PREPARATION OF THORIUM NITRIDES AND THEIR OXIDATION BEHAVIOUR*

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Summary

This paper summarizes the results obtained during a course of study of the preparation of thorium nitrides, Th_3N_4 and ThN.

Well-crystallized Th_3N_4 free from oxide has been prepared by the reaction of powdered Th_4H_{15} with flowing N₂ at 800 °C. Thermal decomposition of Th_3N_4 under various conditions has been studied to prepare ThN containing no ThO_2 .

As part of the study on the oxidation of thorium nitrides, the air-oxidation of Th_3N_4 has been performed around room temperature for different periods extending to one week. From broad diffuse peaks in the X-ray diffraction patterns for the completely oxidized products, it follows that either amorphous ThO₂ or ThO₂ of small crystallite size forms.

A preliminary experiment indicated that ThN was easily soluble in HNO_3 at room temperature.

1. Introduction

The current Japanese interest in thorium-fuelled reactors has led us to make a renewed study of the preparation of thorium nitrides.

There exist two nitrides, Th_3N_4 and ThN, in the Th-N system. Although information is available on the physical and chemical properties of the nitrides, almost all the data have been measured with poorly characterized samples. In order to obtain reliable data on the properties of the nitrides it is necessary to establish preparation methods for pure homogeneous and wellcharacterized thorium nitrides.

Two methods have been reported for the preparation of ThN: (a) the direct nitriding of thorium metal under a nitrogen pressure higher than 1 atm at about 2000 °C [1], and (b) the thermal decomposition of Th₃N₄ at about 1500 °C [1 - 3]. According to Olson and Mulford [1], ThN ingot prepared by method (a) is less unstable in air than ThN samples prepared by method

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(b), even though a black surface film forms on the ThN ingot within seconds of removing it from the furnace. X-ray diffraction examinations revealed the presence of ThO₂ as an impurity in the ThN prepared by method (b) [1 - 3]. Ozaki *et al.* [3] observed ThO₂ in the Th₃N₄, although other authors [1, 2] have not mentioned this point. Little work on the oxidation of thorium nitrides has been reported in the literature. Ozaki *et al.* [3] have made a kinetic study of the oxidation of Th₃N₄ and ThN.

In this paper, representative results obtained from an experimental study of the preparation of thorium nitrides is described.

In addition, oxidation of Th_3N_4 has been studied at about room temperature using an X-ray diffraction technique.

From the viewpoint of the down stream chemistry in the thorium fuel cycle, the solubility of ThN in HNO_3 may be very important. A preliminary experiment has been performed on the dissolution of ThN in HNO_3 at room temperature.

2. Preparation of thorium nitrides

 Th_3N_4 has been prepared by nitriding powdered thorium or Th_4H_{15} . ThN has been obtained by thermal decomposition of Th_3N_4 prepared by the above method. The preparation methods developed in our laboratory for powdered thorium and Th_4H_{15} have already been reported [4].

The phases formed have been identified using an X-ray diffraction technique and [N]/[Th] ratio of the products has been determined by a chemical analysis.

2.1. Preparation of Th_3N_4

A number of experimental trials for the preparation of Th_3N_4 have been done using the reaction of thorium or Th_4H_{15} with nitrogen or NH_3 between 700 and 800 °C. The reaction of thorium with nitrogen or NH_3 has not yielded satisfactory results, probably due to the fact that sintering occurs to some extent during dehydriding. From all the results obtained in our laboratory, it is concluded that the reaction of Th_4H_{15} with flowing nitrogen at about 800 °C may be suitable for the preparation of Th_3N_4 . Insofar as could be judged from the X-ray diffraction pattern shown in Fig. 1, no ThO_2



Fig. 1. X-ray diffraction pattern for Th₃N₄ prepared by the reaction of Th₄H₁₅ with flowing nitrogen at 800 $^{\circ}$ C.

existed. A chemical analysis of the product gives [N]/[Th] = 1.30. The separation between the (211) and (333) peaks of Th₃N₄ is excellent, suggesting the formation of well-crystallized Th₃N₄.

2.2. Preparation of ThN

In an attempt to produce ThN containing no ThO_2 , thermal decomposition of Th_3N_4 has been performed under various conditions.

Thermal decomposition of Th_3N_4 placed in a molybdenum boat in an Al_2O_3 reaction tube was performed for 2 h at 1400 °C under a vacuum of 10^{-3} Pa. The X-ray diffraction pattern of the product in Fig. 2(a) shows that the major phase is ThN (a = 5.159 Å) with a small amount of ThO₂. Chemical analysis of the product gives $[N]/[Th] = 0.95_4$, indicating that the product includes about 5 mol.% ThO₂.

Figure 2(b) shows the diffraction pattern for the sample obtained by thermal decomposition of Th_3N_4 at 1400 °C in flowing argon. Although the major phase is ThN, Th_2N_2O is found to exist as an impurity in addition to ThO_2 . Benz [5] has reported that Th_2N_2O is formed by the reaction between ThN and ThO_2 under a nitrogen atmosphere, according to the equation $6ThN + 2ThO_2 + N_2 = 4Th_2N_2O$. A thermodynamic estimate suggests that Th_2N_2O may form when the partial pressure of nitrogen exceeds about 1 Pa. The formation of Th_2N_2O may, in this case, be attributed to the nitrogen resulting from Th_3N_4 decomposition.

 Th_3N_4 in a quartz boat has been held at 1000 °C for 30 h under a vacuum of 10^{-3} Pa in a quartz reaction tube. As shown in Fig. 2(c), the diffraction pattern of the heat-treated sample consists of the peaks corresponding to ThN and Th_3N_4 . This is consistent with the fact that ThN and Th_3N_4 coexist in equilibrium under the experimental conditions. It should be emphasized, however, that no peak for ThO₂ has been detected.

These three experimental results, together with all other results obtained in our work, suggest that the preparation of pure ThN is possible with a suitable choice of atmosphere and materials for the reaction tube and boat.



Fig. 2. X-ray diffraction patterns for the products obtained by thermal decomposition of Th_3N_4 : (a) at 1400 °C in vacuum; (b) at 1400 °C in argon; (c) at 1000 °C in vacuum.

3. Oxidation of Th_3N_4

Oxidation behaviour of Th_3N_4 in dry air for one week at 0 and 50 °C has been examined with the aid of X-ray diffraction. After oxidation, brown Th_3N_4 was converted to a white substance. As seen in the X-ray diffraction pattern in Fig. 3(a), shown as a typical example, the product at 0 °C generates only two diffuse halos. In the pattern of the product at 50 °C, shown in Fig. 3(b), one additional broad halo appears. From these results, it is suggested that amorphous ThO_2 or ThO_2 of small crystallite size is formed by the oxidation of Th_3N_4 .

The powder sample obtained at 50 °C was heat-treated at 1400 °C in a vacuum of 1×10^{-3} Pa. The diffraction pattern of the product, shown in Fig. 3(c), consists of the 14 peaks appearing in the pattern of well-crystallized ThO₂ when Cu K α radiation is used. Moreover, ThO₂ is the only stable oxide in the Th–O system in the solid state and the [O]/[Th] ratio is very close to 2.00 below 1400 °C. From these results, it follows that the products obtained by air-oxidation of Th₃N₄ at 0 and 50 °C are ThO₂ of poorly crystalline character.

More detailed study of the oxidation of Th_3N_4 will be reported elsewhere.



Fig. 3. X-ray diffraction patterns: curve a, the product produced in the air-oxidation of Th_3N_4 at 0 °C; curve b, the product produced in the air-oxidation of Th_3N_4 at 50 °C; curve c, after heat-treating at 1400 °C in vacuum, the product of air-oxidation at 50 °C.

4. Dissolution of ThN in HNO₃

The ThN powder prepared (containing small amounts of ThO₂) was immersed in HNO₃ (conc.) for 30 h at room temperature. The insoluble residue was filtered out and identified as ThO₂ using X-ray diffraction analysis. The filtrate was evaporated to dryness and the residue was again dissolved in distilled water. The solution was held at 50 °C until evaporation was completed and then the residue was sufficiently air dried at 50 °C. A white platelike crystalline solid was obtained. The X-ray pattern of this solid does not correspond to ThN, ThO₂ or Th₂N₂O. Unfortunately, the crystal structures of Th(NO₃)₄ and Th(NO₃)₄•4H₂O are not to be found in the literature as far as we know. However, this compound may be assumed to be either Th(NO₃)₄ or Th(NO₃)₄•4H₂O since it is easily soluble in H₂O and it is a white plate-like crystalline solid. The determination of the crystal structure of the compound is now under way.

5. Conclusion

(1) A preparation method for well-defined Th_3N_4 has been established, and much information that will aid preparation of pure ThN has been accumulated.

(2) ThO₂ of a poor crystalline nature is found to be produced in the oxidation of Th_3N_4 at about room temperature.

(3) It is found that ThN is easily soluble in HNO_3 at room temperature.

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