

The effect of variable oxygen buffer gas on microstructure development in Cr₂O₃ added UO₂

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1. Introduction

A pellet-clad-interaction (PCI) has been soaring as a key risk to deteriorate integrity of cladding [1]. To enhance its robustness against the failure, many researchers have conducted research related to additive contained UO₂ which has enlarged its grain size because enhanced grain growth has positive effect on a fast creep rate at elevated temperature and fission gas retention capability [2-4].

Among various additives such as Cr₂O₃, Al₂O₃, or SiO₂, chromium oxide in UO₂ is sensitively affected by sintering atmosphere of oxygen potential and transformation to liquid phase of CrO in a certain range of oxygen potential induces fast uranium mass transformation. Namely, oxidation or reduction reaction governing phase transformation of the composite determines the mechanism that mass transportation happens. Therefore, by maintaining oxygen potential where CrO(l) is stable for grain growth, significant microstructural changes occur in Cr₂O₃ doped UO₂ [5-8].

It is difficult to make the sintering atmosphere as extremely as low about 10⁻¹⁰ of oxygen partial pressure by using normal rotary or diffusion pump, which is in stable pressure domain for CrO(l) in Ellingham diagram. Therefore, oxygen buffer gas mixtures such as CO₂ + H₂, H₂O + H₂, or CO + CO₂ in 1 atm are typically used to maintain extremely low oxygen partial pressure instead of mechanical device pumping out sintering furnace chamber to be almost vacuum.

As mentioned above, although the buffer gas mixtures can be applied into UO₂ sintering process and the value of oxygen partial pressure created by the mixtures is equivalently controlled, constituents of the mixtures are different and the variable gases could make different in UO₂ grain growth behavior. For verifying the effect of the various gases on enlargement of microstructure in UO₂, in this study, UO₂ containing 1500ppm of Cr₂O₃ has been sintered in atmosphere using gas mixtures of CO₂ + H₂ and H₂O + H₂, respectively, which are commercially used in industry. The result has been confirmed through estimation of average grain size with optical microscopy.

2. Experimental

2.1 Isothermal sintering in controlled oxygen potential

UO₂ powder (dry conversion) doping 1500 ppm Cr₂O₃ was compacted with a pressure of 2.8~3.1 ton/cm² so that the density of the green pellets was in a range of 5.7~5.9g/cm³. After the sintering temperature reached 1700 °C with heating rate of 300K/h, it was maintained for 6 hours by using an electric alumina tube furnace.

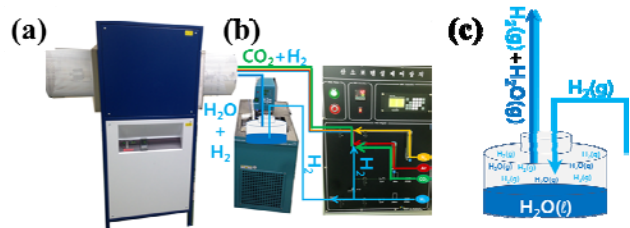


Fig. 1. Oxygen partial pressure controlled sintering system. (a) Alumina tube furnace (b) oxygen potential controller comprising constant-temperature bath filled with water and digital MFC (mass flow controller), (c) glass bottle for evaporating water immersed in water of constant-temperature bath.

Isothermal sintering system capable of maintaining oxygen partial pressure by using oxygen buffer gas mixtures have been shown in Fig. 1. In order to compare the effect of buffer gas mixtures of CO₂ + H₂ and H₂O + H₂, respectively, on grain growth, the oxygen potential controller fabricated in-house used. The gas flow rate of CO₂(g) and H₂(g) has been precisely controlled with digital MFC whereas that of H₂O(g) has been kept by evaporating H₂O(l) in glass bottle immersed in water.

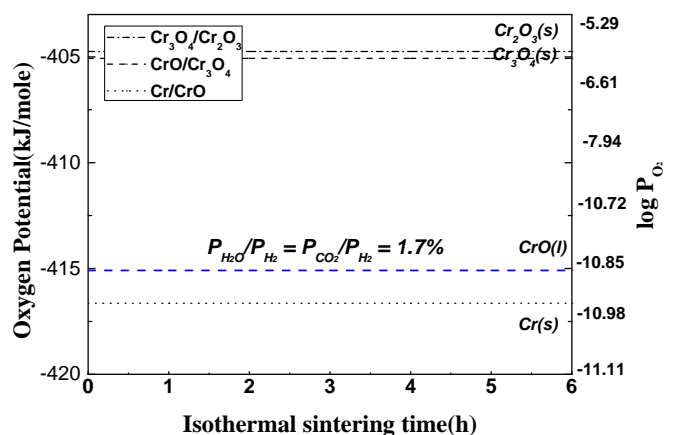


Fig. 2. Atmospheric control where CrO liquid phase is stable by vapor pressure control during isothermal sintering at 1700°C.

For promoting liquid sintering in UO_2 matrix by transforming $\text{Cr}_2\text{O}_3(\text{s})$ to $\text{CrO}(\text{l})$, sintering atmosphere should be maintained in a certain range where $\text{CrO}(\text{l})$ is stable. In this experiment, the oxygen potential has been kept at 415.1kJ/mol coincident with the vapor pressure ratio of 1.7 vol.% in H_2O to H_2 or CO_2 to H_2 . According to N.Y.Toker [6], the pressure ratios of $\text{CO}_2 + \text{H}_2$ and $\text{H}_2\text{O} + \text{H}_2$ correspond mutually. Fig. 2 shows that variable chromium oxides such as $\text{Cr}_2\text{O}_3(\text{s})$, $\text{Cr}_3\text{O}_4(\text{s})$, and $\text{CrO}(\text{l})$ and metallic chromium are existing with oxygen potential.

The grain has been observed with optical microscopy and the grain size was measured by the linear intercept method.

2.2 Verification of oxygen potential in $\text{H}_2\text{O} + \text{H}_2$ gas mixture

For precise flow control of $\text{H}_2\text{O}(\text{g})$, it was inevitable to confirm the exact flow amount of it through pipe connected to the alumina tube furnace because the gas flow was not controlled by the digital system but vaporization at a certain dew point developed by the constant-temperature bath. Namely, water temperature in the constant-temperature bath conducts its temperature to the water in the glass bottle, and then finally, the water in the glass bottle determines dew point which is the amount of vaporized water.

The function of water vapor pressure with temperature is shown in following equation [9]:

$$P_{v, \text{Water}} = \exp\left(20.386 - \frac{5132}{T(\text{K})}\right) \text{mmHg}$$

Through the above equation, the 1.7% of vapor pressure ratio of H_2O to H_2 can be obtained by keeping the water temperature to be about 15 °C.

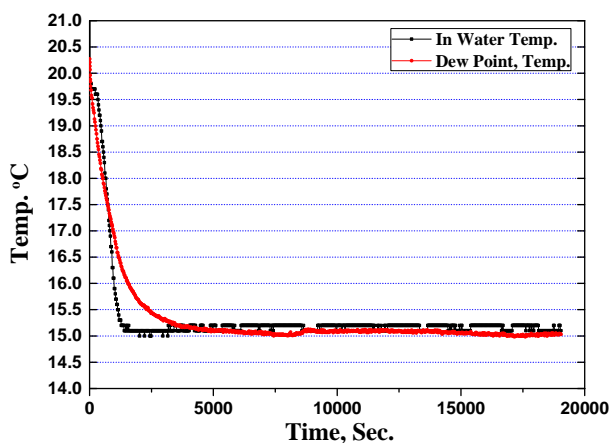


Fig. 3. Water temperature in the glass bottle and dew point of flowing $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2(\text{g})$ mixture through the pipe connected to the alumina tube furnace.

As shown in Fig. 3, after keeping the temperature in the constant-temperature bath and then about 4000s, the temperature variation between water in the glass and

dew point of the gas mixture was negligible. The temperature and the dew point were measured with K type thermocouple and dew point digital meter respectively. With this result, it proves that the amount of vaporized water measured with the digital meter was corresponding to the water temperature and the carrier gas, $\text{H}_2(\text{g})$, take out $\text{H}_2\text{O}(\text{g})$ in exact ratio.

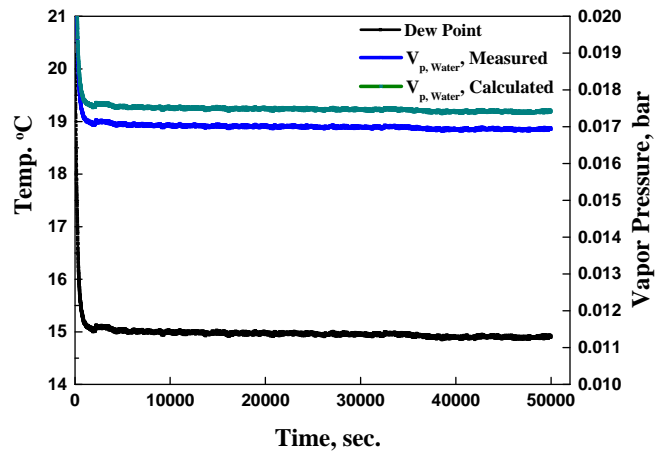


Fig. 4. Dew point (°C) and vapor pressure (bar) measurement in the pipe where the gas mixture of H_2O and H_2 flows.

Fig. 4 shows that dew point and vapor pressure of gas mixture flowing through the pipe connected to sintering tube have been measured with the digital meter. The dew point appears to be maintained at about 15°C and the measured dew vapor pressure of water indicates 0.017bar as 1.7 vol.% in $\text{H}_2(\text{g})$. Therefore, it was confirmed that $\text{H}_2\text{O}(\text{g})$ supply by vaporization in the oxygen potential controller was regulated accurately.

3. Results and discussion

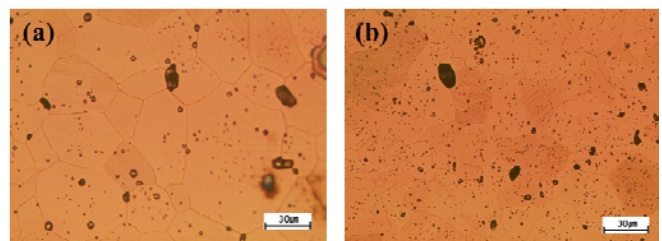


Fig. 5. Optical microstructures sintered in (a) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ mixture, (b) $\text{H}_2\text{O}(\text{g}) + \text{H}_2(\text{g})$ mixture.

Fig. 5 shows optical microstructures sintered in (a) $\text{H}_2 + 1.7$ vol. % CO_2 and (b) $\text{H}_2 + 1.7$ vol. % H_2O . Fig. 5a and Fig. 5b show the average grain size of 33.7 μm and 28.6 μm , respectively. In both pellets, it seemed that grain enlargement was achieved, compared to about 10 μm of pure UO_2 . Based on the result, it is assumed that $\text{CrO}(\text{l})$ has been emerged during the sintering process. However, the grain size variation suggests that although the oxygen potential applied has been

equivalent, the kind of gas mixture caused different grain growth rate which $\text{CO}_2 + \text{H}_2$ gas mixture is more effective on microstructure change than $\text{H}_2\text{O} + \text{H}_2$ gas mixture.

4. Conclusion

In the present work, the grain growth behavior in Cr_2O_3 1500ppm added UO_2 , has been studied with different oxygen buffer gas mixtures of $\text{CO}_2 + \text{H}_2$ or $\text{H}_2\text{O} + \text{H}_2$, respectively. In order to control oxygen potential during isothermal sintering, the oxygen partial pressure controlled sintering system has been used and the oxygen potential controller which was fabricated in-house, was used. Water vaporization method without digital device was introduced to supply $\text{H}_2\text{O}(\text{g})$ and it was confirmed with dew point meter that the almost exact amount of $\text{H}_2\text{O}(\text{g})$ has been developed.

The sintering atmosphere promoted by the vapor pressure ratio of 1.7 vol.% of H_2O to H_2 or CO_2 to H_2 has been in $\text{CrO}(\text{l})$ domain at 1700°C . After sintering for 6 hours, microstructure change was examined and in both pellets, grain enlargement has happened. However, the average grain size in the pellet sintered in $\text{CO}_2 + \text{H}_2$ gas mixture was larger than that in $\text{H}_2\text{O} + \text{H}_2$ gas mixture. Therefore, it is assumed that $\text{CO}_2 + \text{H}_2$ gas mixture promoted faster grain growth behavior than $\text{H}_2\text{O} + \text{H}_2$ gas mixture during Cr_2O_3 1500 ppm doped UO_2 at 1700°C isothermal sintering.

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