Fabrication process of NpO$_2$ pellets

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Abstracts: In order to increase dissolution ratio of the irradiated NpO$_2$ targets, it's necessary to add a little diluent into NpO$_2$ pellet. In this paper, pressureless sintering processes and microstructures of NpO$_2$-10% CaO, NpO$_2$-10% SrO, NpO$_2$-10% MgO and NpO$_2$-5% MgO pellets were studied, sintered at 1730℃ for 2 hours in Ar-5%H$_2$ gases. Only NpO$_2$ solid solution phase structure was found in all the pellets. NpO$_2$-10% CaO pellet melts at the sintering process. NpO$_2$-10% SrO pellet has a sintered density of 60.0% TD with cracking and porous microstructures. NpO$_2$-10%MgO pellet has a sintered density of 83.1%TD with irregular grains. NpO$_2$-5% MgO pellet can be sintered to 90.0%TD with cobble grains. Density of NpO$_2$-5% MgO pellet will increase to 92.5%TD using UO$_2$ powder embedding sintering process.

Keywords: NpO$_2$; pellet ; sinter ; density ; diluent

1. Introduction

Neptunium is one of the minor actinides with long-live and high level radioactive, its partitioning and transmutation is very important in the Advanced Fuel Cycle Initiative (AFCI)[1,2]. But nothing about the fabrication process of NpO$_2$ pellets with high density and stoichiometry was found in the open or classified literature.

Huber (1968) reported that 50-mm diameter by 3.18-mm thick NpO$_2$ wafers were fabricated for heat capacity measurements in the mid 1960s at LANL. The NpO$_2$ powder was blended with 1 to 2 wt% carbowax and pressed and heated in the oxidizing atmosphere to $800\sim1000$℃ to

remove the wax. Then the wafers were sintered at $1400 \sim 1700℃$ to densities of 85 to 90 %TD. Bartscher and Sari (1986) have shown that the sintering atmosphere of stoichiometric NpO_2 is hydrogen containing 1% H_2O at all temperatures. Hypostoichiometric NpO_{2-x} is obtained when sintered in the reducing atmospheres, and NpO_{2-x} will decompose to NpO_2 and metallic neptunium on cooling to room temperature[3]. Blair and Chidester (1994) studied the feasibility of fabrication NpO_2 into various targets configurations for irradiation in FFTF to produce plutonium-238. NpO_2 pellets could be sintered in argon containing 6% hydrogen to a density of 86.5%TD with 20-mm diameter by 0.229-mm thick[4]. In order to increase dissolution ratio of the fast reactor irradiated NpO_2 target, a little diluent which has a high melting point and can be dissolved easily by nitric acid is necessary to be added into NpO_2 pellet. Al_2O_3 or ZrO_2 is excluded because of bad dissolution in nitric acid.

In this study, the effects of additives such as CaO, SrO, and MgO on sintering densification of NpO_2 were experimentally investigated for the purpose of designing compositions of CEFR neptunium target.

2. Experimental

MA-bearing fuels requires special handling due to the high α and γ activities of MA, as well as their high decay heat. For these reasons , the entire fabrication and characterization of MA materials is performed in heavy-shielded cells and glove boxes in the CIAE facility.

NpO$_2$-MgO mixed oxide pellets are prepared by powder metallurgy processes principally consisting of milling-pelletizing-sintering steps. Fig.1 shows the fabrication procedure of NpO$_2$ pellets with additives such as CaO, SrO and MgO, respectively. Characteristics of the used starting powders are given in Table 1. Total γ activity and total α activity of NpO$_2$ powder is 2.852×10^7 Bq/g and 1.863×10^7 Bq/g, respectively.
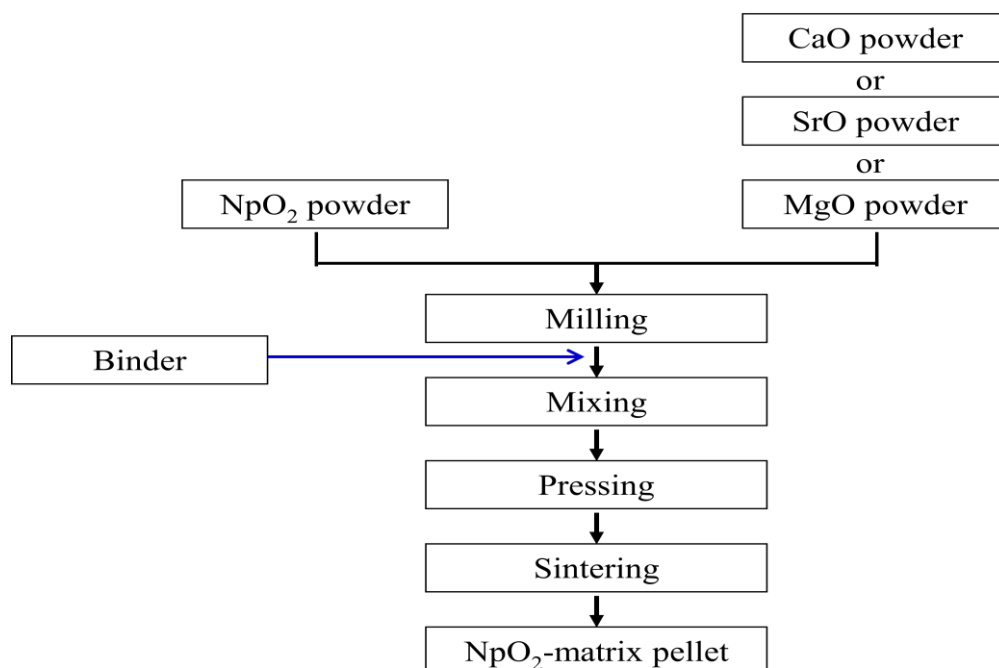

Fig.1 The fabrication procedure of NpO$_2$-matrix pellets with additives

Table 1 Powder characteristics

	NpO$_2$	CaO	SrO	MgO
Purity(%)	99.5	99.0	99.0	99.0
Median particle size(μm)	3.0	1.2	1.5	0.8

Firstly, NpO$_2$ and 5～10 wt% additive powders were milled by planetary ball milling at 300 rpm for 4 h. Secondly, 0.5～1 wt% binder was mixed with the milled powders for 30 min in the three-dimension

movement mixer. Then, mixed powders were pressed at 350 MPa into a compact. At last, pellet sintering tests were carried out at 1700℃ for 2 h in Ar-5%H_2 atmosphere, undergoing solid state reaction. Sintering are performed in a tungsten furnace giving a maximum operation temperature of 2000℃. NpO_2 pellets were placed in the Al_2O_3 crucibles.

Before and after sintering, pellet diameters are measured using digital displaying calliper in the glove. The densification behaviors were characterized by the density and microstructure. The theoretical density of each material was calculated by the mixing rule on the assumption that the sintering additives did not react with NpO_2. The microstructure of the pellet was observed with an optical microscope and SEM, respectively. X-ray diffraction (XRD) analyses are performed on pellets using a Bruker D8 Advance with a Cu anticathode.

3. Results and discussion

3.1 Phase structure

All the sintered NpO_2 pellets were firstly submitted a visual inspection. As shown in Figure 2, NpO_2-10% CaO pellet melts totally at the sintering stage. NpO_2-10% SrO pellet has cracks and a large weight loss, without any shrinkage. Neither crack nor strain was detected in NpO_2-10% MgO and NpO_2-5% MgO pellets with 4.92～5.02-mm diameter by 6.50～7.00-mm thick.

Fig.3 presents the XRD patterns of four NpO_2 pellets. Whether UO_2

powder embedded (covered) sintering process was used, only NpO_2 solid solution phase was found in the pellets of NpO_2-10% MgO, NpO_2-5% MgO and NpO_2-10% SrO. Characteristics peaks of NpO_2-MgO pellet move left compared to NpO_2-SrO pellet.

(a) NpO_2-10%CaO   (b) NpO_2-10%SrO

(c) NpO_2-10%MgO   (d) NpO_2-5%MgO
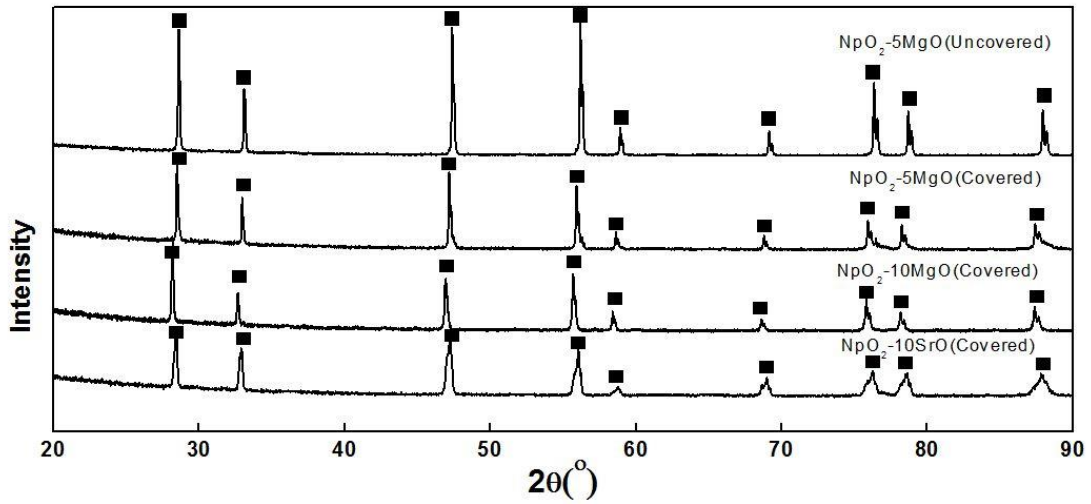
Fig.2 Photographs of NpO_2 pellets

Fig.3 XRD patterns of NpO$_2$ pellets

3.2 Density

NpO$_2$-10% SrO pellet has a sintered density of 60.0% TD without any shrinkage. NpO$_2$-10% MgO pellet has a sintered density of 83.1%TD with a little shrinkage. NpO$_2$-5% MgO pellet can be sintered to 92.5%TD with a shrinkage of about 13.3% using a UO$_2$ powder embedding sintering process, but only 90.0% TD for NpO$_2$-5% MgO pellet without embedding sintering .

Table 2 Pellet characteristics

	NpO$_2$-10%CaO	NpO$_2$-10%SrO	NpO$_2$-10%MgO	NpO$_2$-5%MgO
Sintered density(%TD)	melting	60.0	83.1	92.5
Diameter shrinkage(%)	--	--	9.2	13.3

3.3 Microstructure

NpO_2-10% CaO pellet melts at the sintering process because of forming eutectic liquid phase. NpO_2-10% SrO pellet has a sintered density of 60.0% TD with a lot of cracks and porous and loose microstructures (see Fig.4). It seems the SrO had been reacted with the NpO_2 to form a arborescent structure, and the low-melting component in the arborescent structure had evaporated at the sintering process to form the pores in the grain. NpO_2-10%MgO pellet has a sintered density of 83.1%TD with irregular grains, as shown in Fig.5. NpO_2-5%MgO pellet which use UO_2 powder embedding sintering process can be sintered to 92.5%TD. The pellet has cobble grains, also some liquid phase can be found in the grain boundary(see Fig.6).

Surface of the NpO_2-5% MgO pellet is very clear without UO_2 powder embedding sintering process, as shown in Fig.7, but the embedding sintering pellet is rough and dirty.
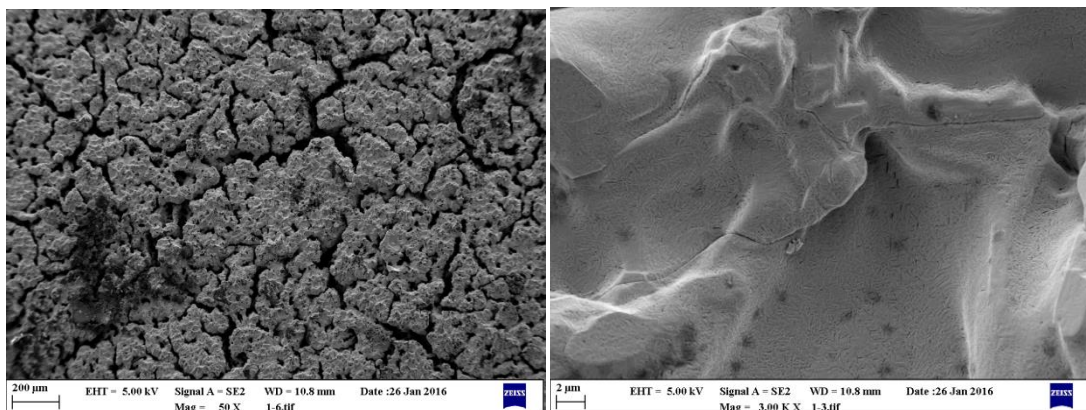

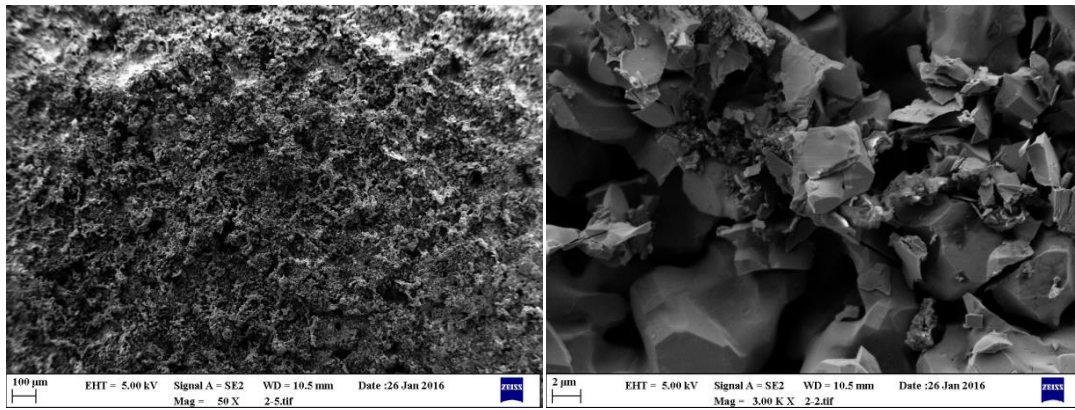Fig.4 SEM microstructures of the NpO_2-10%SrO pellet

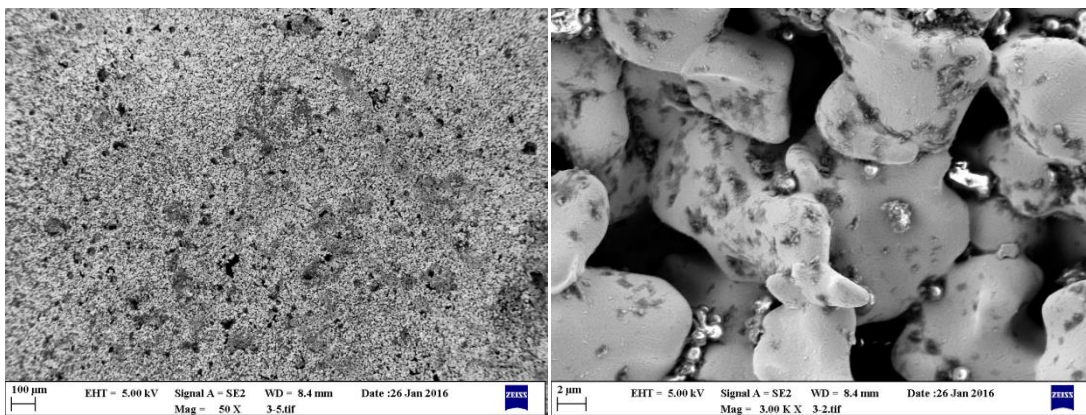Fig.5 SEM microstructures of the NpO_2-10%MgO pellet

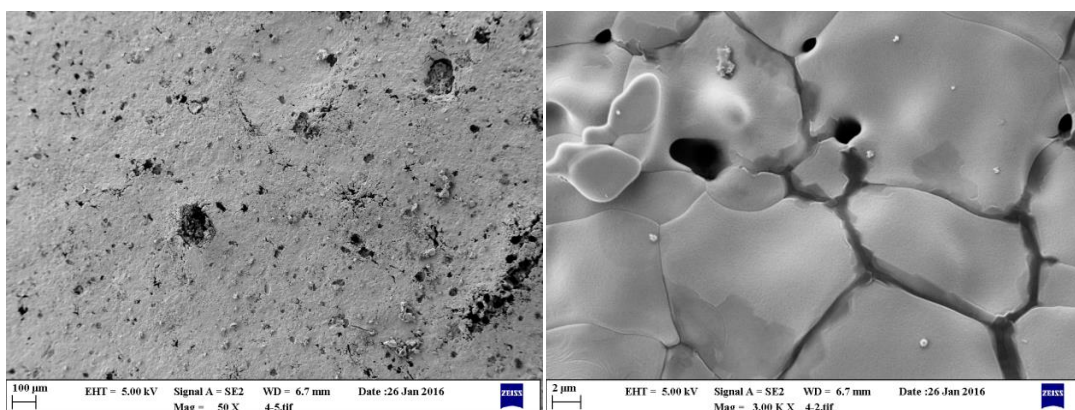Fig.6 SEM microstructures of the NpO_2-5%MgO pellet using UO_2 powder embedding
sintering process

Fig.7 SEM microstructures of the NpO_2-5%MgO pellet without UO_2 powder
embedding sintering process

In the experiment of UO_2-MgO pellets, we found the MgO particles

had not reacted with UO_2, as shown in Fig.8. So the liquid phase in the

NpO_2-MgO pellet will be a result that NpO_2 reacts with MgO (see Fig.7),

but no literature has reported that NpO_2 will react with MgO[5]. Also we

found a little second phase distributing along NpO_2 grain boundary in the

NpO_2-5%MgO pellet without UO_2 powder embedding sintering process.

The second phase is so little that it is very difficult to be detected by the

XRD analysis technique.

UO_2-5% UO_2 pellet has a density of above 98% TD. Fig.9 shows

that porosity of NpO_2-5%MgO pellet is more than that of UO_2-5%MgO

pellet. We can include in this paper that MgO particle promotes sintering

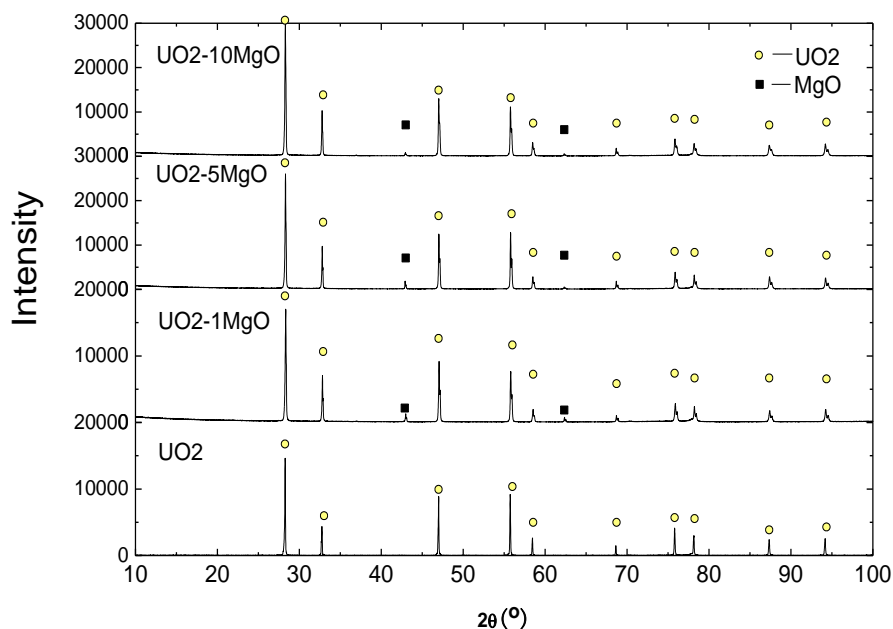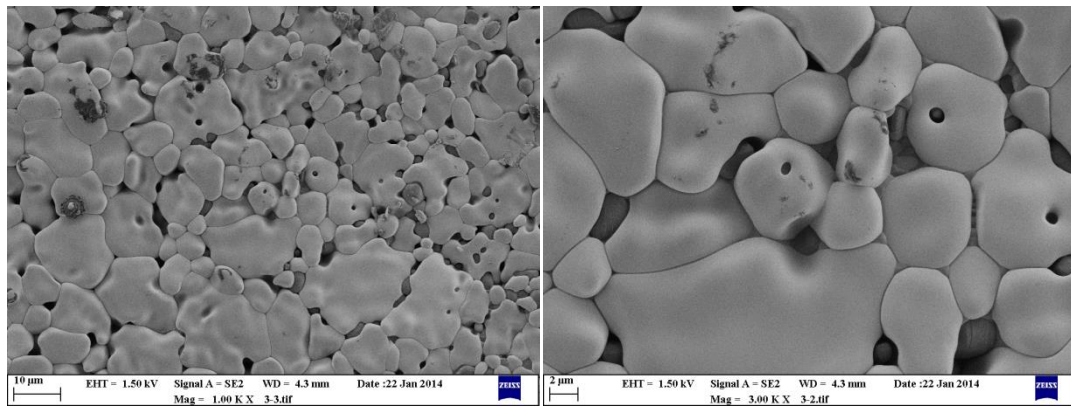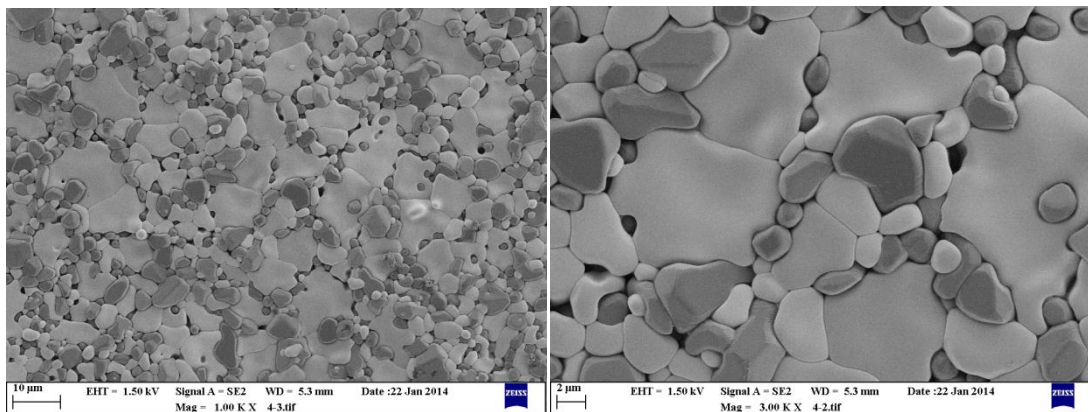densification of UO_2, but hinders densification of NpO_2.

Fig.8 XRD patterns of UO_2-MgO pellets

(a) UO$_2$-5wt%MgO

(b) UO$_2$-10wt%MgO

Fig.9 SEM microstructures of UO$_2$-MgO pellets

4. Conclusion

NpO$_2$ pellet is very difficult to be sintered to high density in the reducing atmosphere. Additive of 10% CaO into NpO$_2$ results in melting when sintering at 1700℃. Additive of 10% SrO has no effect on densification but producing cracks in the pellet. Additive of 10% MgO and 5% MgO can produce high-densitied pellets without defects. But the sintered density of NpO$_2$-5%MgO pellet is lower than that of UO$_2$-5%MgO pellet.

References

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