Turkish Journal Of Nuclear Science (2018), Cilt. 30, No. 2.
http://www.turkishnuclearscience.com http://dergipark.gov.tr/tjns

INVESTIGATION OF THE FIRST STAGE SINTERING KINETICS OF ADDITIVE FREE UO_2 PELLETS

S. AKBAL*, A. YAYLI,

Çekmece Nuclear Research and Training Center, İstanbul, Turkey

sevgi.akbal@taek.gov.tr

KATIŞKISIZ UO_2 YAKIT PELETLERİNİN İLK AŞAMA SİNTERLEME KİNETİĞİNİN İNCELENMESİ

Abstract

The purpose of this study is to investigate the first stage sintering kinetics and to calculate activation energy of additive free UO_2 pellets. UO_2 pellets and U_3O_8 added UO_2 pellets were fabricated by powder metallurgy route. Pellets were sintered in the Ar+ 5% H_2 atmosphere using a dilatometer. Activation energy calculations carried out by constant heating rate. The influence of U_3O_8 addition on the properties of sintered UO_2 pellets was also investigated.

Özet

Bu çalışmanın amacı katışkısız UO_2 yakıt peletlerinin birinci sinterleme kinetiği ve aktivasyon enerjilerinin incelenmesidir. UO_2 ve U_3O_8 ilave edilmiş UO_2 yakıt peletleri toz metalurji yöntemiyle üretilmiştir. UO_2 ve U_3O_8 ilave edilmiş UO_2 yakıt peletleri dilatometrede, Ar+%5 H_2 atmosferinde sinterlenmiştir. Aktivasyon enerjilerini hesaplamak için sabit ısıtma hızı yöntemi kullanılmıştır. Ayrıca, sinterlenen peletlerin özelliklerine U_3O_8 etkisi incelenmiştir.

Keywords: Nuclear fuel pellet, UO_2, U_3O_8, activation energy, constant heating rate

Anahtar kelimeler: Nükleer pelet, UO_2, U_3O_8, aktivasyon enerji, sabit ısıtma hızı

1. Introduction

Most of nuclear reactors use UO_2 as nuclear fuel. UO_2 powder is pressed into green pellets and then heated in high temperature furnace at about for 4 hours at 1700 ^{0}C under reducing atmosphere containing H_2. Most of these sintered UO_2 pellets met the manufacturing specification of UO_2 pellets. However, in the manufacturing process of UO_2 pellets, defective UO_2 pellets that do not provide the manufacturing specification or scrap of fuel pellets, such as grinding sludge, are produced [(Santos & Riella, 2009), (Ganguly & Jayaraj, 2002)]. These defective pellets are reused in manufacturing new UO_2 pellets. It is common recycling method that defective UO_2 pellets are oxidized in air at 400-500 ^{0}C to make U_3O_8 powder and then added to UO_2 powder [(Kang, et al., 2008), (Song, Kim, Kang, & Jung, 2002)].

Generally, a content of U_3O_8 powder only up to about 15 wt. % is allowed since larger content of U_3O_8 powder makes a deviation from the acceptable density required by fuel specification (Kang, et al., 2008), (Song, Kim, Ki, Kim, & Yang, 1999). The addition of U_3O_8 powder would be a more economical method for obtaining large-grained fuel pellets without a long sintering time and a high sintering temperature (Kang, et al., 2008).

The sintering process is diffusion controlled one, whose rate is controlled by the slower moving metal atoms. Sintering is completed in three stages, first, intermediate and last.

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018

When the density of pellet is between 60% and 90% TD (theoretical density) this stage is defined as the intermediate stage and the stage below 60% is defined as the first stage, the stage over 90% is called the final stage (Aybers, 1989). Uranium diffusion at grain boundaries controls the initial stages of uranium dioxide sintering (Lahiri, Ramana Rao, & Hemanta Rao, 2006). The activation energies for initial stages of UO_2 pellets sintering, reported by different works varies in a wide range from 84 kJ/mol to 420 kJ/mol (Aybers, 1989). The dilatometer operating values used to calculate the activation energies were investigated taking into account the initial sintering phase. In the first phase of sintering, after cold pressing, the contact starts with the transport of the substance to the contact point and the contact point also starts to grow. Other contact points come into contact with each other and radial growth occurs. This stage generally corresponds to a 3% increase in the density and its value is below 65%. In the first phase of sintering, the density values are calculated for the temperature ranges examined with the assumption that there is no grain growth and structural change.

If the use of U_3O_8 powder affects the formation of large-grained pellets, it is also expected to affect the activation energy at the same time. In this study, sintering activation energy of U_3O_8 added UO_2 powder is investigated. . Constant heating rate method was used to calculate the activation energy. The influences of U_3O_8 on the properties of sintered pellets were discussed. In addition, the effect of U_3O_8 on the densification behaviour was investigated in first sintering stage.

2. Materials And Methods

2.1 UO_2 and U_3O_8 added UO_2 pellets production

In this study, U_3O_8 added (5%, 10% weight ratio) UO_2 pellets were prepared using by conventional powder metallurgical route. UO2 powders were prepared by ADU (Ammonium Di-Urinate) method. U_3O_8 powder was obtained by oxidation of UO_2. Figure 1 shows the flow-sheet used for the preparation of UO_2 -5%U_3O_8 and UO_2- %10U_3O_8 pellets.

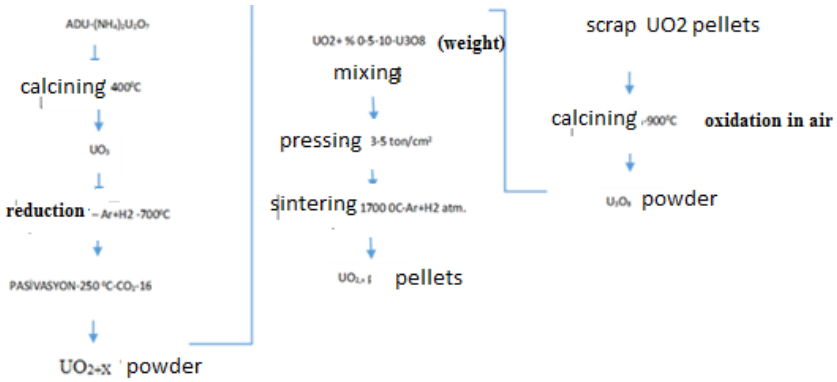

Figure 1. The preparation of U_3O_8 added UO_2 pellets

2.2 The physical properties of powders and pellets

In this study the densities of UO_{2+x} and U_3O_8 powders were measured by helium pycnometer. The particle size of powders was measured by laser diffraction method. The specific surface

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018

area of powders was measured by Brunaue Emmett-Teller (BET) method. Powders were compacted into green pellets of 6 mm diameter at 400 MPa.

Sintering was performed in axial direction using a push rod type dilatometer. Sintering behaviour of the U_3O_8 added UO_2 pellets were investigated by dilatometer technique (NETZSCH DIL 402 C DIL 402C). Green pellet densities were determined by geometrical method; sintered pellet densities were determined by the immersion method. All the process parameters for the pellets used in this study were exactly same. The effect of U3O8 on sintering and activation energy was carried out by experiments consisting of six isothermal steps (800, 900,1000, 1100, 1200,1300 °C with waiting for 120 minutes at each steps) with a heating rate of 5 °C /min in atmosphere of Ar + %5 H2 up to1400 °C.

The effect of U_3O_8 impregnation on the activation energy.

The activation energies of the pellets were calculated using the constant heating rate method which is also called as the Wang and Ranj method (Dehaudt, Bourgeois, & Chevrel, 2001), (Lahiri, Ramana Rao, & Hemanta Rao, 2006). The experimental shrinkage curve obtained from the dilatometer is expressed by the Arrhenius constant as given in Equation 2. In this equation, y= $\frac{\Delta L}{L_0}$ refers to the relative shrinkage, K (T) is Arrhenius constant, m is constant due to the sintering mechanism (m = 1 / n), L_0 represents the length of the raw pellet, ΔL is size change, T is temperature and t is time.

$$y^m = \left(\frac{\Delta L}{L_0}\right)^m = [K(T)t] \quad \textbf{(E-2)}$$

when the derivative of Equation 2 is taken Equation 3 is obtained:

$$\frac{dy}{dt} = \frac{K(T)y^{1-m}}{m} = K(T)f(y) \quad \text{(E-3)}$$

$$K(T) = \frac{AD_0\gamma\Omega}{G^{\alpha k}}\frac{exp\left(\frac{-Q}{RT}\right)}{T} = \left(\frac{k_0}{G^{\alpha k}T}\right)\exp\left(-\frac{Q}{RT}\right) \quad \text{(E-4)}$$

The terms in Equation 4 γ is the free surface energy, Ω the atomic volume, D_0 the pre-exponential factor of the diffusion coefficient, G the grain size, Q the activation energy, R the molar gas constant (8,314 J / K), and the symbols A and α are constants dependent on the geometry of the particle.

The K (T) value is inserted to by Equation 3, and if it is modified, Equation 5 is obtained as in the following:

$$\mathrm{dy/dt} = \frac{k_0 f(y)}{G^{\alpha k}}\frac{exp\left(\frac{-Q}{RT}\right)}{T} \quad \text{(E-5)}$$

When we re-arrange the relative shrinkage rate constant heating rate a = dT / dt, then the relative shrinkage rate equation can be written as

$$dy/dt = a(dy/dT) \quad \text{(E-6)}$$

Using equation (4) and (5) and taking logarithms of the expression the following equation is obtained.

$$ln\left(T\frac{dy}{dT}a\right) = -\frac{Q}{RT} + lnk_0 + lnG^{\alpha} + lnf(y) \quad \text{(E-7)}$$

When the graph of ln (T dy/dT a) is plotted as a function of 1 / T, the slope gives Q / R. Here, terms other than Q / RT on the right hand side of Equation 7 are considered fixed.

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018

In addition, if sintering is defined as densification, the dimensional change will also result in the change in density. The shrinkage data from the dilatometric runs were converted into %TD using the following relation (Kutty, et al., 2003):

$$\rho = \rho_0 \left[\frac{1}{\left(1+\frac{\Delta L}{L_0}\right)} \right]^3 \quad \text{(E-8)}$$

Where ρ and ρ_0 are the density of sintered and green pellets, respectively.

3. Results

In this study, the measured densities of the UO_{2+x} and U_3O_8 powder are 10.86 and 8.46 g/cm^3 respectively. The theoretical density of UO_2 is 10.96 and U_3O_8 is 8.39 g/cm^3. The characteristics of UO_2 and U_3O_8 added UO_2 powders are given in Table 1.

Table 1. Characteristics of UO_2 and U_3O_8 added UO_2 powders

Property	**UO_2**	**UO_2+ 5%U_3O_8**	**UO_2+ 10%U_3O_8**	**U_3O_8**
Theoretical density (g/cm^3)	10.96	10.83	10.68	8.39
Specific surface area (m^2/g)	5.4	-	-	9.99
The pycnometer density (g/cm^3)	10.86	10.74	10.69	8.46
Particle size (μm)	**4,9**	**-**	**-**	**11**

The densities of green pellet was determined by geometrical method. The relative density values of the 0%, 5% and 10% U_3O_8 added green pellets are 52%, 53% and 54% TD (Theoretical density) , respectively. The relative density is the ratio of the sintered density to the theoretical density.

The dilatometer data of the dimensional change or shrinkage (dl / l0) of the pellets are given in Figure 2 depending on temperature and time.

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018

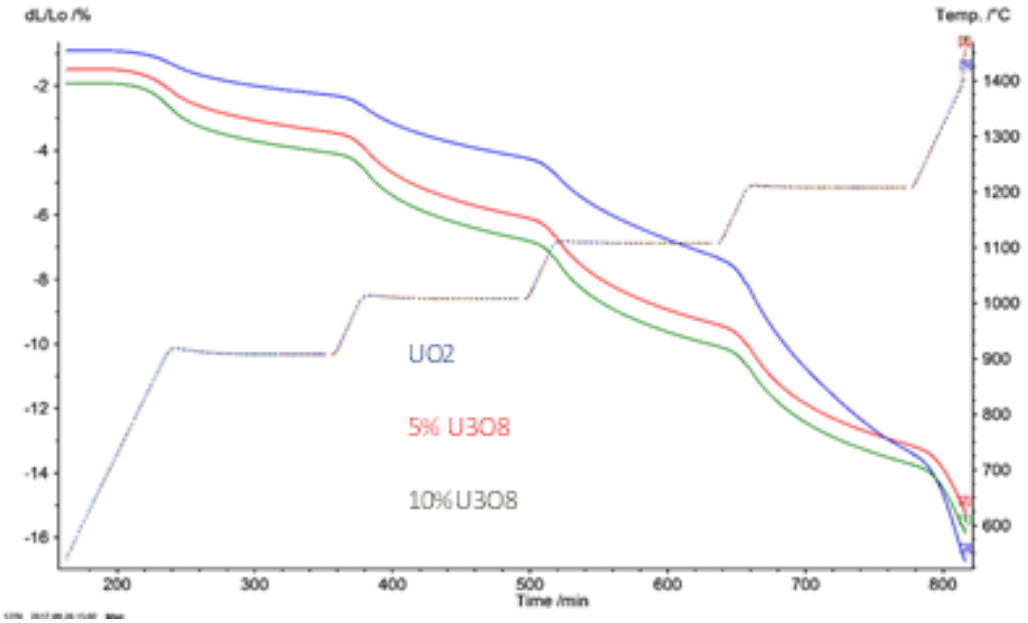

Figure 2. The shrinkage behaviours of UO_2 pellets with 0%, 5% and 10% U_3O_8 addition versus time and temperature.

The dilatometer data of the dimensional change or shrinkage (dL/L0) and shrinkage rate (dL/dt) of the pellets in the first stage sintering zone is given in Figure 3 depending on temperature and time. Figure 3 clearly shows that as the U_3O_8 impurity increases, the shrinkage rate increases and densification begins earlier. Sintering in pure UO_2 was started at 900 °C, with 5% U_3O_8 addition at 870 °C and 10% addition at 840 °C. It is clear that the shrinkage rate increases as the amount of U_3O_8 increases.

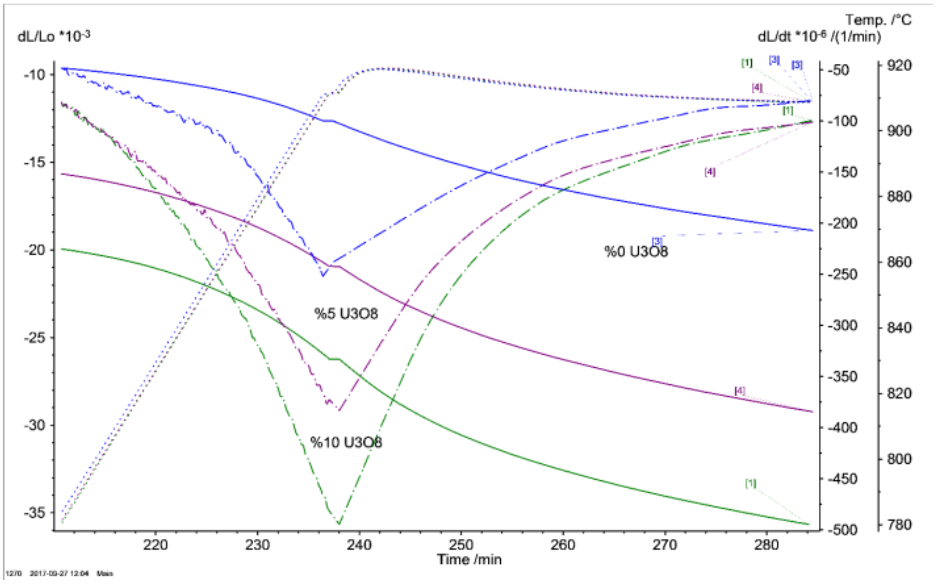

Figure 3. The Shrinkage and shrinkage rate of UO_2 pellets with the ratio of U_3O_8 to time and temperature at initial stage

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018

Using Equation 8, the density change of the pellets was calculated. Figure 4 shows the density of UO_2 pellets depending on the ratio of U_3O_8 added.

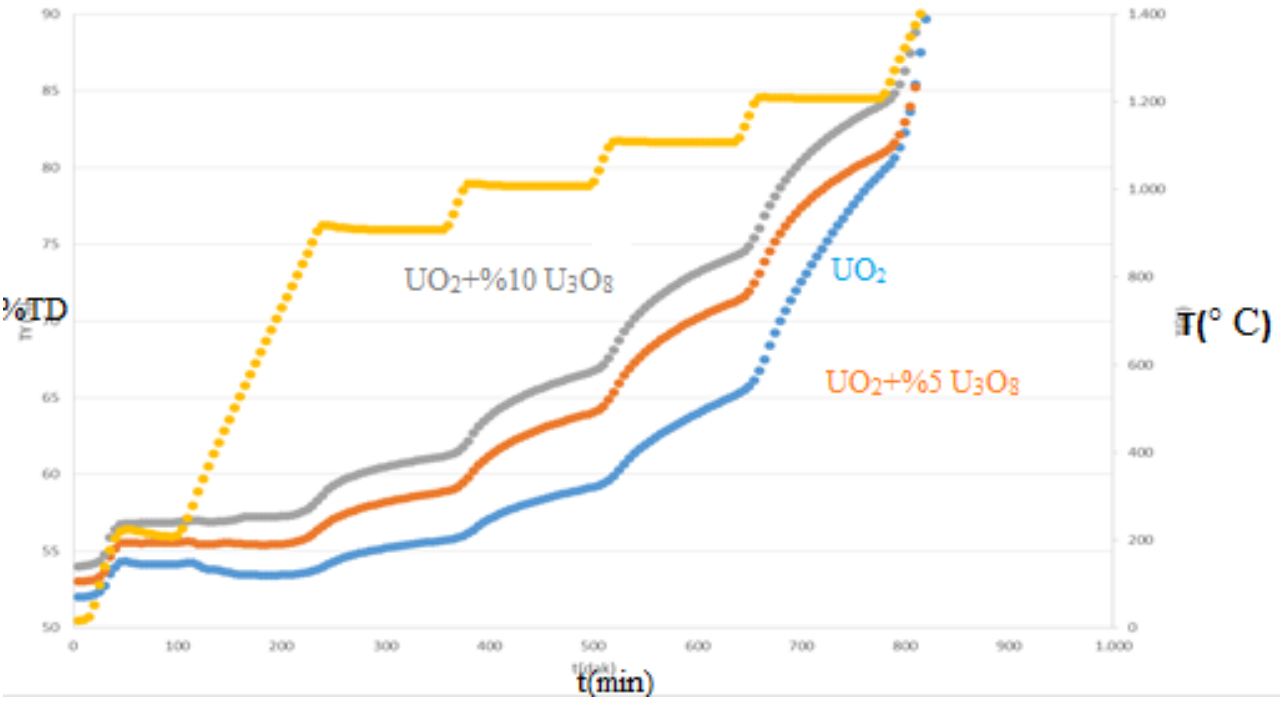

Figure 4. The relative Density of UO_2 pellets depending on the ratio of U_3O_8

In Table 2, relative theoretical density values related to U_3O_8 ratio and temperature are given. Sintering, which is 60% below the relative theoretical density, is considered to be the first stage of sintering. It is seen that the density values are increased with the increasing of temperature and U_3O_8 in Table 2. UO_2 pellets reach about 1100-1200 ^{0}C at about 60% TD, while 10% U_3O_8 pellets reach at 900-1000 ^{0}C.

Table 2. Theoretical density values depending on the amount of U_3O_8 ratio and the temperature

	TD(%)		
T (^{0}C)	UO_2+%0 U_3O_8	UO_2+%5 U_3O_8	UO_2+%10 U_3O_8
25	52	53	54
800	54	56	57
900	55	58	60
1000	58	62	65
1100	63	68	72

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018

Activation energies were calculated at about 800 ° C to 1300 ° C with an increase of about 100 ° C. The results are given in Table 3. In the calculation, the dimensional and structural changes are neglected at the initial sintering. It is assumed that there is no dimensional and structural change up to about 60% TD. The activation energies are indicated by "*****" at ≤ 60% TD.

Table 3. Activation energies calculated by the constant heating rate method

	Q(kJ/mol)		
Temperature range (^{0}C)	UO_2	UO_2+5 %U_3O_8	UO_2+10% U_3O_8
800-900	191	**123**	**146**
900-1000	**240***	**262***	**279***
1000-1100	**277***	**298***	308
1100-1200	**293***	319	332
1200-1300	80	169	128
Average	216	234	239

The average activation energies of the 0%, 5% and 10% U_3O_8 added pellets are calculated 216, 234 and 239 kJ/mol, respectively. In the literature the calculated activation energy of UO_2 are 215 and 243 kJ/mol, (Sökücü, 2015) and (Dehaudt, Bourgeois, & Chevrel, 2001).

4. Counclusion

The change in the density and activation energy of different amount of U_3O_8 added UO_2 pellets were investigated. The results are given below.

- The starting temperature for sintering pellets with 10% U_3O_8 addition was seen approximately 840 ° C. The increasing of the U_3O_8 ratio means increasing of the shrinkage and decreasing of sintering temperature.
- The results show that the density of UO_2 pellets increases with the added amount of U_3O_8 with the assumption of no the structural change and grain growth at the first stage sintering.
- The activation energy values calculated by the constant heating rate method showed that there is no clear dependincy on the added amount of U_3O_8. The activation energy for UO_2, 5% U_3O_8 and 10% U_3O_8 adding UO_2 pellets were calculated as 293 kJ/mol, 298 kJ/mol and 279 kJ/mol, respectively (at 60%TD).
- Between 800-1100 ^{0}C sintering results show that the similarity with same studies.

5. References

1) Aybers, M. T. (1989). UO_2, ThO_2 ve (u,Th)O_2 peletlerinin birinci safha sinterleme kinetiğinin incelenmesi. İstanbul, Türkiye: İstanbul Teknik Üniversitesi-Nükleer Enerji Enstitüsü.

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018

2) Banerjee, J., Kutty, T., Kumar, A., Kamath, H., & Banerjee, S. (2011). Densification behaviour and sintering kinetics of ThO_2-4%UO_2 pellet. Journal of Nuclear Materials, pp. 224-230.

3) Dehaudt, P., Bourgeois, L., & Chevrel, H. (2001). Activation energy of UO_2 and UO_2+x sintering. Journal of Nuclear Materials(299), s. 250-259.

4) Ganguly, C., & Jayaraj, R. N. (2002). Characterisation and quality control of nuclear fuels. New Delhi: Alled Publishers Pvt. Limited.

5) Kang, W. K., Yang, J. H., Kim, J. H., Rhee, Y. W., Kim, D. J., Kim, K. S., & Song, K. W. (2008). Improvement of UO2 pellet Properties by Controlling the powder morphology of recycled U3O8 powder. journal of Nuclear Science and Techonology, 1150-1154.

6) Kutty, T., Khan, K., Hegde, P., Sengupta, A., Majumbar, S., & Kamatha, H. (2003). Deterrmination of activation energy of sintering of ThO2-U3O8 pellets using the master sintering curve approach. Science of Sintering, 35, 125-132.

7) Lahiri, D., Ramana Rao, S. V., & Hemanta Rao, G. V. (2006). Study on sintering kinetics and activation energy of UO2 pellets using three different methods. Journal of Nuclear Materials(357), s. 88-96.

8) Santos, L. R., & Riella, H. G. (2009). Effect of deffect of densification additive (Al (OH)and U_3O_8 recycle in sintering UO_2-7wt%Gd_2O_3 fuel pellets. 2009 ınternational Nuclear Atlantic Conference-INAC 2009. Rio de Janeiro, Brazil: ABEN. May 9.5.2017, 2017 tarihinde alındı

9) Song, K. W., Kim, K. S., Kang, K. W., & Jung, Y. H. (2002). Large-grained UO_2 pellets without impurity additives. CQCNF-2002. INDIA.

10) Song, K. W., Kim, K. S., Ki, W. K., Kim, Y. M., & Yang, J. H. (1999). Effect of TiO_2 on sintering behavour of mixed UO_2 and U_3O_8. Jurnal of the Korean Nuclear Society, 455-464.

11) Sökücü, A. S. (2015). SOL-GEL Prosesinin Jelleşme Tekniği İle Üretilen UO_2, ThO_2 ve (Th,U)O_2 Peletlerinin Birinci Safha Sinterlem E Kinetiğinin İncelenmesi. İstanbul, Türkiye.

Makale Gönderim Tarihi :01/05/2018
Makale Kabul Tarihi :24/12/2018