



Letter to the Editors

Preparation and characterization of PuN pellets containing ZrN and TiN

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Abstract

PuN pellets containing inert matrix nitrides such as ZrN and TiN were prepared and characterized. Formation of (Pu,Zr)N solid solution was confirmed by X-ray diffraction analysis and metallographic examination of the dense pellets. On the other hand, the pellets were constituted by two phases when PuN was heated with TiN. The dissolved amount of TiN was negligibly small. Several thousands ppm of oxygen was found in both samples owing to the oxidation of ZrN and TiN powders. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Incineration of plutonium (Pu) and minor actinides (MA) is important from the viewpoint of burning surplus plutonium [1] and alleviating the burden of high-level waste (HLW) disposal [2]. Various methods of incineration have been proposed so far, in which the use of nitride fuel with fast neutron spectrum is one of their options. They are (MA,Pu,Zr)N for accelerator driven system (ADS) [3], (MA,U)N for actinide burning reactors (ABR) [4], pure PuN in CAPRA core [5], (MA,Zr)N dispersed in inert matrix by hybrid concept [6] and so on. The superior thermal and neutronic characteristics of nitride fuel are advantageous for realizing high burnups with wide safety margins. But their physical and chemical properties have been little understood for the moment.

The purpose of the present study is to provide the basic information for evaluating the feasibility of nitride fuel for incineration. Plutonium nitride (PuN) pellets containing inert matrix nitrides such as ZrN and TiN were prepared and characterized.

2. Experimental*2.1. Sample preparation*

PuN was prepared by carbothermic reduction of PuO₂. Powders of PuO₂ and graphite [7] were mixed at a C/PuO₂ molar ratio of 2.2 and the mixed powder was compacted into thin disks under a pressure of ~100 MPa. The discs were heated in an N₂ gas stream at 1823 K for 36 ks for carbothermic reduction and consecutively heated in an N₂-H₂ mixed gas stream at 1723 K for 72 ks for removal of excess carbon.

PuN pellets containing inert matrix nitrides were prepared by mechanical blending method. The contents of Pu were arbitrarily chosen at 40 and 60 wt% for the reaction with ZrN and 50 wt% for the reaction with TiN. The powders of ZrN and TiN (purity: >99.5%) were obtained from CERAC.

The nitrides were mixed at the Pu/(Pu + Zr) molar ratios of 0.234 (Pu: 40 wt%) and 0.420 (Pu: 60 wt%) and at the Pu/(Pu + Ti) ratio of 0.216 (Pu: 50 wt%) in an agate mortar. The mixed powder was compacted into thin disks, then heated in an N₂-H₂ mixed gas stream at 1673 K for 18 ks for homogenization. After repeating these procedures (mixing, compacting and heating) for three times, the disks were ground and compacted into green pellets under a pressure of ~300 MPa without any organic binder. They were sintered in an Ar gas stream

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at 2003 K for 18 ks, followed by heating in an N_2 - H_2 mixed gas stream at 1673 K for the control of stoichiometry. PuN pellets without inert matrix nitrides were also prepared as reference.

The preparation experiment was carried out in the gloveboxes with purified Ar gas atmosphere. The impurity levels of oxygen and moisture in the gloveboxes were controlled below 2 and 3 ppm, respectively.

2.2. Characterization

X-ray powder diffractometry was applied to identify the phases and to determine the lattice parameters. The diffraction pattern was taken immediately after cooling the heated sample (1673 K) for stoichiometry control to avoid the effect of self-radiation damage accumulated in the lattice. Lattice parameters were calculated from high angle reflections ($2\theta > 90^\circ$) by a least square method.

Nitrogen, oxygen and carbon contents in the pellets were determined by combustion gas chromatography, inert gas fusion coulometry and high frequency heating coulometry, respectively [8]. The samples for chemical analysis were sealed into tin or platinum capsules in the glovebox with Ar gas atmosphere. The metallic elements (Pu, Zr and Ti) were not subjected to chemical analysis. It was considered that their mixing ratios remained unchanged during the experiments.

Metallographic examination of the dense pellets was carried out. The microstructures were observed after chemical etching in a mixture of nitric acid and lactic acid with one drop of fluoric acid.

3. Results and discussion

3.1. Solubility of PuN in inert matrix nitrides

Typical X-ray diffraction pattern of the sintered pellets prepared in this study is shown in Fig. 1 besides those of ZrN and TiN powders as received. Each of the pure PuN pellet and the received ZrN and TiN powders was of a single phase with NaCl-type structure. On the other hand, the small peaks corresponding to the oxides were also present in the pellets containing inert matrix nitrides. It is considered that slight oxidation occurred during the preparation of pellets containing ZrN and TiN.

The diffraction patterns of the pellets of PuN + ZrN consist of only one NaCl-type fcc phase except small oxide-bearing peaks. However, two separate phases were identified for the pellet of PuN + TiN. The lattice parameters of the pellets were plotted in Fig. 2 as a function of Pu/(Pu + Zr) or Pu/(Pu + Ti) atomic ratio. The lattice parameters of the pellets containing ZrN are in good agreement with those assumed by the Vegards law between PuN and ZrN. These results suggest that the

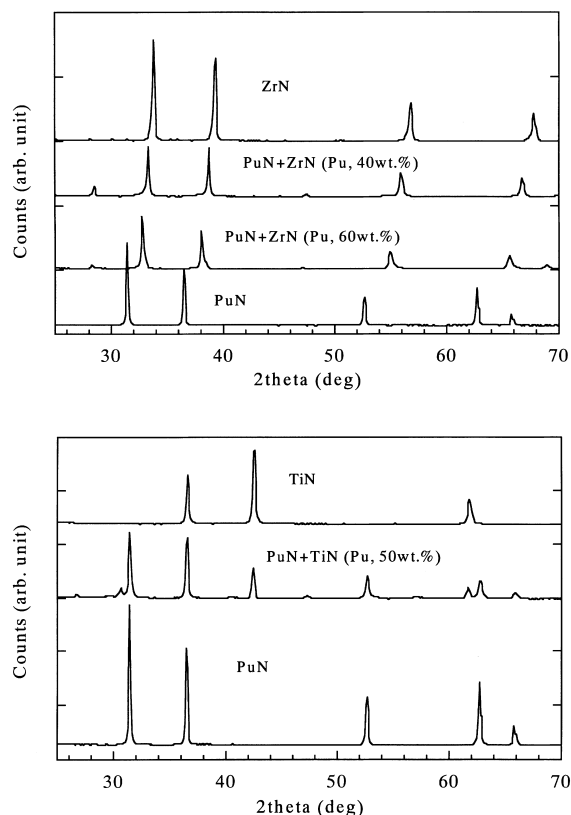


Fig. 1. X-ray diffraction patterns of PuN pellets containing ZrN (upper) and TiN (lower) besides those of PuN pellet and ZrN and TiN powders as received.

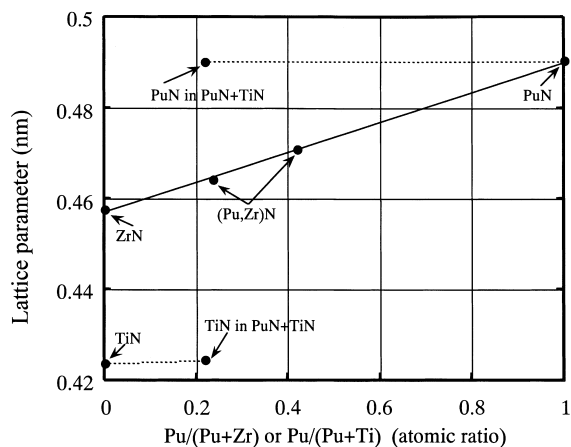


Fig. 2. Composition dependence of the lattice parameter of fcc phase with NaCl-type structure.

solid solution of (Pu,Zr)N was formed in the pellets containing ZrN. On the other hand, the lattice parameters of two NaCl-type phases in the pellet containing TiN almost did not change from those of PuN and TiN.

This result suggests that the amount of PuN dissolved in TiN and that of TiN in PuN were very small under the present experimental conditions; the values calculated from the lattice parameters were 0.7 and 0.3 at.% for PuN in TiN and TiN in PuN, respectively. Benedict [9] has investigated the solubility of solid fission products in actinide carbides and nitrides based on the relative lattice parameter difference (RLPD). According to his assumption, there is complete solubility in case of $-7.5\% < \text{RLPD} < +8.5\%$, limited solubility in case of $-16\% < \text{RLPD} < -7.5\%$ and negligible solubility in case of $\text{RLPD} < -16\%$. In the present case, RLPD corresponds to -6.7% and -13.6% for PuN–ZrN and PuN–TiN, respectively. The present results qualitatively agreed with Benedict's assumption. In case of the PuN + TiN pellet, it may be possible to increase the solubility by increasing sintering temperature or by reducing the particle size of the powders. However, it will be impossible to make a solid solution with single phase of NaCl-type structure.

3.2. Chemical composition

The results of chemical analysis and sintered density are summarized in Table 1. In the pure PuN pellet, oxygen and carbon impurity contents were quite low for the nitride fuel prepared by carbothermic reduction. The nitrogen content almost corresponds to the stoichiometric composition of mononitride. On the other hand, a fairly large amount of oxygen was present in the pellets containing inert matrix nitrides. Further, the oxygen contents apparently increased with ZrN contents in this case. Indeed, 1.47 wt% of oxygen was found in the ZrN powder after being heated in the $\text{N}_2\text{--H}_2$ stream at 1673 K. So it is considered that the large amount of oxygen was caused by the oxidation of ZrN and TiN during preparation stage. The carbon contents, 0.25 wt%, were considered as the carbon impurities contained in the ZrN and TiN powder as received.

In contrast to PuN that is recognized as so-called a line compound, ZrN [10] and TiN [11] have a large homogeneous region especially in hypostoichiometric region although there is no clear relationship between temperature, nitrogen pressure and phase boundaries. So the last heating was carried out in an $\text{N}_2\text{--H}_2$ mixed gas stream in the present study so as to control stoichiometry. Here, an equivalent nitrogen content (ENC,

wt%), which is defined as $\text{N content (wt\%)} + (14/16) \cdot \text{O content (wt\%)} + (14/12) \cdot \text{C content (wt\%)}$ assuming the solution of oxygen and carbon into mononitride phase, is calculated to be 10.26 and 8.63 wt% for the PuN + ZrN pellets and 13.17 wt% for the PuN + TiN pellet. Comparing them with their theoretical stoichiometric compositions, 10.01, 8.37 and 13.57 wt%, the present ENC values are higher than the theoretical values for the pellets containing ZrN but lower than that for the pellet containing TiN. It is considered that the (Pu,Zr)(N,O,C) solid solution has a near stoichiometric composition and the surplus oxygen is contained in the oxide phase precipitated. In the pellets containing TiN, however, it is likely that TiN itself still has a hypostoichiometric composition in spite of the heat treatment in an $\text{N}_2\text{--H}_2$ mixed gas stream.

A contrastive result was found for the density of sintered pellets containing ZrN and TiN. The former pellets were sintered to higher density than 90% TD but only 76% TD was attained for the latter pellet under the same sintering condition. It is suggested that the formation of solid solution promotes sintering to high density and also leads to toughness of the pellet in this case. The difference of sintered density in two PuN + ZrN pellets shown in Table 1 might be related to the oxygen impurity contents. Indeed, there is a patent for the use of oxide as a sintering aid in UN [12]. Microstructures of PuN + ZrN (Pu: 40 wt%) and PuN pellets are shown in Fig. 3. They had a similar grain size of 7–8 μm . In contrast to single phase structure of PuN pellet, the 'gray' oxide precipitates were observed among the matrix of (Pu,Zr)N. The appearance of the precipitates was similar with those in UN or (U,Pu)N containing oxygen impurity up to ~ 1 wt% [13].

3.3. Applicability to transmutation by ADS

The mononitride solid solution, (MA,Pu,Zr)N, was chosen as a potential fuel for ADS mainly from neutronic consideration [3]. Here, plutonium is added to control the effective multiplication coefficient nearly constant at ~ 0.95 . From a material science viewpoint, the requirement for fuel is structural stability under operating temperature and high neutron fluence, high heat conduction, compatibility with cladding material and reprocessing technology, and so on.

Table 1

Results of chemical analysis and density for PuN + ZrN and PuN + TiN pellets compared with PuN pellet

Samples	Pu content ^a (wt%)	Nitrogen (wt%)	Oxygen (wt%)	Carbon (wt%)	Bulk density (% TD)
PuN + ZrN	40	9.15	0.94	0.25	95
PuN + ZrN	60	7.95	0.44	0.25	90
PuN + TiN	50	12.21	0.76	0.25	76
PuN	94.5	5.57	0.04	0.03	96

^a Nominal amount.

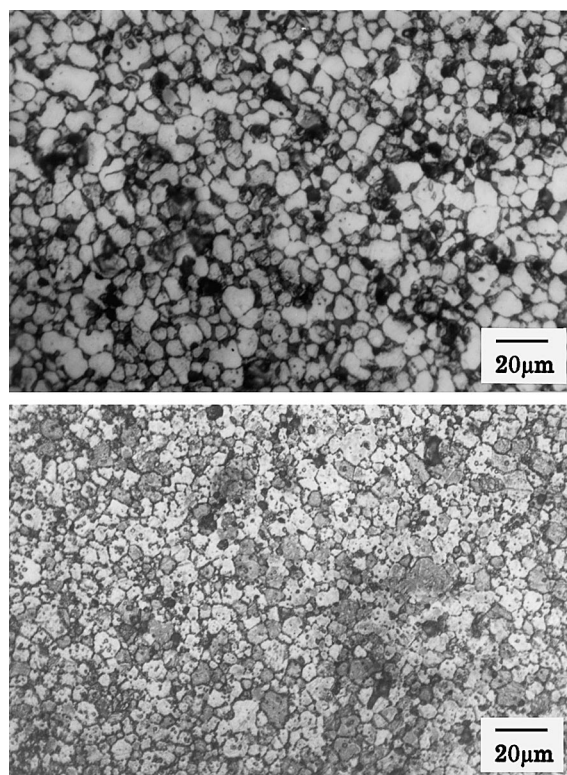


Fig. 3. Microstructure of PuN + ZrN pellet with Pu of 40 wt% (upper) and pure PuN pellet (lower).

In this study, MA such as Np, Am and Cm, were substituted by Pu since mononitrides of actinide elements have the same crystal structure with similar molecular volumes. The present PuN + ZrN pellets have high densities with one NaCl-type fcc phase except a small amount of oxide. It will lead to toughness and structural stability of fuel under operation. Although many other physical and chemical properties and irradiation behavior have to be examined, the solid solution containing ZrN is a potential fuel for transmutation use. On the other hand, it was shown that TiN does not easily dissolve into actinide mononitrides in spite of the same crystal structure. The single phase is not a strict requirement, but the control of microstructure becomes more important if the nitrides are the mixture of two phases. Further, special consideration is needed to attain high density leading to structural stability.

The present samples contained a fair amount of oxygen impurities. It might deteriorate the irradiation behav-

ior and applicability to reprocessing. But recent supplementary experiments on (Pu,Zr)N revealed that the oxygen content can be lowered to ~ 0.2 wt%, which is a similar value for (U,Pu)N fuel of technological grade, by adding small amount of carbon before the initial mixing without increasing carbon impurities in the product.

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