

THE EFFECTS OF HYDROGEN CONCENTRATION IN REDUCING ATMOSPHERE ON MICROSTRUCTURE OF UO_2 FUEL PELLETS

Birsen AYAZ* and A Nezihi BILGE**

**Istanbul Technical University, Institute for Nuclear Energy, 80626Maslak-Istanbul*

***Marmara Res., Mater. & Chem. Tech. Research Institute, Gebze-Kocaeli-TURKEY*

ABSTRACT

In both conventional high temperature and low temperature sintering techniques, hydrogen is used as sintering and reducing atmosphere to prepare uranium dioxide fuel pellets. It is well known that hydrogen is a dangerous gas to work with. In this work it was aimed to investigate the effects of low-level hydrogen concentration used in reducing atmosphere on micro structure of UO_2 fuel pellets produced by low temperature sintering. Different ratios of H_2/Ar (0.1% H_2 +99.9%Ar, 0.5% H_2 +99.5%Ar, 1% H_2 +99%Ar and 0% H_2 (pure argon)) atmospheres were used as reducing atmosphere for 1, 2, 3 and 6 hours. It was determined that using very low-level hydrogen (1%) in reducing atmosphere prevents the formation of other oxides.

1. INTRODUCTION

Uranium dioxide (UO_2) as a reactor fuel is of great interest in the world. Conventionally uranium dioxide fuel pellets are sintered at high temperatures in hydrogen atmosphere in order to obtain high densities, however in last 20 years many researchers have showed that by using low temperature sintering it is possible to obtain the required high-density (93 %-97%theoretical) UO_2 pellets [1-6], In oxidative (low temperature) sintering technique the green compacts are sintered first at 1100°C in CO_2 atmosphere and then reduced in hydrogen atmosphere. However for reactor use stoichiometric UO_2 compacts are required. The composition of the furnace atmosphere can effect final density and microstructure of UO_2 . The use of CO_2 leads to high O/U ratios and the formation of higher oxides, so that a reduction stage is necessary following to sintering step.

Both in high temperature sintering and low temperature sintering technique hydrogen is used as furnace atmosphere. It is well known that the hydrogen is a dangerous gas to work with. So the usability of the hydrogen should be limited in sintering and reducing atmosphere. In this work it was aimed to investigate the effects of low level-hydrogen concentration used in reducing atmosphere on microstructure of UO_2 fuel pellets produced by low temperature sintering.

2. EXPERIMENTAL PROCEDURE

The uranium dioxide powder used in this work was supplied from the Nuclear Fuel Technology Department of Çekmece Nuclear Research and Training Centre (CNRTC). Ex-ADU

(Ammonium diuranate) uranium dioxide powder was used in this work. The fuel compacts were prepared by adding 0.2% zinc stearate as a binder and formed into disc specimens by pressing at 300 MPa (10 mm in diameter by 11 mm thick). Green densities were about 50% of theoretical density. The pressing operations were performed by means of a hydraulic press. The pellets were placed in alumina boats and were heated in an alumina tube by means of a kanthal-wound furnace. For firing, these specimens were first heated with the CO₂ flowing through the furnace tube and then raised to final sintering temperature at the rate of 7°C/min and then, the CO₂ gas used at low temperature is saturated with moisture. The sintering temperature was determined in previous work as 1150°C in order to obtain 95% theoretical density [6]. Gas flow was at 100 ml/min. Sintering was performed in CO₂+steam atmosphere for 1 hour at 1150°C (partial pressure=3.2x10⁻² atm., total pressure=1 atm.). Different ratios of H₂/Ar atmosphere were used as a reducing atmosphere following the sintering step. The sintered pellets were reduced at 1100°C (partial pressure=3.1x10⁻⁵ atm., total pressure=1 atm.) in 0.1%H₂+99.9%Ar, 0.5%H₂+99.5%Ar, 1%H₂+99%Ar and 0%H₂ (pure argon) atmospheres for 1, 3 and 6 hours. After sintering each pellet was cooled in the furnace atmosphere.

For microstructural observation, the specimens were cut using diamond wafering blade. The UO₂ pellets were mounted in a polyester resin, and polished. Specimens were etched by holding in CO₂ atmosphere at 1100°C for 1 hour. Grain and pore sizes were measured with the aid of an image analyser. More than 1000 grains and pores were counted quantitatively for the determination of average pore size and grain size. The absolute densities of sintered specimens were measured on each pellet, using the immersion technique according to Archimedes' principle.

A diffractometer (Shimadzu-XRD 6000) equipped with monochromator was used to obtain X-ray diffraction patterns from the specimens reduced in 0.1%H₂+99.9%Ar, and 0%H₂ (pure argon) atmospheres under CuK_α (A= 1.5418 Å) radiation. These obtained data were analysed according to Hanawald procedure; the phases of the specimens were later determined by using ASTM cards.

3. RESULTS AND DISCUSSION

The microstructure of the UO_{2+x} specimens sintered at 1150°C in CO₂+steam and reduced in 1%H₂+99%Ar, 0.5%H₂+99.5%Ar, 0.1%H₂+99.9%Ar and 0%H₂ (pure argon) atmospheres at 1100°C are shown in Figs. 1 to 4 respectively. Figs. 1-4(a), (b) and (c) correspond to the microstructure of the pellets the reducing time of 1, 3 and 6 h, respectively. The grain shapes are irregular and with the increasing reducing time, the shapes and sizes stay nearly constant except the Fig. 4(c) which represents the microstructure of the pellet reduced in pure argon for 6 h. The pores can be considered to be of an elongated elliptic shape. The morphology of the surface of

the pellet reduced in pure argon changes with the increasing reducing time (Figs 4(a) to 4(c)). A different microstructural morphology can be observed in Fig. 4(c), compared with the other specimens. The X-ray diffraction pattern obtained from the surface of the pellet reduced in pure argon atmosphere, shown in Fig. 5(a), may explain the different structure of this specimen. This X-ray diffraction pattern was compared with the X-ray diffraction pattern of the pellet reduced in 0.1% H_2 +99.9%Ar atmosphere for 6 h as shown in Fig. 5(b). The peaks were determined as cubic UO_{2+x} in Fig 5(a), which represents the X-ray diffraction pattern of the pellets, reduced in 0.1% H_2 +99.9% Ar atmosphere. As can be seen in Fig. 5(b) which represents the X-ray diffraction pattern of the pellet reduced in pure argon (0% H_2) atmosphere for 6 h, mainly UO_{2+x} peaks and some weak peaks were found which could be indexed as orthorhombic U_3O_8 , and orthorhombic UO_3 . The formation of U_3O_8 and UO_3 shows that there is an oxidation process during reducing of this pellet. The subsequent formation of U_3O_8 and UO_3 is probably due to the lack of hydrogen gas in reducing atmosphere. Even a very low-level hydrogen (0.1%) in reducing atmosphere prevents the formation of U_3O_8 and UO_3 as can be seen from Fig. 5(b). The disadvantage of using low-level hydrogen (0.1%) in reducing atmosphere requires long reducing time as explained in previous work of Ayaz and Bilge [7]. In this work Ayaz and Bilge suggested the use of 1% H_2 +99%Ar mixture as reducing atmosphere in order to obtain stoichiometric fuel pellets.

Fig. 6 shows grain size distribution of the pellets reduced in different H_2 /Ar atmosphere for 6 h. It indicates that the pellet reduced in 1% H_2 +99%Ar, 0.5% H_2 +99.5%Ar and 0.1% H_2 +99.9%Ar atmospheres have the similar distribution and the pellet reduced in pure argon (0% H_2) has a narrower distribution. We suggest that again some other oxide formation of U_3O_8 and UO_3 cause such narrow peak formation for the pellet reduced in pure argon atmosphere (see Fig. 4(c)).

The average grain and pore size relationship with reducing time for the reducing atmospheres of 1% H_2 +99%Ar, 0.5% H_2 +99.5%Ar, 0.1% H_2 +99.9%Ar and 0% H_2 (pure argon) are demonstrated in Fig. 7. The effect of reducing atmosphere on microstructure can also be seen from this Figure. The average grain size and average pore size for 1% H_2 +99%Ar, 0.5% H_2 +99.5%Ar and 0.1% H_2 +99.9%Ar reducing atmospheres are shown in Figs. 7(a) to 7(c) respectively. As can be seen from these Figures the changes in average grain and pore size are not great with the increase in reducing time. Whereas the representative curve of the pellet reduced in pure argon (Fig. 7(d)) shows a slight increase in average grain size with the reducing time until 3 h but then a sharp decrease can be observed. The same behaviour is not observed for the average pore size distribution. The average pore size stay nearly constant with the reducing time for 3 h and then a slight increase is observed on the contrary of average grain size curve. The contrary is believed to originate from the existence of other oxides in the structure. Phase changes occur from cubic UO_{2+x} to orthorhombic U_3O_8 and UO_3 . in the structure These phase changes may cause some small cracks in structure, thus an increase in average pore size.

4. CONCLUSION

Studies have been carried out to investigate the effects of the low-level hydrogen containing reducing atmosphere for ex-ADU uranium dioxide fuel pellets on microstructure. It has been shown that;

- It is supposed that the lack of hydrogen in reducing atmosphere influences the formation of U_3O_8 and UO_3 . Low level hydrogen (0.1%) in reducing atmosphere prevents the formation of phase change in structure from cubic UO_{2+x} to orthorhombic U_3O_8 and UO_3 . The formation of these oxides causes changes in grain size distribution; decreases the average grain sizes, causes some small cracks in structure, thus an increase in average pore size.
- This work provides a base for obtaining high density UO_2 pellets in reducing atmospheres having low-level hydrogen concentration, which means better working conditions since the dangerous hydrogen gas is not required enormously.

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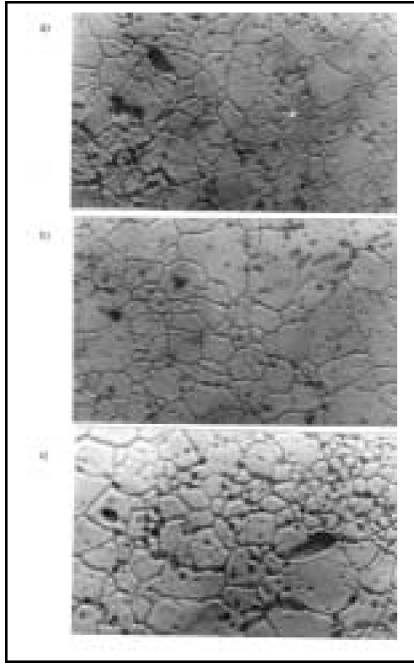


Figure 1. The microstructure of the pellets reduced in 1% H_2 +99%Ar atmosphere for a) 1 h, b) 3 h and c) 6 h.

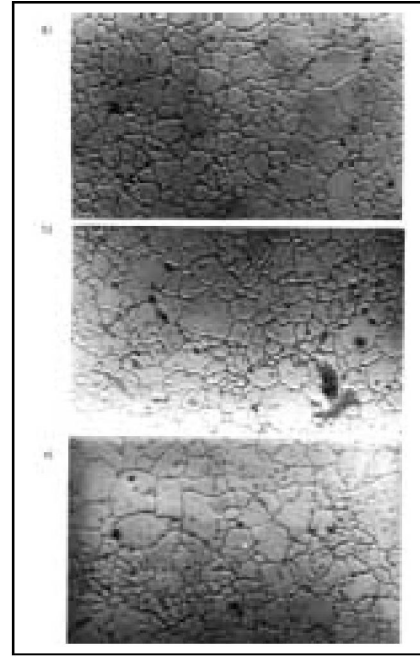


Figure 2. The microstructure of the pellets reduced in 0.5% H_2 +99.5%Ar atmosphere for a) 1 h, b) 3 h and c) 6 h

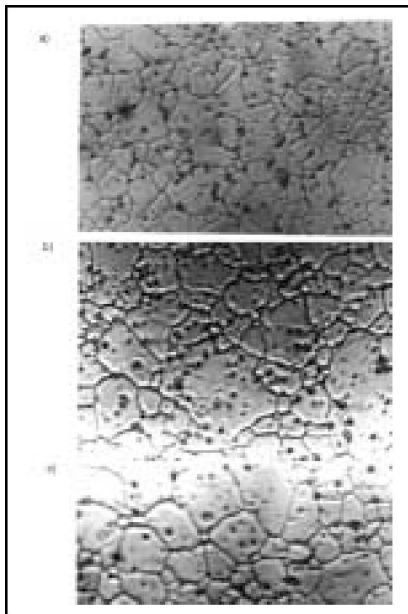


Figure 3. The microstructure of the pellets reduced in 0.1% H_2 +99.9%Ar atmosphere for a) 1 h, b) 3 h and c) 6 h.

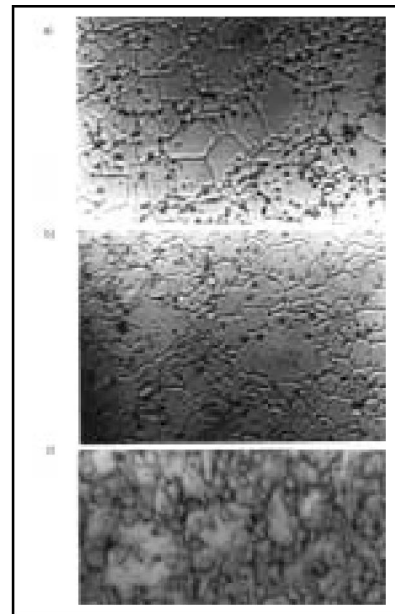


Figure 4. The microstructure of the pellets reduced in 0% H_2 (pure argon) atmosphere for a) 1 h, b) 3 h and c) 6 h

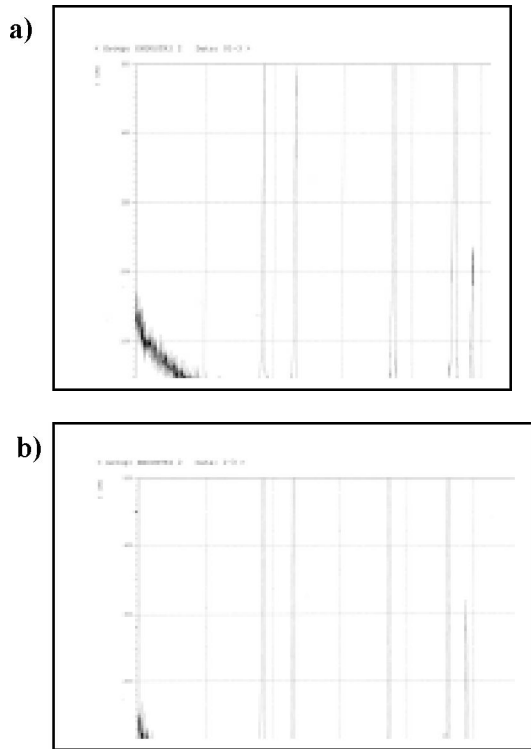


Figure 5. X-ray diffraction pattern of the oxide phases. Figs. 5(a) and 5(b) are corresponding to the layers in Figs. 3(c) and 4(c), represent the pellets reduced in 0.1% H_2 +99.9%Ar and 0% H_2 (pure argon), respectively.

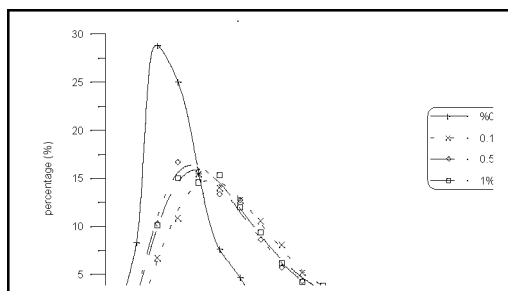


Figure 6. Grain size distribution of the uranium Dioxide pellets reduced in 1% H_2 +99% Ar, 0.5% H_2 +99.5% Ar, 0.1% H_2 +99.9% Ar and 0% H_2 atmospheres at 1100 °C for 6 h.

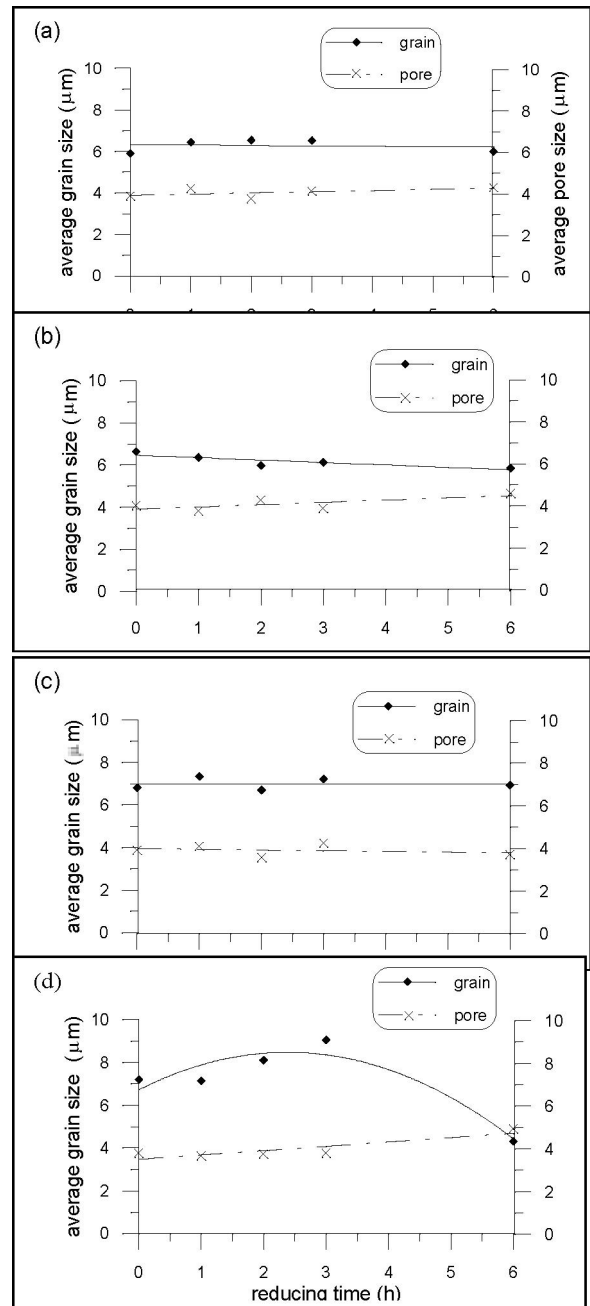


Figure 7. The average grain and pore size and reducing time relationship of the pellets for a) 1% H_2 +99%Ar, b) 0.5% H_2 +99.5%Ar, c) 0.1% H_2 +99.9% Ar and d) 0% H_2 for 6