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Thermal and mechanical properties of uranium nitride prepared by SPS technique

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Abstract Nitride fuel is a promising nuclear fuel in fast breeder reactor (FBR) or accelerator-driven subcritical reactor (ADSR) system. In this study, high-density UN pellets were prepared by Spark plasma sintering (SPS) technique. The sample density strongly depended on the sintering temperature and pressure, and the pellets with 90% of theoretical density were easily obtained with low sintering temperature and short sintering time without any milling process. The grain size and pore size were much smaller compared with those for samples prepared by conventional sintering process. Despite of the small grain size, the thermal conductivity remains the high value. The SPS process permits easy densification of nitrides without any deterioration of thermal and mechanical properties, considered to be suitable as a preparation method of nitride fuels.

Introduction

The nitride such as (U,Pu,MA)N and (Pu,MA,Zr)N, MA is minor actinide, are good candidates as nuclear fuels of fast breeder reactor (FBR) and accelerator-driven subcritical reactor (ADSR) [1] due to the high thermal conductivity, high melting point, and the wide solubility between uranium/plutonium nitride and minor actinide nitride with NaCl type structure. These superior properties provide secure and manageable reactors. However, several problems exist in the fabrication processes for practical utilization of the nitride fuel. One of the problems is costly extraction of 15-nitrogen [2]. Another problem is the high sintering-resistance of the nitride fuel [3–8]. Conventionally, long milling process, sintering additive, and high sintering temperature were necessary for fabrication of the high-density nitride pellets. For example, UN pellets were prepared with sintering temperature of 2073 K from 40 h-milled powders. However, the fabrication processes must be operated remotely due to the high radioactivity, hence the long milling process were not desired. In addition, the fuel includes some amount of americium nitride, which easily decomposes and evaporates at high temperature. It means that high temperature and long time heat treatment is not acceptable for the sintering process. Therefore, new preparation method for high density nitride pellets has been desired.

Spark plasma sintering (SPS) is a pressure-assisted sintering that utilizes an electric current [9, 10]. The sample temperature was raised and controlled by Joule heating in the sample and electronically conductive dies. It is known that the sintering temperature and time can be drastically lowered compared with those in conventional sintering. High-density pellets of some nitride-based ceramics were successfully prepared by the method [11–14]. The superior feature appeared to be suitable for densification of the nitride fuel pellet. In this study, UN powders were palletized using the SPS technique with different sintering conditions. Sample density, the microstructure, and several thermal and mechanical properties were measured and compared with those for samples prepared by conventional way.

Experiment

UN powder was purchased from Mitsubishi Materials Corporation. The powder was fabricated by carbothermic

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reduction of carbon–UO_2 mixed pellets in a flow of nitrogen gas, followed by heat treatment in a flow of nitrogen–hydrogen mixed gas for removal of the unreacted carbon. The impurity amount of oxygen and carbon were 78 ppm and 93 ppm, respectively. Some of the powders were ball-milled for 40 h at argon atmosphere using WC pot and balls.

The distribution of particle diameter is shown in Fig. 1. The average diameters were about 81 μm for as-cast powder and 1.3 μm for ball-milled powder.

The UN powder was packed to graphite die and sintered in SPS apparatus (SPS-515S, Sumitomo Coal Mining, Japan) in vacuum. The graphite die was covered with carbon–wool for thermal insulation. Several UN pellets were prepared by SPS with different sintering temperature, heating rate, and pressure.

The sintering conditions are listed in Table 1. The sintering temperature was measured on surface of the graphite die by an optical pyrometer. Holding time was set to 10 min, consequently the SPS process finished within 40 min for most of the samples. For comparison, one UN sample was fabricated by conventional sintering method. The ball-milled UN powder was cold-pressed at a pressure of 300 MPa, then the pellet was sintered at 2073 K for 4 h at a flow of argon gas.

The crystal structure and phases were examined by powder X-ray diffraction analysis using Cu $K\alpha$ radiation. The polished surface of samples was observed by SEM analysis. In addition, the grain orientation of the sample surface was evaluated by electron backscattering pattern (EBSP) analysis. The thermal conductivity was evaluated as a product of the thermal diffusivity, the heat capacity, and the experimental density at room temperature. The thermal diffusivity was measured by a laser flash method using TC-7000 equipment (ULVAC Co. Ltd.) in vacuum. Heat capacity was measured using TG–DSC Jupiter (Netzsch Co.) at a flow o argon gas. Young's modulus was evaluated from the sound velocity measured by ultrasonic pulse echo method using Echometer 1062 (NIHON MATEC Co.). It is noted that the thermal diffusivity and sound velocity were measured in axial direction of the sample pellet. Additionally, elastic modulus of UN was evaluated by electronic state calculation using Cambridge Serial Total Energy Package (CASTEP), which is a pseudpotential plain-wave code based on the density functional theory.

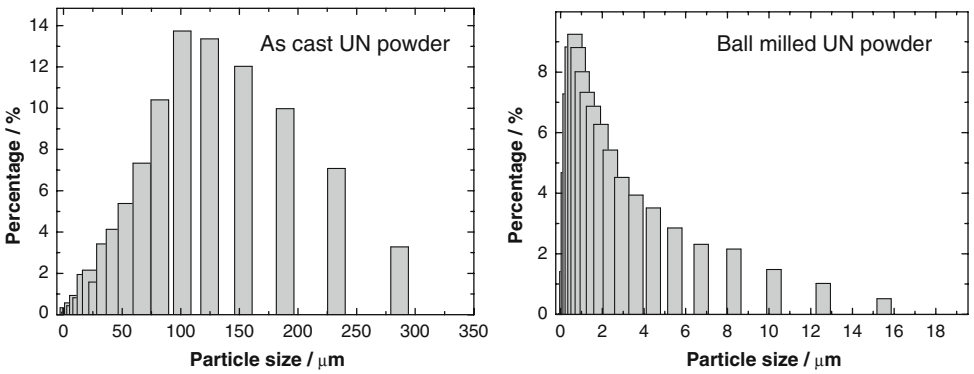

Fig. 1 Distribution of particle diameter of UN powders

Table 1 Sintering condition of UN pellets

Sample	Powder	Sintering temperature (K)	Heating rate (K/min)	Pressure (MPa)
A1573/50/50	As cast	1573	50	50
A1673/50/50		1673	50	50
A1773/50/50		1773	50	50
A1873/50/50		1873	50	50
A1773/20/50		1773	20	50
A1773/100/50		1773	100	50
A1773/50/20		1773	50	20
A1773/50/100		1773	50	100
B1573/100/50	Ball milled	1573	100	50
B1673/100/50		1673	100	50
B1773/100/50		1773	100	50
Ref		2073	–	–

Results and discussion

The XRD pattern of UN powders and pellets sintered at 1773 K was shown in Fig. 2. Small amount of the UO_2 was detected for the sample of A1773/20/50, which has relatively long sintering time due to the low heating rate. The impurity peak for other samples was very small, hence single phase of NaCl type UN was obtained.

Figure 3a and b shows SEM photograph of polished sample surface prepared by conventional sintering method and SPS technique, respectively. Relatively large pores were observed for sample prepared by conventional method. Most of pores existed at the grain boundary for the sample. On the contrary, very small intra-grain pores were observed for all the samples prepared by SPS. It indicates that the grain and pore growth were inhibited due to the lowered sintering temperature and sintering time. The pore size and distribution were independent of the sintering condition, hence the pore was considered to be generated in the carbothermic reduction process. Pores were nearly spherical and no crack was observed for both samples.

Figure 4 shows relative sample density of sintered UN pellets. The theoretical density is assumed to be 14.32×10^3 kg/m^3. The sample density strongly depended on the SPS temperature and pressure. With sintering temperature of >1773 K and pressure of >50 MPa, relatively high sample density of about 90% TD was obtained from as-cast UN powder. Compared with conventional sintering temperature of 2073 K and sintering time of 4 h, they were drastically reduced in the SPS process. The result indicated that application of SPS technique enables to omit the long milling process. Additionally, the evaporation of americium nitride in the sintering process could be negligible due to the reduced sintering temperature and sintering time.

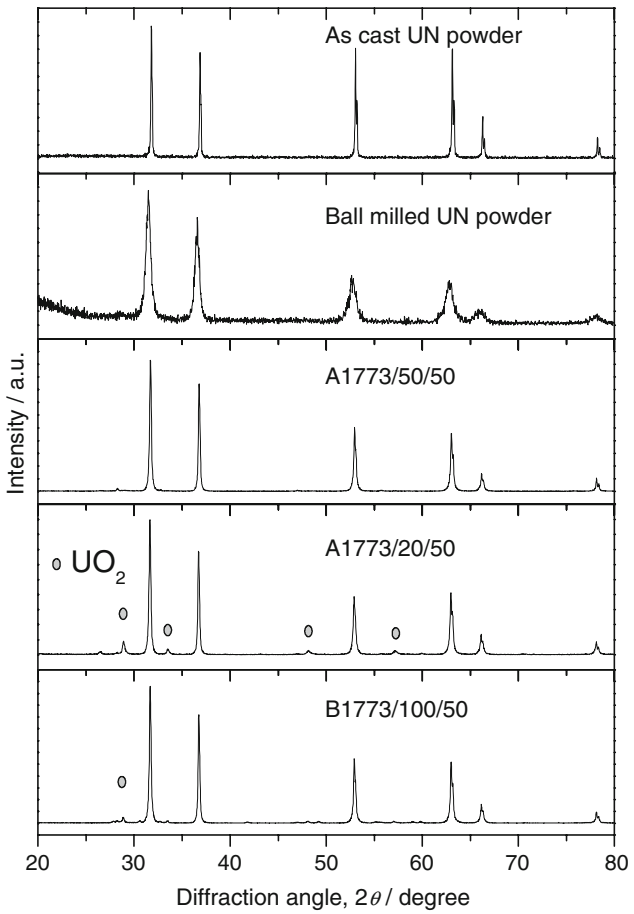

Fig. 2 XRD pattern of UN powder and sintered UN pellet

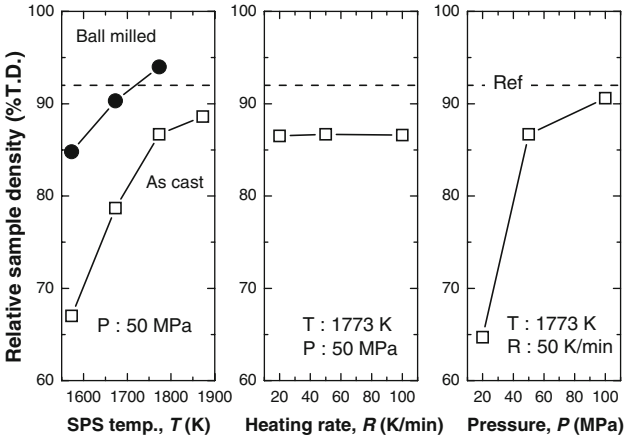

Fig. 4 Sample density of UN pellets

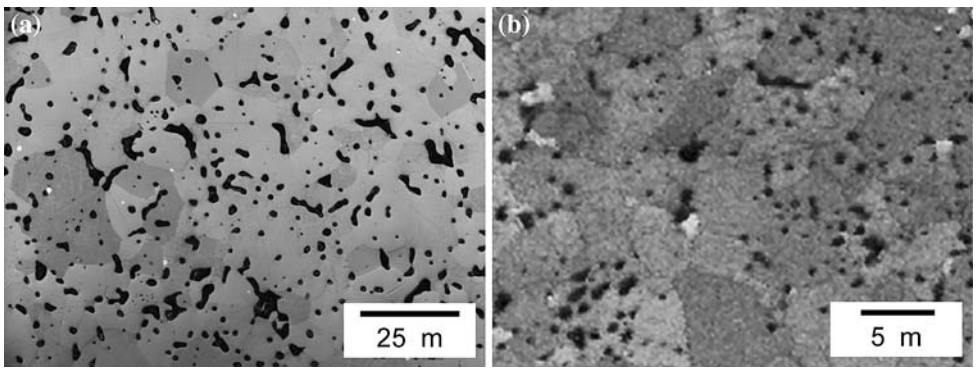

Fig. 3 SEM photograph of polished sample surface prepared by (**a**) conventional sintering method and (**b**) SPS technique

Thermal expansion of UN pellet was shown in Fig. 5 with the reported data. The value and temperature dependence of samples prepared by SPS are in good agreement with the previous data.

The temperature dependence of thermal conductivity of samples that SPS temperature is 1773 K was shown in Fig. 6a with reported values [15–17]. The thermal conductivity gradually increased with increasing temperature for all the samples, which is in agreement with the previous data. Figure 6b shows thermal conductivity at 300 K for the samples. The value was corrected with consideration of sample density by using following Maxwell–Eucken formula,

$$\lambda = \lambda_{100}\frac{1-P}{1+\Phi P}$$

where P is volume fraction of pore and λ_{100} is thermal conductivity of sample with the theoretical density. Φ is adjusting parameter that depends on the pore shape. The value of 1.0 is proposed for UN pellet with spherical pores. In this study, same value of 1.0 is used because observed pore shape of our samples is also spherical as seen in Fig. 2. The sample of A1773/20/50 showed the lowest value in our data due to the impurity UO_2 phase that was detected by XRD analysis. Other samples prepared by SPS show higher thermal conductivity than previous data reported by Hayes. The result confirms that the high thermal conductivity of nitride fuel remains for SPS prepared sample.

Figure 7 shows porosity volume dependence of Young's modulus with previous data [18, 19]. In whole porosity volume range, the samples prepared by SPS exhibited higher Young's modulus. The higher Young's modulus and higher thermal conductivity in Fig. 6b, which are also measured in axial direction of the pellet, should be attributed to difference of the fabrication process. Since SPS is a pressure-assisted sintering, the grain orientation should be considered as in the case for hot-pressed samples.

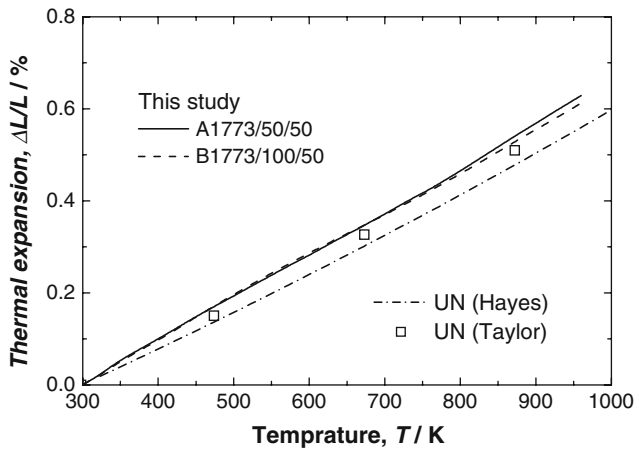

Fig. 5 Thermal expansion of UN pellet

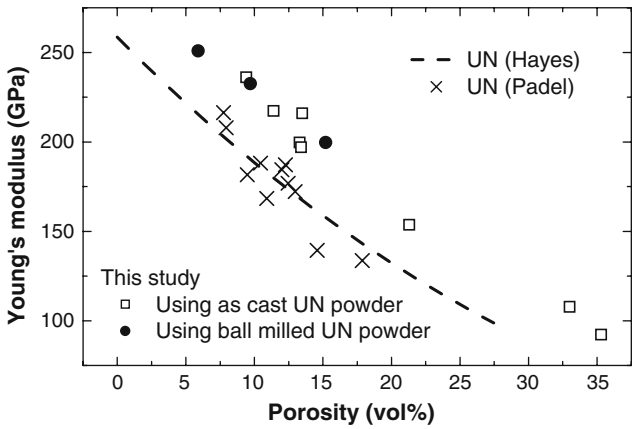

Fig. 7 Porosity volume dependence of Young's modulus estimated by sound velocity at 300 K. The sound velocity was measured in axial direction

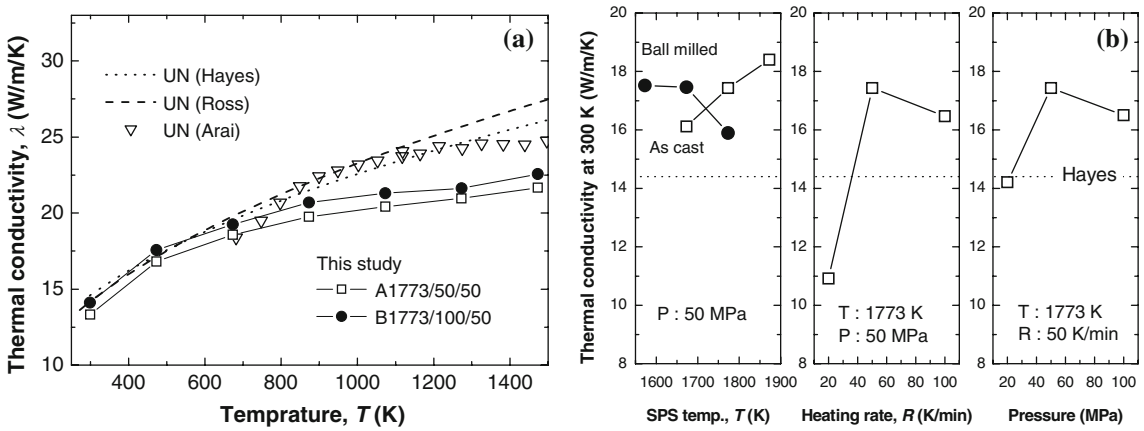

Fig. 6 Thermal conductivity of UN pellets. (**a**) Temperature dependence of samples sintered at 1773 K. (**b**) The corrected thermal conductivity at 300 K. The value is corrected to 100% TD by Maxwell–Eucken formula

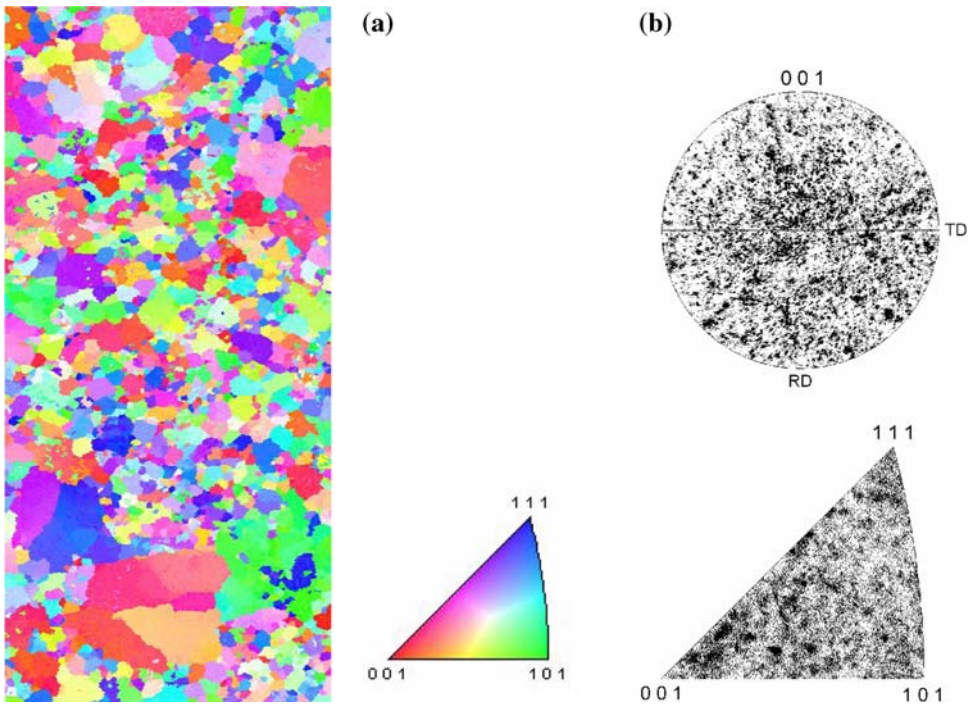

Fig. 8 (**a**) IPF map and (**b**) pole figure for sample of A1773/50/50. The measurement was served for sample surface perpendicular to axial direction

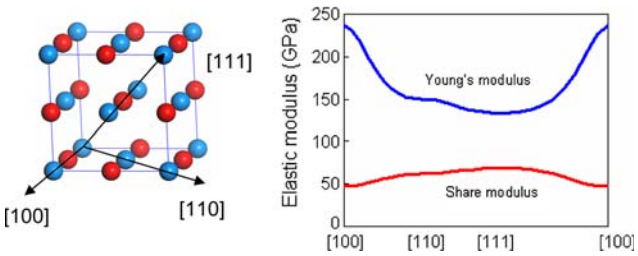

Fig. 9 Crystal structure and elastic modulus of UN. The elastic modulus was evaluated by electronic calculation

Figure 8 shows inverse pole figure and the map for sample surface of A1773/50/50. The grain orientation was measured perpendicular to axial direction. It is not clear, however, weak grain orientation in [100] direction was observed.

Figure 9 showed crystal structure of UN and elastic modulus evaluated by electronic calculation. According to the result, the elastic modulus strongly depends on the crystal direction, and UN takes high Young's modulus in [100] direction. EBSP analysis indicates weak grain orientation in that direction, therefore, the results suppose that the experimental high Young's modulus was caused by the grain orientation in [100] direction. The high thermal conductivity can also be explained by the grain orientation because high elastic modulus means the high sound velocity, which is related to the phonon velocity. However, it calls for further investigation about other factors, such as oxygen contamination, change of stoichiometry, and bonding strength between the grains.

Summary

Several dense UN pellets have been prepared by SPS technique without milling process and sintering additive. Sintering temperature and total sintering time were drastically decreased compared to those for conventional method. It indicates that the vaporization of americium actinide in sintering process could be neglected by application of the SPS technique. The thermal expansion, thermal conductivity, and Young's modulus were measured and compared with those for the sample prepared by conventional method. No deterioration of the thermal and mechanical properties was observed for the SPS sample. At room temperature the thermal conductivity and Young's modulus in axial direction were slightly higher than previous data, which supposed to be caused by the weak grain orientation in [100] direction. These results indicate that the SPS process is suitable as a preparation method of nitride fuels.

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