6}$ (*9*) and ZrN were accompanied. These phases seem to result from the thermal decomposition of β-ZrNCl. At a lower reaction temperature of 400°C, $(NH_4)_2ZrCl_6$ (*7*) and α-ZrNCl were formed. As for the products containing β-ZrNCl as a single phase, apparent conversion of zirconium hydride to β-ZrNCl or yield was calculated on the basis of the weight changes observed before and after the reactions. The calculated values are shown in Table I. The conversion as high as 75% was attained in the temperature range from 550 to 700°C.

Analyses. The chemical analysis data for the product obtained from zirconium hydride at 650°C are shown in Table II. The data are in good agreement with the values calculated for β-ZrNCl. The product is contaminated with about 2% of oxygen. It is reasonable to assume that the oxygen is bound to zirconium in the form of ZrO_2. The contamination of oxygen probably comes from zirconium hydride powder which may be covered with thin oxidized surfaces.

Figure 2a shows the XRD pattern of the product obtained at 650°C. Although the pattern is broad, almost all the reflections can be indexed on the basis of a hexagonal cell of $a = 2.08$ and $c = 9.35$ Å, the dimensions of which are in good agreement with those for β-ZrNCl reported by Juza and Friedrichsen ($a = 2.08$ and $c = 9.23$ Å). The remaining unindexed peaks appearing at the diffraction angles ranging from 28 to 32° can be attributed to a mixture of monoclinic and tetragonal zirconia, which are designated by m and t in the XRD pattern, respectively. The product obtained from zirconium metal also showed a very similar XRD pattern. It appears that the β-ZrNCl from zirconium metal is also contaminated with ZrO_2 to the same extent.

Chemical transport. So long as zirconium hydride or zirconium powder reactants are used, the contamination of zirconia seems to be unavoidable. However, it

TABLE II

CHEMICAL ANALYSIS DATA OF β-ZrNCl OBTAINED AT 650°C

	Calcd/%	Found/%	Atomic ratio*
Zr	64.8	64.8	1.07
N	9.96	9.30	1
Cl	25.2	23.7	1.01
O		2.07	0.19
Total	100.0	99.9	

* With reference to nitrogen.

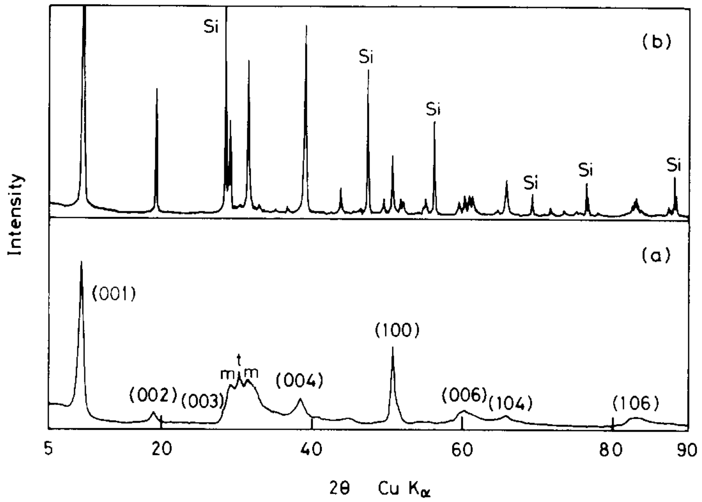

FIG. 2. X-ray powder diffraction patterns of β-ZrNCl (a) as-prepared and (b) chemically transported. Diffraction peaks for silicon used as an internal standard are marked by Si in (b).

has been found that the product can be purified by the chemical transport. The as-prepared sample was vacuum sealed in a fused silica tube, and placed in a furnace with a temperature gradient from 750 to 850°C. β-ZrNCl was transported into the higher temperature zone in a few days. The transported sample was highly crystalline and contaminated with little oxide. The analytical data of the transported β-ZrNCl are shown in Table III. The oxygen contamination is reduced to less than 0.3%. Its XRD pattern is shown in Fig. 2b in comparison with that of the as-prepared sample. The XRD data for the chemically transported sample are given in Table IV. It should be noted that the reflections for the transported sample can be indexed on the basis of a $\sqrt{3}\,a \times 3c$ supper cell, 3.6055(4) Å × 27.664(4) Å, rather than the hexagonal cell previously used for the as-prepared sample.

TABLE III

CHEMICAL ANALYSIS DATA OF β-ZrNCl OBTAINED BY CHEMICAL TRANSPORT

	Calcd/%	Found/%	Atomic ratio*
Zr	64.8	65.4	1.04
N	9.96	9.68	1
Cl	25.2	24.4	1.00
O		0.30	0.03
Total	100.0	99.8	

* With reference to nitrogen.

Juza and Friedrichsen (*1*) proposed a random CdI_2–$CdCl_2$ structure for β-ZrNCl, since the XRD pattern can be indexed on the basis of a fractional hexagonal cell containing only a 2/3 ZrNCl unit, so that a random stacking sequence of the layers is suggested. On the contrary, the XRD pattern of the highly crystalline sample can be indexed on the basis of the $\sqrt{3}\,a \times 3c$ supper cell and as seen from the table, only the reflections for which $-h + k + l = 3n$ are present. This indicates that the symmetry is rhombohedral rather than hexagonal. It is reasonable to assume that the structure of the chemically transported sample is of $CdCl_2$ type.

Discussion

In most reactions, ammonia was used as a flowing gas. However, even by using ar-

TABLE IV

X-RAY DIFFRACTION DATA OF β-ZrNCl OBTAINED BY CHEMICAL TRANSPORT

d_{obs}	I_{obs}	$h\ k\ l$*	d_{calcd}
9.213	100	0 0 3	9.221
4.604	15	0 0 6	4.610
3.101	5	1 0 1	3.103
3.072	10	0 0 9	3.074
2.844	15	1 0 4	2.846
2.718	1	0 1 5	2.720
2.448	1	1 0 7	2.450
2.317	10	0 1 8	2.318
2.305	20	0 0 12	2.305
2.070	5	1 0 10	2.071
1.9589	1	0 1 11	1.9586
1.8431	1	0 0 15	1.8442
1.8019	10	1 1 0	1.8029
1.7696	1	1 1 3	1.7694
1.7586	1	1 0 13	1.7585
1.6797	1	1 1 6	1.6791
1.6706	1	0 1 14	1.6697
1.5555	1	1 1 9	1.5551
1.5362	5	0 0 18	1.5368
1.5221	5	0 2 4	1.5230
1.5117	5	1 0 16	1.5126
1.4427	1	0 1 17	1.4431
1.4194	5	1 1 12	1.4202
1.3171	1	0 0 21	1.3173
1.2892	1	1 1 15	1.2892
1.2642	1	0 1 20	1.2646
1.2592	1	0 2 13	1.2588
1.2254	1	2 0 14	1.2251
1.1797	1	2 1 1	1.1792
1.1700	1	1 1 18	1.1696
1.1670	1	1 0 22	1.1664
1.1630	5	2 1 4	1.1635
1.1549	1	1 2 5	1.1543
1.1165	1	1 2 8	1.1170

* Indexed on the basis of a hexagonal unit cell of a = 3.6055 Å and c = 27.664 Å.

gon or nitrogen gas, β-ZrNCl was obtained in a similar manner, although the yield was about 20% lower. Evidently, ammonia is not essential for the formation of β-ZrNCl from zirconium metal or zirconium hydride. The fundamental reactions can be written by the following equations:

$$\mathrm{Zr} + \mathrm{NH_4Cl} \rightarrow \mathrm{ZrNCl} + 2\ \mathrm{H_2}$$

$$\mathrm{ZrH_2} + \mathrm{NH_4Cl} \rightarrow \mathrm{ZrNCl} + 3\ \mathrm{H_2}$$

In a previous study (*7*), we showed that $(NH_4)_2ZrCl_6$ was an easily formed phase in the reaction systems $ZrCl_4$–NH_3, $ZrCl_4$—NH_4Cl and $ZrCl_3(NH_2)\cdot x NH_3$–NH_4Cl, and began to vaporize at about 400 ° C by raising the temperature. As mentioned in the foregoing paragraph, in the preparation of β-ZrNCl by the method of Juza and Heners (*6*), the vaporization of $(NH_4)_2ZrCl_6$ does occur during the course of the second heating step and results in very low yield of β-ZrNCl. Even in the present reaction systems of zirconium metal or zirconium hydride with ammonium chloride, $(NH_4)_2ZrCl_6$ also appears at a low reaction temperature of 400°C. The reactions may be written as

$$\mathrm{Zr} + 6\ \mathrm{NH_4Cl} \rightarrow (\mathrm{NH_4})_2\mathrm{ZrCl_6} + 4\ \mathrm{NH_3} + 2\ \mathrm{H_2}$$

$$\mathrm{ZrH_2} + 6\ \mathrm{NH_4Cl} \rightarrow (\mathrm{NH_4})_2\mathrm{ZrCl_6} + 4\ \mathrm{NH_3} + 3\ \mathrm{H_2}$$

It seems reasonable to consider that similar reactions occur even at higher reaction temperatures. However, if the temperature of zirconium metal or zirconium hydride is high enough, it is likely that the $(NH_4)_2ZrCl_6$ is decomposed to β-ZrNCl as soon as it is formed on the surface of the zirconium metal or zirconium hydride.

$$(\mathrm{NH_4})_2\mathrm{ZrCl_6} \rightarrow \beta\text{-}\mathrm{ZrNCl} + \mathrm{NH_4Cl} + 4\ \mathrm{HCl}$$

As shown in Table I, the yield for β-ZrNCl is only 30% at 500°C, which is remarkably low compared with the yields for the reaction above 550°C. It seems reasonable to conclude that the rate of the above decomposition is not fast enough at 500°C, and large portions of $(NH_4)_2ZrCl_6$ are carried away with the flowing ammonia before converting to β-ZrNCl.

Savranskii *et al.* (*10*) investigated the reactions of zirconium metal and zirconium nitride with ammonium chloride under a high pressure of 30–40 kbar and at a high temperature of 1000–1500°C. They found that ZrN and β-ZrNCl were obtained from the systems Zr–NH_4Cl and ZrN–NH_4Cl, respectively. We have also examined the reactions of ZrN with the vapor of NH_4Cl at atmospheric pressure in the temperature range of 500 to 800°C. Although β-ZrNCl was also obtained, ZrN was less reactive than zirconium and zirconium hydride, and part of the ZrN remained unreacted. It should be emphasized that in the method developed in this study, no high pressure nor high temperature was necessary.

The mechanism for the chemical transport of β-ZrNCl remains to be solved. In a preliminary study, we have found that the transport is much accelerated by the addition of a small amount of ammonium chloride. Detailed mechanism for the chemical transport and the nature of the vapor phases involved are now under way.

Acknowledgment

This study was partly supported by the Grant-in-Aid for Developmental Scientific Research (No. 61850148) of the Ministry of Education, Science and Culture.

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