



Preparation and Characterization of Large Grain UO_2 for Accident Tolerant Fuel

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Large grain UO_2 is considered as an accident tolerant fuel with great application potential due to its competitive advantage of good fission gas retention. In this paper, the influence of preparation parameters such as sintering atmosphere, mixing process, powder pretreatment and grain growth additives on the grain size of UO_2 is systematically studied. The result shows that the factors mentioned above have different effects on the grain size of UO_2 . The grain growth of UO_2 pellet sintered in oxidizing atmosphere is better than those in reducing atmosphere. The wet mixing process has a significant advantage over the dry mixing process. In addition, the powder pretreatment has little effect on grain growth while the influence of additives plays the main role. Large grain UO_2 pellets with uniform grain size up to 150 μm are successfully prepared. Finally, the thermo-physical properties of the pellets are investigated.

Keywords: large grain UO_2 , accident tolerant fuel, additive, atmosphere sintering, preparation process parameters

INTRODUCTION

After the Fukushima accident in 2011, the Accident Tolerant Fuels (ATFs) has been paid much attention by researchers. As a kind of ATF fuels, large grain UO_2 fuel is characterized as the significantly increased UO_2 grain size in the fuel pellet, by adding trace additives and optimized preparation process. Grain boundaries and open pores are the main means of fission gas release (FGR). The specific surface area of grain decreases with the grain size increasing, and thus the pores will be distributed in the grain as far as possible. Moreover, the diffusion distance of fission gases from the grain interior to the grain boundary is increased accordingly. This means a higher fission gas retention rate for large grain UO_2 . On the other hand, the plasticity and thermal creep properties of large grain UO_2 are higher than normal UO_2 (Kang et al., 2010). Then the radiation swelling, which is of great significance to reduce the Pellet-Cladding Interaction (PCI), could be reduced. Thus, the large grain UO_2 fuel is capable to achieve higher burn-up than the normal UO_2 fuel (Turnbull, 1974; Hastings, 1983; Une et al., 1993). Meanwhile, the large grain UO_2 fuel is almost composed of pure UO_2 . It can completely inherit the advantages of normal UO_2 fuel, such as high melting point, good thermal stability, good compatibility with coolant and cladding material, excellent irradiation stability and water corrosion resistance. Besides, the large grain UO_2 fuel owns perfect compatibility to the present Light-Water Reactor plants (LWRs) fuel manufacturing and operating system. This is much favorable for nuclear power plants and nuclear fuel plants. Based on the advantages in terms of safety, economy, and compatibility, the large grain UO_2 fuel is considered as one of the most promising ATFs.

TABLE 1 | The basic information of the additive powders in this paper.

Additive	Particle size	Purity (%)	Source
Cr	5~20 μm	99.9	
Cr ₂ O ₃	5~20 μm	99.9	
Al ₂ O ₃	100 nm	99.99	Aladdin Bio-chem Technology co
CaO	<160 nm	99.9	
MgO	50 nm	99.9	
NiO	30~50 nm	99.5	Macklin scientific co

Many studies have been carried out in the past to investigate the factors that contribute to the grain growth of UO₂ pellets. In general, sintering temperature, holding time and sintering aids were reported to be important for increasing the grain size of UO₂ pellets (Singh, 1977). However, much higher temperature could lead to abnormal growth of UO₂ grains (MacEwan and Lawson, 1962). Long-term heat preservation had little effect on grain growth (Glodeanu et al., 1987), but would increase the cost of fuel production. The most effective way was adding additives to the UO₂ matrix. The common additives included Cr₂O₃ (Bourgeois et al., 2001; Arborelius et al., 2006; Yang et al., 2012), TiO₂ (Amato et al., 1966; Ainscough et al., 1974; Yao et al., 2016), Nb₂O₅ (Killeen, 1975; Song et al., 1994), Al₂O₃ (Oh et al., 2014; Une et al., 2000) and MgO (Sawbridge et al., 1980). Recently, Yang et al. (2012) studied the grain growth of Cr₂O₃ doped UO₂ under different oxygen potential sintering atmospheres. Then, a thermodynamic solubility model of Cr in UO₂ was established by Martial et al. using the electron probe microanalysis (Riglet-Martial et al., 2014). Che et al. used the BISON fuel performance code to calculate the FGR of Cr₂O₃ doped UO₂ fuel (Che et al., 2018). Satisfactory simulation results have been obtained. However, few of the above literatures reported the influence of the preparation process on the grain size of UO₂.

In this work, the effects of different additives, mixing methods, powder pretreatment processes, forming pressure, and sintering atmosphere on the grain growth of UO₂ were systematically studied. Additionally, the thermo-physical properties of the large grain UO₂ were also discussed.

EXPERIMENTAL

Starting Powder and Preparation Process

UO₂ powders were obtained from CNNC Jianzhong Nuclear Fuel Co., Ltd. The powders purity was 99.9%, and its sizes ranged from 10 to 20 μm. The O/U ratio of the UO₂ powders was 2.17 detected by thermogravimetric analysis. The zinc stearate (99% purity, 50 μm particle size, Macklin Scientific Co., LTD., China) was used as binder and lubricant to enhance the strength of the green body, and the addition amount in the pellets is 0.1 wt%. Six types of additive powders were used, as listed in Table 1.

Firstly, the raw materials were mixed. During the mixing process, three different mixing methods were studied. The difference between the two dry mixing methods was with or without grinding media. The Dry mixing was performed on a planetary mixer using a WC container, while the wet mixing was performed on a horizontal mixer using a nylon tank. Both mixing processes run at a speed of 300 r/min for 24 h. The powder of wet

mixing was obtained by heating at 100°C for 5 h. Secondly, the mixed powders were granulated. Two kinds of granulation processed were adopted. Spark Plasma Sintering (SPS) can activate the powder and realize the densification of high melting point materials in a short time. In this experiment, the difference between SPS pre-sintering granulation and traditional cold press granulation was investigated. The SPS pre-sintering granulation process was heating the powder at 800°C for 1 min. A pressure of 25 MPa was applied on the powders during the whole sintering process. After the SPS pre-sintering process, the density of pellets reached 68%. The Cold press granulation was to hold the powder under 300 MPa for 5 min. Then, the green body was crushed and sieved with a 50-mesh screen. Thirdly, the mixed particles were introduced into a cemented carbide mold for biaxial pressing with 100 MPa, 200 MPa, and 300 MPa respectively. The green density of pellets formed under different processes were distributed within the range of 5.7–6.5 g/cm³. Finally, the green body was sintered at temperature of 1680 and 1700°C. The holding times were 1.5 and 4 h. For comparison, pure UO₂ pellets were prepared by the same technological process. H₂, H₂-H₂O, and H₂-CO₂ were used as sintering atmosphere. The content of H₂O or CO₂ in H₂ were 1 vol% and 2 vol%, respectively. The details of the above process conditions and parameters were listed in Table 2.

Microstructure Characterization

The pellets were successively grinded by 500, 1000, 2000 mesh SiC sandpaper, then polished with 1 μm diamond suspension, and finally eroded with H₂O₂/HCl etching solution. The erosion time is 1–3 min. The grain morphology was analyzed by laser confocal microscopy (LSCM, LEXT OLS4000, Olympus). Grain size was determined by the linear intercept method, and more than 200 intercepts were counted for each sample.

Thermal Physical Performance

The thermal diffusivity (TD) of the pellet was determined by a laser testing equipment (LFA 427, Netzsch, Germany). The sintered pellet was processed into the final size of Φ8 × 3 mm for the thermal diffusivity test. The testing temperature range was 25–1000°C, with an interval of 200°C. The density (ρ_p) of UO₂ pellet was measured by the Archimedes method. The thermal expansion coefficient of the pellet was measured by a thermal expansion tester (DIL 402, Netzsch, Germany). The testing temperature range was 25–1200°C. The sintered pellet was processed into the final size of Φ8 × 13 mm for the thermal expansion test.

The thermal conductivity (TC) λ_c (W m⁻¹ K⁻¹) was determined from the following formula:

$$\lambda_c = \rho_p \times T_d \times C_p \quad (1)$$

where ρ_p (g cm⁻³) is the density of pellet, D_d (mm² s⁻¹) is the thermal diffusivity of pellet, C_p (J g⁻¹ K⁻¹) is the specific heat capacity of pellet. The value of C_p is dominated by UO₂ where the additives is ignored due to its low mass fraction (≤0.5 wt%). The specific heat capacity of UO₂ can be derived from the following equation (Fink, 2000):

TABLE 2 | Process conditions and parameters used in the experiment.

Mixing method	Powder pre-treatment	Forming pressure	Sintering atmosphere	Additive	Additive content
Dry mixing (with balls)	Cold press granulation	200 MPa	H ₂ -CO ₂	Cr	0.50 wt%
				Cr ₂ O ₃	
				Al ₂ O ₃	
				CaO	
				MgO	
Dry mixing (no balls)				Cr	
Dry mixing (with balls)				Cr	
Wet mixing (with balls)				Cr	
	SPS pre-sintering			Cr ₂ O ₃	
		100 MPa			
		200 MPa		Cr	
		300 MPa			
		100 MPa	H ₂ -CO ₂		
		200 MPa		Cr ₂ O ₃	
		300 MPa			
Dry mixing (with balls)	Cold press granulation	200 MPa	H ₂		
			H ₂ -H ₂ O	Cr	
			H ₂ -CO ₂		
			H ₂		
			H ₂ -H ₂ O	Cr ₂ O ₃	
			H ₂ -CO ₂		
			H ₂	Additive free	—
			H ₂ -CO ₂		
					0.10 wt%
				Cr	0.25 wt%
		0.50 wt%			
		0.10 wt%			
	Cr ₂ O ₃	0.25 wt%			
		0.50 wt%			

$$C_{UO_2}(T) = 52.1743 + 87.951a - 84.2411a^2 + 31.542a^3 - 2.6334a^4 - 0.71391a^{-2} \quad (2)$$

where C_{UO_2} refers to the heat capacity of UO₂ in J mol⁻¹ K⁻¹, and a ($a = T/1000$) refers to the temperature in K.

The coefficient of thermal expansion (CTE) was calculated from the following computational formula:

$$E_T = \frac{L_T - L_{ref.}}{L_{ref.}(T - T_{ref.})} \quad (3)$$

where E_T (K⁻¹) is the CTE of UO₂ pellet at temperature T, T (K) is the temperature, $T_{ref.}$ (K) is the reference temperature, L_T (mm) is the length of pellet at temperature T, $L_{ref.}$ (mm) is

the length of pellet at temperature $T_{ref.}$ In this work, $T_{ref.}$ is set at 25°C. For comparison, the CTE of UO₂ can be derived from the following equation (Martin, 1988):

For 273–923 K:

$$L_{UO_2}(T) = L_{(273)} \times (9.9734 \times 10^{-1} + 9.802 \times 10^{-6}T - 2.705 \times 10^{-10}T^2 + 4.391 \times 10^{-13}T^3) \quad (4)$$

and for 923–3120 K:

$$L_{UO_2}(T) = L_{(273)} \times (9.9672 \times 10^{-1} + 1.179 \times 10^{-5}T - 2.429 \times 10^{-9}T^2 + 1.219 \times 10^{-12}T^3) \quad (5)$$

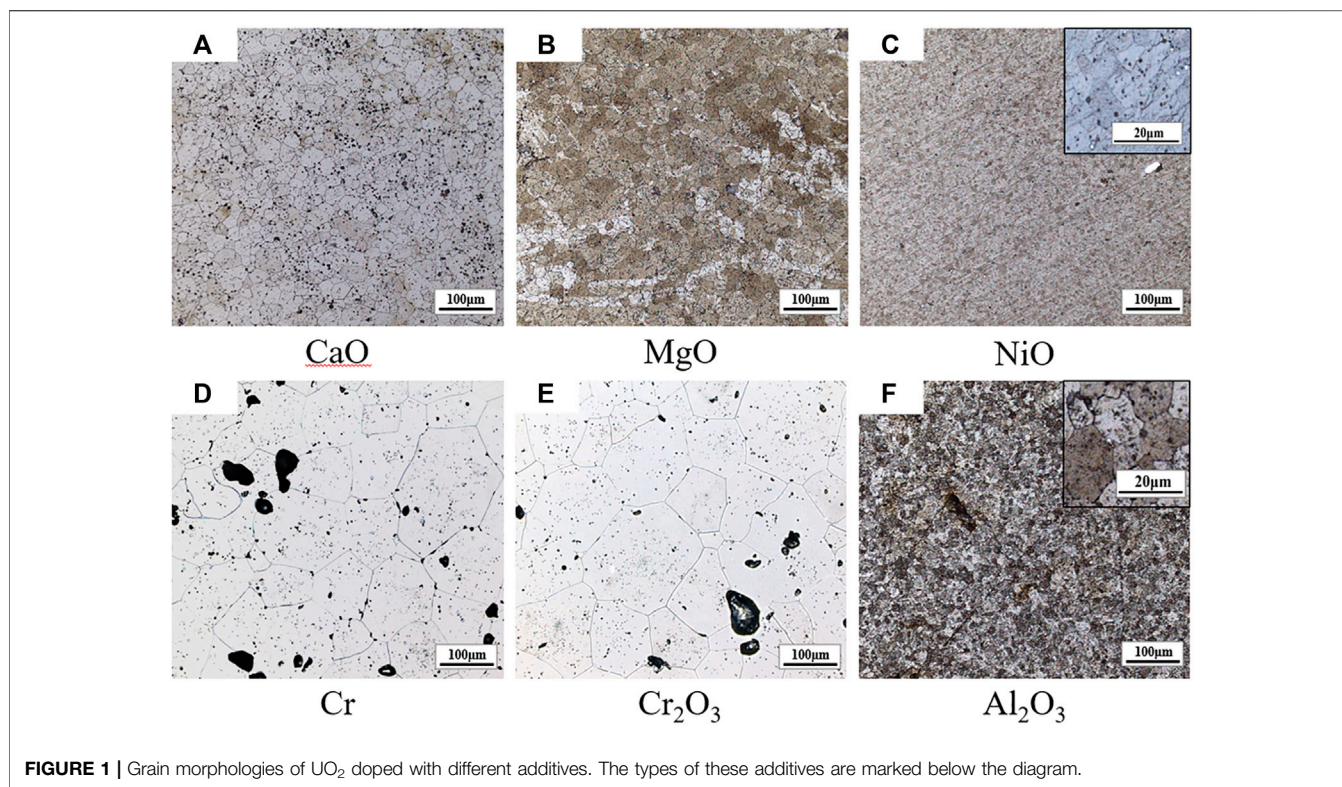


FIGURE 1 | Grain morphologies of UO₂ doped with different additives. The types of these additives are marked below the diagram.

TABLE 3 | The average grain size of UO₂ pellets sintered with different additives.

Property	Additives					
	CaO	MgO	NiO	Cr	Cr ₂ O ₃	Al ₂ O ₃
Average grain size (µm)	28	20	8	121	134	16

where $L_{UO_2}(T)$ and $L_{(273)}$ are lengths of UO₂ at temperatures of $T(K)$ and 273 K, respectively.

RESULTS AND DISCUSSIONS

The Effect of Different Additives on UO₂ Grain Growth

Figure 1 shows the metallographic photos of UO₂ doped with different additives. The sintering process is performed at 1700°C for 1.5 h. The average grain size of doped UO₂ with different additives is listed in Table 3. In this experiment, the average grain size of pure UO₂ sintered under H₂-CO₂ atmosphere is about 16 µm. It can be found that Al₂O₃ has almost no effect on the growth of UO₂ grains. This is consistent with the calculation results reported by Cooper et al. (2018). CaO has a similar promoting effect with MgO. Cr₂O₃ shows the best promotion effect on grain growth of UO₂. This can be attributed to the higher concentration of uranium vacancies produced by doped Cr₂O₃ and the liquid phase behavior of Cr₂O₃ in the sintering process. Therefore, Cr and Cr₂O₃ are using as the additives in the

following experiments. The effect of doped NiO is reported for the first time. However, the effect is contrary to expectations. The grain size of UO₂ doped with NiO is smaller than pure UO₂ under the same condition. This indicates that NiO can inhibit the grain growth of UO₂. According to the defect chemistry theory by Cooper, additives can increase the concentration of negatively charged uranium vacancies and thus promote UO₂ grain growth (Cooper et al., 2018). Therefore, the doping of NiO may cause a decrease of the uranium vacancy concentration during the sintering process. On the other hand, NiO can be reduced by H₂ above 400°C (Janković et al., 2008). So, there is the possibility of interaction between Ni and UO₂, and thereby reducing the effect of oxygen potential on UO₂. At the same time, the dispersion of liquid Ni on the grain edge may pin the migration of UO₂ grain boundaries. In summary, the doping effect of NiO needs further research and analysis.

The Effect of Mixing Method on UO₂ Grain Growth

Figure 2 shows the metallographic photos of Cr doped UO₂ pellets fabricated by different mixing processes. The sintering process is performed at 1700°C for 4 h. As shown in Figure 2, the grain morphologies obtained by the three different mixing processes are uniform, but the grain growth effect is quite different. Table 4 shows the average grain size of the Cr-doped UO₂ pellets in Figure 2. The average grain size of pellets from dry mixing with balls and without balls are 28 and 57 µm, respectively. The grain size of pellets from wet mixing with balls reaches 75 µm. It seems that the additive dispersion

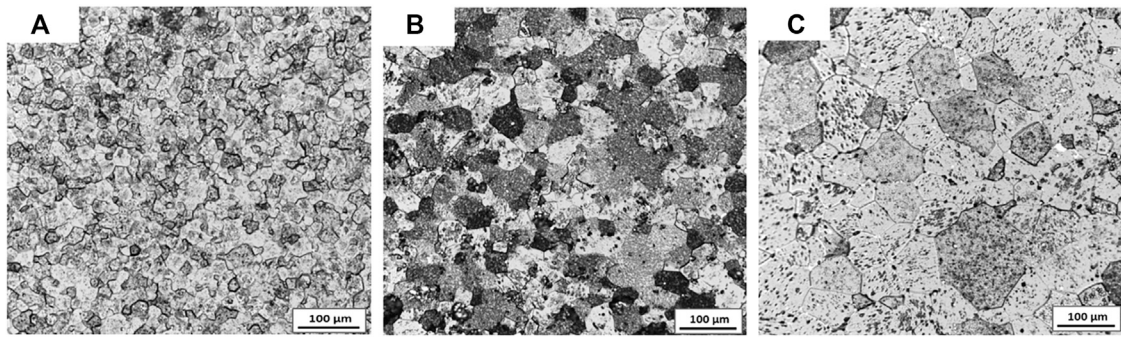


FIGURE 2 | Grain morphologies of Cr-doped UO₂ sintered under different mixing methods. **(A)** Dry mixing (no balls); **(B)** Dry mixing (with balls); **(C)** Wet mixing (with balls).

TABLE 4 | The average grain size of UO₂ pellets mixed in different processes.

Property	Mixing processes		
	Dry mixing (no balls)	Dry mixing (with balls)	Wet mixing (with balls)
Average grain size (μm)	28	57	75

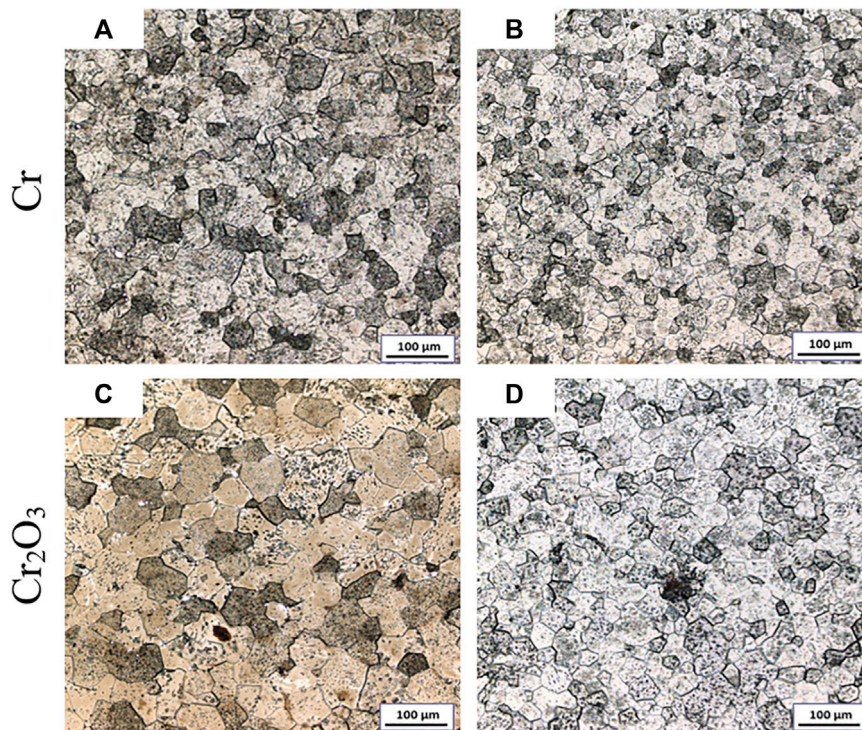


FIGURE 3 | Grain morphologies of Cr and Cr₂O₃ doped UO₂ under different powder pretreatment processes. **(A)** Cold press granulation; **(B)** SPS pre-sintering; **(C)** Cold press granulation; **(D)** SPS pre-sintering.

in the matrix is an important factor affecting the grain growth. Due to the difference in the density of raw material density and the agglomeration characteristics of fine powders, the dry mixing process without any mixing medium leads to the worst dispersion

effect of additive. As a result, the grain size of pellets from such a mixing process was small. In comparison, the introduction of a stirring medium promotes the powders to be mixed. So the grain size obtained by dry mixing with balls is much larger than that of dry mixing

TABLE 5 | The average grain size of doped UO₂ pellets with different powder pretreatments.

Property	Additive	Powder pre-treatment	
		Cold press granulation	SPS pre-sintering
Average grain size (μm)	Cr	54	34
	Cr ₂ O ₃	63	42

samples without balls. The wet mixing process always leads to the most uniform dispersion of the additive in the UO₂ matrix, which is beneficial to the dissolution and diffusion of Cr additive. Thus, the pellets from the wet mixing process own the largest grain size.

The Effect of Powder Pretreatment on UO₂ Grain Growth

Figure 3 shows the metallographic photos of Cr and Cr₂O₃ doped UO₂ under different powder pretreatment processes. The sintering process is performed at 1700°C for 4 h. The UO₂ grain morphologies shown in **Figure 3** are uniform. This indicates that the additive achieved a good mixing effect with UO₂ during the process of dry mixing with balls. **Table 5** shows the average grain size of the doped UO₂ after different powder treatments. Obviously, with the same additive, the average grain size of the doped UO₂ pellet obtained by cold press granulation is larger than that obtained by the SPS pre-sintering method. The reason may be that the UO₂ is slightly sintered at 800°C (Ge et al., 2013). Therefore, the densification of the pellets becomes more difficult, and the diffusion of additives during the sintering process is inhibited. Under the same fabrication condition, the grain size of Cr₂O₃ doped UO₂ is larger than that of Cr doped UO₂. The reason for this difference should be related to the oxidation state of Cr in UO₂. Martial found that the solubility of Cr in UO₂ increased with the growth of the oxidation state of Cr in the solid phase (Riglet-Martial et al., 2014). This indicates that the solubility of Cr₂O₃ in UO₂ is much higher than that of metallic Cr. Johnson et al. studied the binary phase diagram of Cr₂O₃ and Cr, and reported the existence of a eutectic at 1665°C (Johnson and Muan, 1968). So, the possible reason for the difference between the two additives may be caused by the easier formation of Cr-O liquid phase with Cr₂O₃ than Cr, which is more conducive to the growth of UO₂ grains.

The Effect of Different Pressing Pressures on UO₂ Grain Growth

Figure 4 shows the metallographic photos of Cr and Cr₂O₃ doped UO₂ under different forming pressures. The sintering process is performed at 1700°C for 1.5 h. The forming parameters and average grain size of the pellets are listed in **Table 6**. As shown in **Figure 4**, the morphology of UO₂ grains is clear and uniform. However, due to the similar grain size, it is difficult to distinguish the influence of different forming pressures on the grain size of the UO₂ pellet. The grain size distribution of two kinds of doped UO₂ by statistical method is calculated and shown in **Figure 5**. It is found that the ratio of 150–200 μm grain size increases rapidly with the increasing of

TABLE 6 | Green density, sintered density and average grain size of UO₂ pellets under different forming pressures. ρ and ρ_{th} are the density measured by the geometric method and the theoretical density, respectively.

Additive	Property	Forming pressure		
		100 MPa	200 MPa	300 MPa
Cr ₂ O ₃	Green density (g/cm ³)	6.16	6.34	6.50
	ρ/ρ_{th} (%)	56.20	57.85	59.31
	Sintered density (g/cm ³)	10.73	10.76	10.77
	ρ/ρ_{th} (%)	97.90	98.18	98.27
Cr	Average grain size (μm)	117	127	137
Cr ₂ O ₃	Average grain size (μm)	131	127	158

forming pressure. For example, from 100 to 300 MPa, the percentage of grain size between 150 and 200 μm for the Cr-doped UO₂ increases from 6.57 to 14.28%. In general, the average grain size of UO₂ increases with the forming pressure. Since the additives content in the pellet is very small, the green density of the UO₂ pellet doped with Cr and Cr₂O₃ is nearly the same. As shown in **Table 6**, the green density of UO₂ pellets varies with different forming pressures, but the density tends to be similar after sintering. This shows that the forming pressure has little effect on the sintered density with certain strength. However, the average grain size of the pellet increases with the density of the green body. When the binder content is low, the UO₂ grain size increases with the density of the compacted body (Amato and Colombo, 1964). Besides, higher body density means less porosity. Pores are an important microstructural feature of powder compacts and have been considered to have an impediment to grain boundary migration (Nichols, 1968). During the sintering process, the pores will be located at the intersection of grain boundaries or distributed along individual boundaries (Coble, 1961). Thereby, the pores will hinder the growth of grains. Therefore, under the same sintering process, the grain sizes of pellets with higher green density are larger.

The Effect of Different Sintering Atmosphere on UO₂ Grain Growth

Figures 6 and **7** are the metallographic morphologies of normal UO₂ and doped UO₂ in different sintering atmospheres, respectively. The sintering process is performed at 1680°C for 4 h. As shown in **Figures 6** and **7**, the morphology of UO₂ grains is clear and uniform in size. The grain size data are listed in **Table 7**. It can be seen that the grain size of pure UO₂ sintered in H₂-CO₂ is larger than that in H₂. In addition, the grain growth of Cr and Cr₂O₃ doped UO₂ under H₂-CO₂ is obvious. The grain size of pellets under H₂-H₂O is equivalent to that under pure H₂. By comparing the result in **Table 7**, the effect of Cr₂O₃ on grain growth is still better than that of Cr. Moreover, when comparing the results of Cr doping in **Figures 6** and **7**, it indicates that metallic Cr is easier to form oxidation state at 1700°C than at 1680°C. In the past, the importance of oxygen potential for grain growth during UO₂ sintering has been confirmed (Assmann et al., 1986; Harada, 1997). Additionally, the results shown in **Figure 7** also prove that the grain growth of UO₂ is directly related to the oxygen potential during the sintering process. The essence of grain

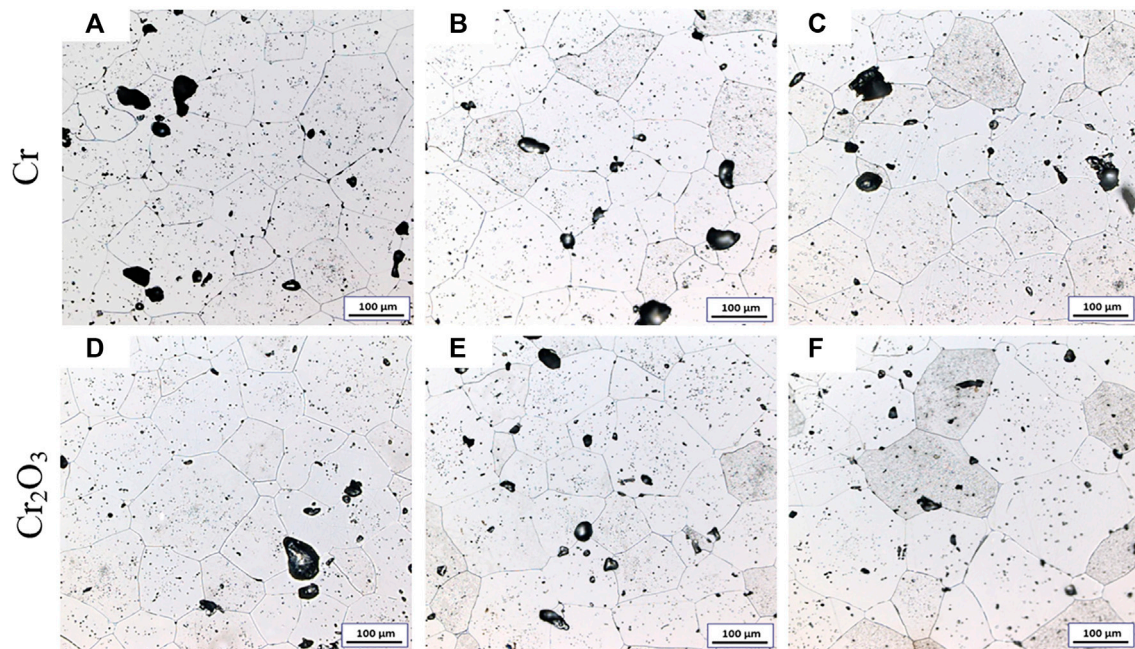


FIGURE 4 | Grain morphologies of Cr and Cr₂O₃ doped UO₂ sintered under different pressing pressures. (A) Cr-100 MPa; (B) Cr-200 MPa; (C) Cr-300 MPa; (D) Cr₂O₃-100 MPa; (E) Cr₂O₃-200 MPa; (F) Cr₂O₃-300 MPa.

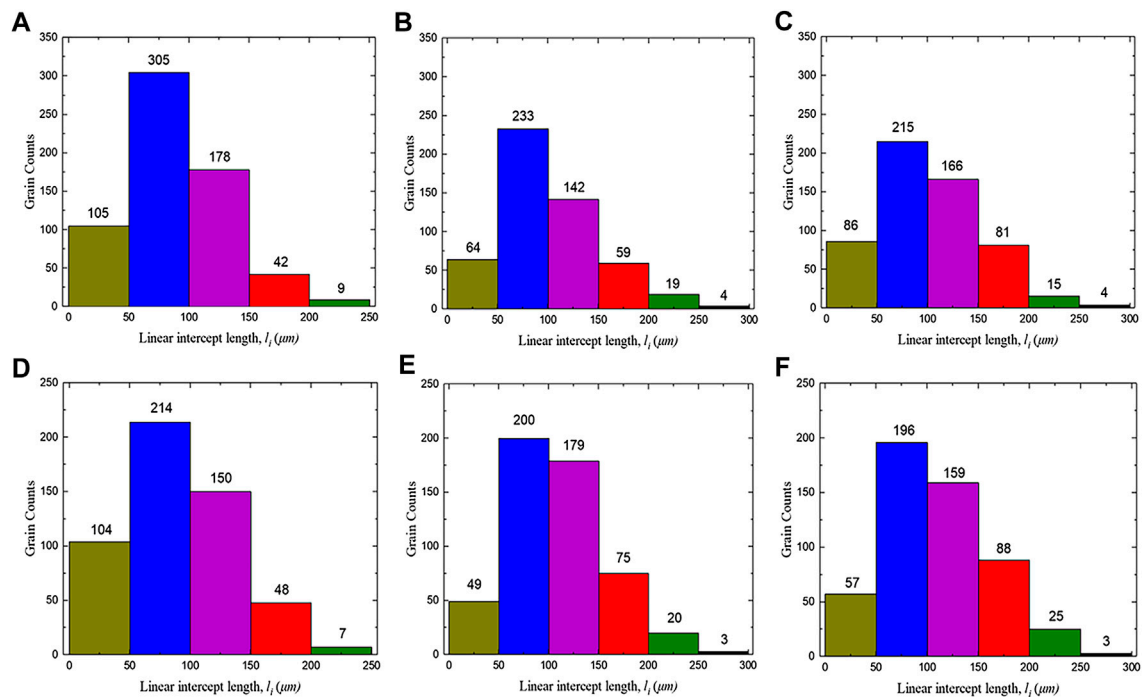


FIGURE 5 | Statistical distribution of sintered UO₂ grain size under different forming pressures. (A) Cr-100 MPa; (B) Cr-200 MPa; (C) Cr-300 MPa; (D) Cr₂O₃-100 MPa; (E) Cr₂O₃-200 MPa; (F) Cr₂O₃-300 MPa.

growth is a process of grain boundary displacement. Grain boundary displacement is a process in which atoms adjacent to the grain boundary are activated, and diffuse to the vacancies

or dislocations in the grain boundary. These are mainly affected by the lattice diffusion rate and the vacancy concentration. Matzke pointed out that the main defects in

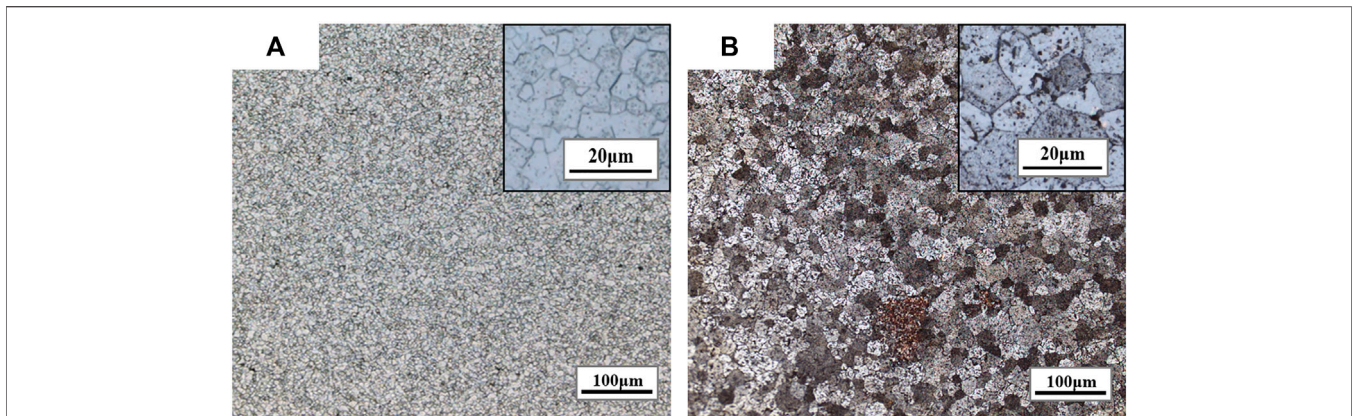


FIGURE 6 | Grain morphologies of pure UO₂ sintered under different sintering atmospheres. (A) H₂; (B) H₂-CO₂.

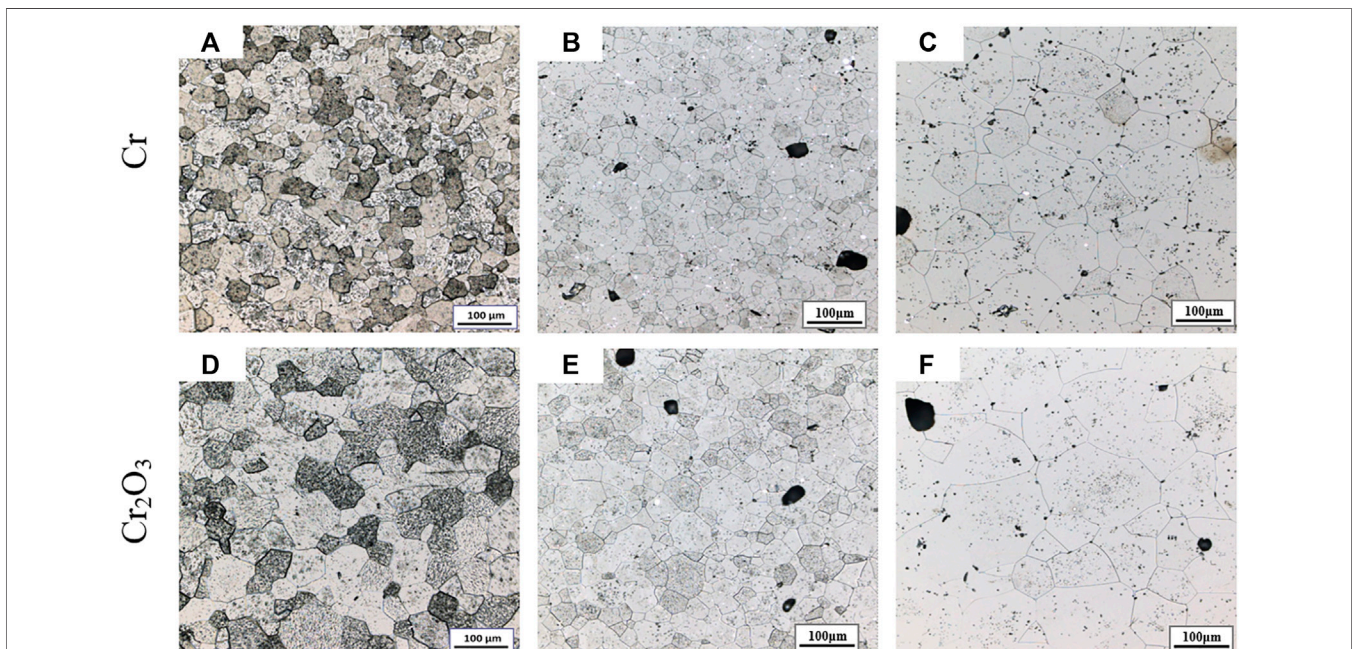


FIGURE 7 | Grain morphologies of Cr and Cr₂O₃ doped UO₂ sintered under different sintering atmospheres. (A) H₂; (B) H₂-H₂O; (C) H₂-CO₂; (D) H₂; (E) H₂-H₂O; (F) H₂-CO₂.

TABLE 7 | The average grain size of UO₂ pellets sintered in different oxygen potential atmospheres.

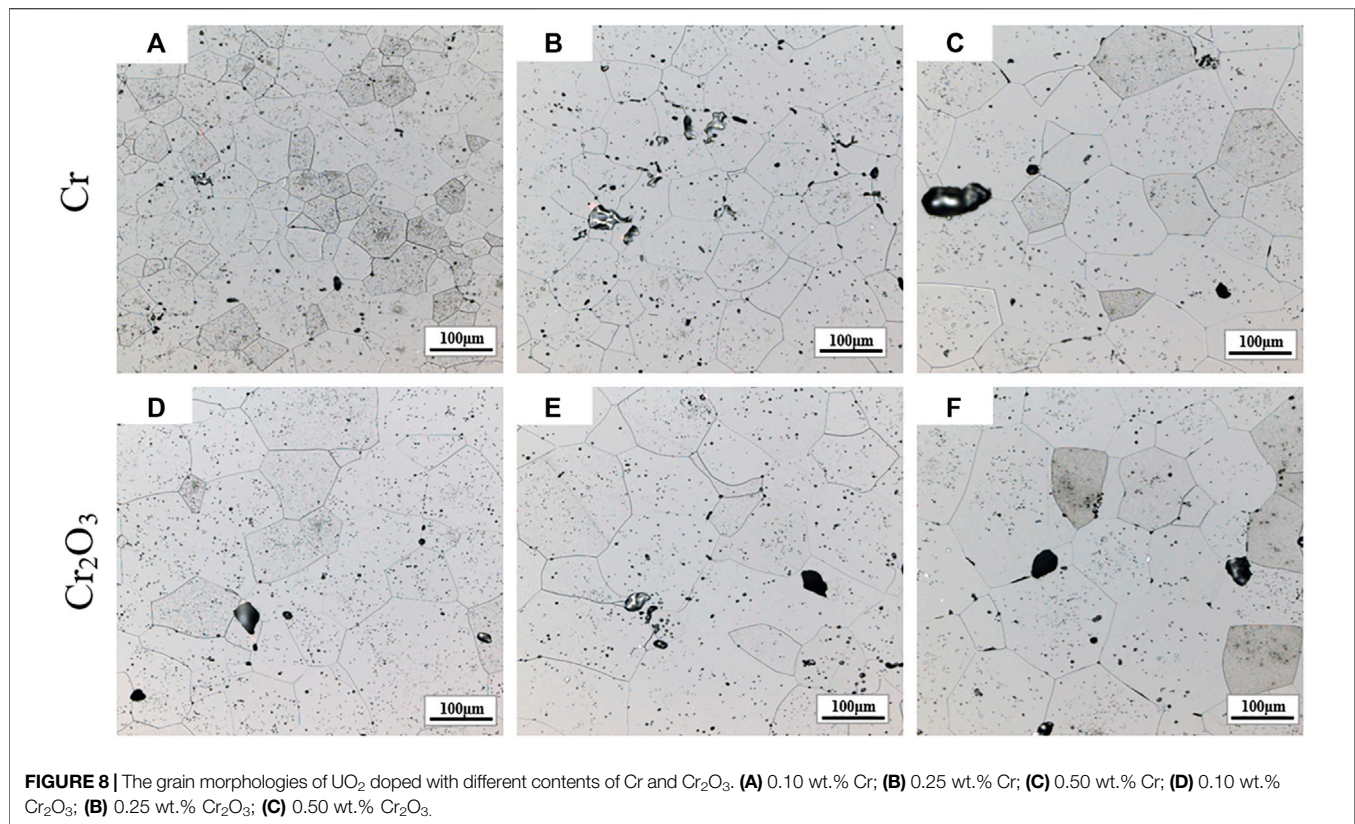
Property	Additive	Sintering atmosphere		
		H ₂	H ₂ -H ₂ O	H ₂ -CO ₂
Average grain size (µm)	Undoped	8	—	16
	Cr	33	41	83
	Cr ₂ O ₃	52	45	123

UO₂ were oxygen interstitials and uranium vacancies, and the self-diffusion rate of uranium was squared with the x of UO_{2+x} (Matzke, 1969; Matzke, 1983). Assuming that UO_{2+x} is related

to the oxygen potential, then the value of x will be in equilibrium with the oxygen partial pressure (Ohse et al., 1985). The results obtained in this work are also consistent with these theories. This indicates that the grain growth of UO₂ is enhanced by increasing the oxygen partial pressure.

The Effect of Additive Content on UO₂ Grain Growth

Figure 8 shows the metallographic photos of UO₂ doped with different contents of Cr and Cr₂O₃. The sintering process is performed at 1700°C for 4 h. As shown in the Figures, the morphology of UO₂ grains is visible after erosion and the size



is relatively uniform. The corresponding average grain size results are listed in **Table 8**. It can be seen that the grain sizes of Cr and Cr₂O₃ doped UO₂ both increase with the growth of the additive amount. In general, the promotion effect of Cr₂O₃ on the grain growth of UO₂ is better than that of metallic Cr under the same content. The increase of Cr content under the same oxygen potential will increase the number of Cr ions and thus create more uranium vacancies. So, the grain size of Cr doped UO₂ increases with the increase of Cr content in the range of 0.1 wt% to 0.5 wt%. By contrast, the increase of Cr₂O₃ content above 0.25 wt% has a gentler effect on grain growth promotion. Regarding this, Kuri et al. combined the quantitative analysis of micro-beam XRD and EPMA data to determine that the average concentration of dissolved Cr in the UO₂ matrix was 0.07 ± 0.01 wt% (Kuri et al., 2014). However, there are still many differences between the results of this experiment and those of others. Firstly, unlike the results by Bourgeois, there is no obvious pinning phenomenon with the increase of Cr₂O₃ content in this experiment. As shown in **Table 7**, the grain growth effect of UO₂ doped with Cr and Cr₂O₃ in H₂-CO₂ atmosphere is much better than that in H₂-H₂O. This indicates that the oxygen potential of CO₂ is much higher than H₂O. Therefore, the difference between the results of this experiment and those obtained by Bourgeois was probably related to the different atmospheres in the sintering process. Secondly, Yang et al. believed that the continuous introduction of CO₂ suppressed the grain growth of Cr₂O₃ doped UO₂, and claimed that the UO₂ grain size was only 12.2 µm when the doping amount was 0.103 wt% (Yang et al., 2012). By contrast, in this

work, with a similar Cr₂O₃ doping amount, the grain size obtained by continuously introducing CO₂ can reach 117 µm.

Thermal-Physical Properties of the Large Grain UO₂

According to formulas (1, 2), the TD and TC of large grain UO₂ doped with Cr are presented in **Figure 10**. The TD and TC of normal UO₂ and values according to the empirical formula recommended by Fink (Fink, 2000) are also plotted for comparison. The calculated density of the sintered pellets in **Figure 10** is about 97%. The average grain size of the 0.25 wt% Cr doped UO₂ pellet used in this TC test is about 102 µm and metallographic photo is shown in **Figure 9**. The preparation process was dry mixing with balls and cold press granulation. The sintering process was performed at 1700°C for 4 h under H₂-CO₂. It is worth noting that the TD and TC of large grain UO₂ are slightly lower than those of the normal UO₂ at lower temperatures. This can be attributed to the fact that impurities can reduce the thermal conductivity of UO₂ (Mei et al., 2014). However, As the temperature rises, the TD and TC of the large grain UO₂ turn higher than those of the normal UO₂ above 600°C. The explanation for this may be that UO₂ crystals are not isotropic, and the presence of grain boundaries will reduce TC to a certain extent (Gofryk et al., 2014). In addition, the TC increase may also relate to the higher specific heat capacity of Cr.

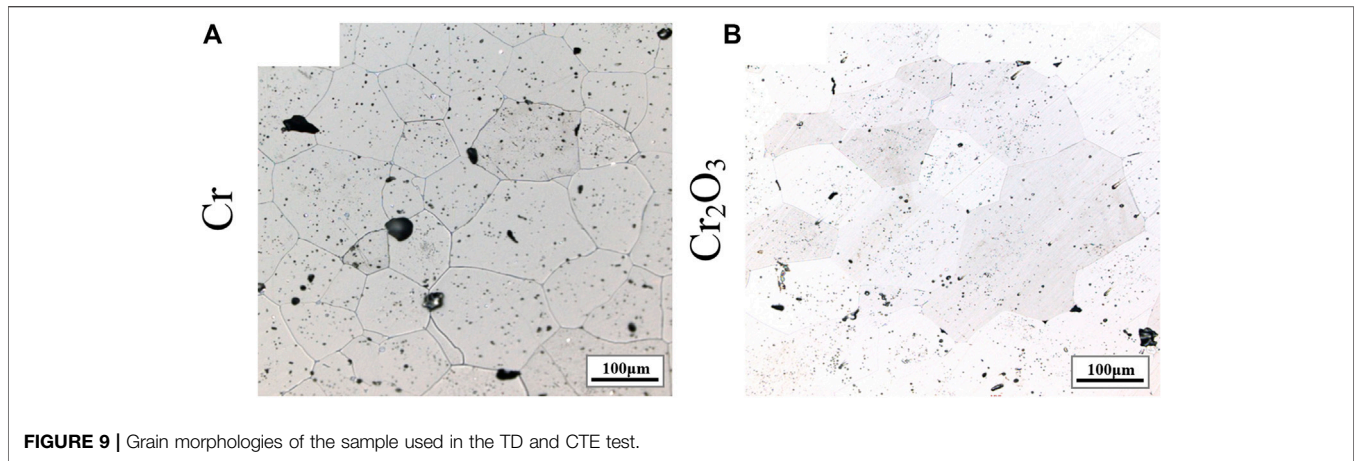


TABLE 8 | The average grain size of UO₂ pellets doped with different contents of Cr and Cr₂O₃.

Property	Additive	The mass fraction of additive		
		0.10 wt%	0.25 wt%	0.50 wt%
Average grain size (μm)	Cr	57	109	133
	Cr ₂ O ₃	117	145	159

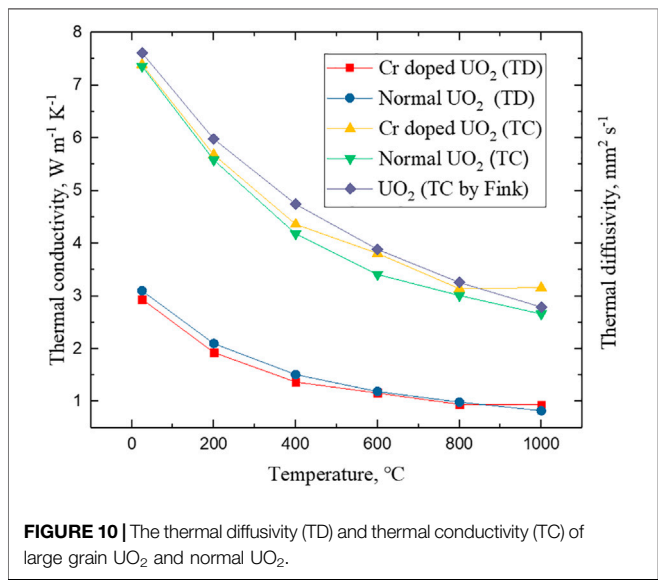


FIGURE 10 | The thermal diffusivity (TD) and thermal conductivity (TC) of large grain UO₂ and normal UO₂.

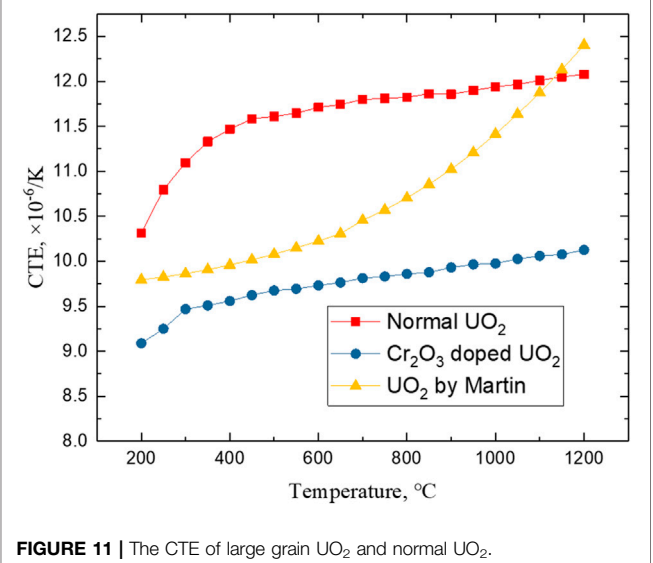


FIGURE 11 | The CTE of large grain UO₂ and normal UO₂.

The CTE of large grain UO₂ doped with 0.5 wt% Cr₂O₃ and normal UO₂ sintered in this experiment can be calculated by formulas (3–5), and the results are shown in **Figure 11**. The preparation and sintering processes of the samples for CTE were consistent with those for the TC testing. For comparison, the CTE of UO₂ is calculated according to the recommendation of Martin (1988). The average grain size

of the Cr₂O₃-doped UO₂ pellet used in this CTE test is about 159 μm and the metallographic photo is shown in **Figure 9**. The CTE of large grain UO₂ and normal UO₂ grows with temperature. However, the CTE of large grain UO₂ is lower than that of the normal UO₂ at the same temperature. The decrease range is maintained at 11.8–16.9% in the temperature range of 200–1200°C. Thermal expansion is the result of volume expansion caused by the aggravation of the lattice vibration of the solid material during heating process. For the effect of grain size on the thermal expansion, it can be explained by the reduction of the interface which leads to the weakening of the anharmonic effect. There are larger anharmonic atomic vibrations at the grain boundaries, and the thermal expansion of the grain boundaries is 2.5–5 times that of the crystalline state (Klam et al., 1987). In addition, two experiments both show that the thermal expansion coefficient will decrease when the grain size

increases (Parker and Rice, 1989, Lu and Sui, 1995). In summary, the reduction in CTE is beneficial to alleviate PCI at high temperatures, and also is of great significance to improving fuel safety.

CONCLUSION

In the current work, the influence of mixing technology, sintering atmosphere, forming pressure, powder pretreatment, additives, and content on the grain growth of UO₂ was systematically studied. The results showed that the influence of additives on the grain growth of UO₂ is the most obvious. Cr₂O₃ shows the best promotion effect among the selected additives. On the contrary, NiO shows an inhibitory effect on the grain growth of UO₂. The preparation process and the sintering atmosphere also play an important role in the grain growth of UO₂. Different mixing and powder pretreatments processes can affect the dispersion effect of UO₂ powder and additives. The best promotion effect is achieved by the wet mixing process. The introduction of CO₂ into the sintering atmosphere can effectively promote the grain growth of UO₂. The average grain size of UO₂ increases with the growth of forming pressure and additive content. However, due to the low solubility of Cr in UO₂, the grain growth effect of Cr₂O₃ tends to be saturated above 0.25 wt%. In this work, UO₂ doped with 0.5 wt% Cr₂O₃ shows the largest grain size, and the average grain size reaches up to 159 μm.

Compared with normal UO₂, large grain UO₂ exhibits obvious advantages in CTE and also shows higher TC at temperatures higher than 600°C. Such enhancement effect has unique

advantages in improving the properties of UO₂ fuel and reducing the swelling effect of the pellets at high temperatures, which can remarkably improve the service performance and the safety of the fuel system.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

YZ: Investigation, Data curation, Writing—original draft preparation; RG: Conceptualization, Investigation; BL: Conceptualization, Investigation; ZY: Validation, Writing—Reviewing and Editing; QH: Investigation; ZW: Investigation; LD: Investigation; XL: Investigation; MC: Conceptualization, Funding acquisition; PZ: Supervision, Funding acquisition; BB: Supervision, Reviewing and Editing; YW: Conceptualization; LC: Conceptualization; BY: Conceptualization; TL: Conceptualization; RL: Conceptualization.

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Conflict of Interest: TL and RL were employed by the company China Nuclear Power Technology Research Institute.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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