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# The Use of Carbon Monoxide in Low-temperature Sintering of High-density $UO_2$ Pellets[*1]

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The fundamental effects of carbon monoxide on $UO_2$-pellet densification are described. A high density of more than 95% of the theoretical level is attained using carbon monoxide as the sintering atmosphere at a low sintering temperature of 1400°C for laboratory-processed $UO_2$ powders. An approximate prediction of the density for any given $UO_2$ powder may be made from the following two experimental criteria: (a) The experimental activation energy for the rate of dissolution of the material into nitric acid may be taken as a measure for the low-temperature sinterability. The density of sintered oxides rises to a maximum at a point where the value of the activation energy for dissolution is about 20 kcal/mol, which is actually very close to the value for the diffusion of oxygen in uranium oxides. (b) The relative intensity of the (220) peak of the X-ray diffraction pattern furnishes another foundation for judging the densification behavior of the $UO_2$ sample.

The present investigation is primarily concerned with basic data aimed at uncovering the role of carbon monoxide, which has seldom been used in uranium dioxide industries, in obtaining high-density $UO_2$ pellets at a low sintering temperature. The sinterabilities are, therefore, examined in the neighborhood of 1400°C instead of in the conventional 1600—1800°C range.

Various approaches have long been taken by many workers to lower the sintering temperature of uranium dioxide. For instance, non-stoichiometric uranium oxide containing an excess of oxygen[1)] increases the degree of sintering. Small amounts of such additives as $TiO_2$ and CaO have been proposed[2,3)] as binding materials between grains of sintered uranium dioxide. In some cases, uranium dioxide has been blended with $U_3O_8$ to prepare a non-stoichiometric uranium oxide mixture and the sintering temperature has been reduced to as low as 1300°C; however, the sintered product here was actually $UO_{2.30}$.[4)] Moreover, an irradiation test elsewhere has indicated that the O/U ratio of the fuel should be less than 2.15 if we are to minimize cracking and fission gas release.[5)]

In the present work, experimentation is carried out to examine the possibility of lowering the sintering temperature by using carbon monoxide to participate in a reduction-sintering schedule for a high-density pellet of more than 95% of the theoretical level. Also, we propose to describe the densification behavior in terms of the activation energy for the rate of dissolution in nitric acid and a specific X-ray diffraction peak of $UO_2$ powder as practical criteria for judging the feasibility of the material for use in low-temperature sintering.

## Experimental

**Materials.** The materials were prepared at an elevated temperature by the simultaneous thermal decomposition and reduction of the ammonium diuranate

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[*1] A part of this work was presented to The 15th Annual Meeting of The Chemical Society of Japan, Kyoto, 1962.

1) P. Murray *et al.*, *TID-7546*, 432 (1957).

2) C. Y. Ang and E. W. Burkhammer, *J. Nucl. Mat.*, **2**, No. 2, 176 (1960).

3) H. G. Sowman and G. L. Ploetz, *KAPL-1556*, 1956.

4) K. Langrod, *Ceram. Bull.*, **39**, No. 7, 366 (1960).

5) O. J. C. Runnalls, *Nucleonics*, **17**, 104 (1959).

precipitate obtained from a purified nitrate solution. Commercially-available tank hydrogen and/or carbon monoxide were used as the reducing gas; the purities of these gases were graded as 99.9% $H_2$ and 99.5% CO respectively. Reducing gas was introduced into the inlet of the laboratory tube furnace with a static charge for several hours at an elevated temperature. The O/U ratio determinations were performed by the oxidation method, which involved igniting the original uranium dioxides to $U_3O_8$ in air and establishing the weight gain,[6,7] the composition of the starting materials was in the range of $UO_{2.07-2.11}$. The thermobalance technique was employed to simultaneously observe the thermogravimetric characteristics of the starting uranium dioxides in the course of the O/U ratio determinations. The $UO_2$ powders were stored in $N_2$-filled polyethylene containers.

**Sintering Tests.** The straight cold-press-and-sinter powder metallurgical technique was used. The granulations were performed by a method similar to that described by Langrod.[4] A high-chromium stainless steel-lined mold was designed to obtain an optimum lubrication of compact $UO_2$ under pressing as well as to eliminate the need for costly carbide dies. No additives were used to flux the grain boundaries of $UO_2$ at a low sintering temperature, the granulated powder was compacted into pellets 1.0 cm in diameter at a pressure of 3 tons/cm². The rather low compacting pressure of 3 tons/cm² was employed to insure a amooth release from the die and to minimize the cracking frequently incurred on green products under higher compacting pressures. The pellets were then sintered at 1400°C with an experimental furnace, either in an atmosphere of carbon monoxide or in hydrogen gas flowing through the furnace, and the densities were measured with the lapse of the sintering time. The density of the sintered $UO_2$ pellet was determined from the weight and geometrical dimensions of the pellet.[7] A dial-depth gauge was used to read the mean values of the diameter and length of the sintered $UO_2$ body.[8]

**Characterization of $UO_2$ Powder in Relation to the Sintering Behavior.** Two tests were performed in an attempt to devise a measure to characterize the sinterability of $UO_2$ powder. The various $UO_2$ powders used were prepared either by the pyrolysis of various precipitates of ammonium diuranate or by the partial air-oxidization of the reduced $UO_2$ samples. Oxide samples with O/U ratios in the range of 2.05—2.16 were thus obtained. In this paper a new experimental criterion will be proposed for judging the low-temperature sinterability of $UO_2$ in terms of another physico-chemical property rather than the well-known O/U ratio of the material.

*(a) Determination of the Activation Energy for Nitric Acid Dissolution.* One gram of the oxide was immersed in 100 m*l* of 1 N nitric acid. A test tube-type glass container was used as the dissolution cell, and the dissolution temperature was controlled to ±1°C throughout the run by means of a water-bath. After a given time has elapsed the cell was incorporated into a centrifugal machine and a 1-m*l* aliquot of the supernatant liquid was pipetted out, thus the dissolved amount of $UO_2$ milligrams could be determined over several time-intervals as measured in minutes. The total liquid volume consumed for the analysis of the dissolved $UO_2$ was not more than 5 m*l* per 100 m*l*. Arrhenius plots of the dissolution rate constant for the nitric acid solution were made at 15, 30, 40, and 60°C.

*(b) Intensities of X-ray Diffraction Peaks.* The deviation in relative intensities of the X-ray diffraction peaks of a given $UO_2$ powder was examined in terms of the density of the pellet when sintered. As a standard of the intensities, the ASTM Card listing the Swanson and Fuyat data[9] for $UO_{2.03}$ was used. An X-ray instrument was operated with the following set of conditions: Target, Cu; filter, Ni; voltage, 30 kV; current, 10 mA; divergency, 1°, and G. M. counting self-rocorder.

## Results and Discussion

Figure 1 shows that, when a hydrogen atmosphere is used for sintering, the use of carbon monoxide in part or wholly as the reducing gas replacing the conventional $H_2$ reduction will be effective in obtaining more densified products in the relatively shorter period of sintering time of less than about 9 hr at 1400°C. However, the conventional hydrogen-reduced $UO_2$ powder gradually exceeds the pellet's density with the lapse of sintering time. The maximum density shown in Fig. 1 was still less than 95% as a fraction of the theoretical density, 10.97 g/cc, obtained by the use of carbon monoxide as the reducing gas.

On the other hand, the use of carbon monoxide as the sintering atmosphere densificates significantly higher when hydrogen-reduced $UO_2$ powder is provided for sintering, as is shown in Fig. 2. It is interesting to note that the combination of hydrogen reduction and carbon monoxide sintering is particularly beneficial for a low-temperature operation. In this case a density of more than 10.6 g/cc (*i. e.*, 96.6% of the theoretical level) is achieved in a firing time of 10 hr. Otherwise, however, the participation of carbon monoxide in the reduction gas will not appreciably contribute to the densification. It may be seen that carbon monoxide can more advantageously be employed as a sintering atmosphere than as a reducing gas.

A further comparison of carbon monoxide and hydrogen as a sintering atmosphere was made by two-stage sintering tests through the medium of nitrogen gas. At the firing temperature of 1400°C green compacts pressed with a hydrogen-reduced $UO_2$ sample were first sintered in an atmosphere of nitrogen, and then the atmosphere was successively switched over either to hydrogen or carbon monoxide. Figure 3 illustrates the surprising result that the successive introduction of hydrogen

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6) W. T. Bourns and L. C. Watson, *A. E. C. L.-757, CRCE-716*, 3 (1958).

7) N. Fuhrman, L. D. However, Jr., and R. B. Holden, *J. Am. Ceram. Soc.*, **46**, 114 (1963).

8) H. K. Lonsdale, *Nucl. Sci. Abstr.*, **16** (17); Abstr. No. 22590 (1962).

9) H. E. Swnson and R. K. Fuyat, *Natl. Bur. Standards (U. S.) Circ.*, No. 539, Vol. **II**, 33 (1953).

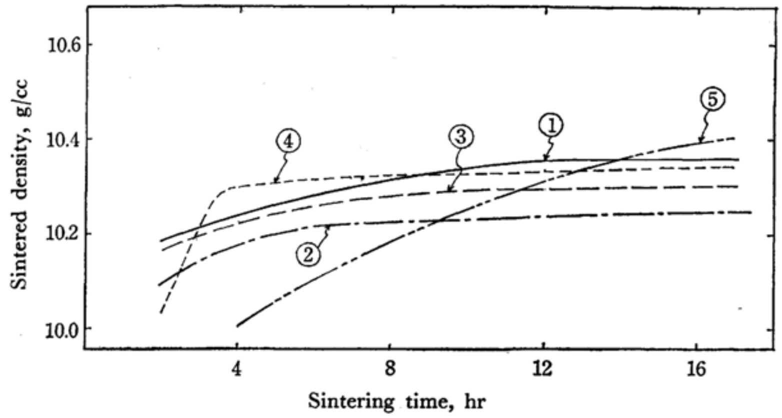

Fig. 1. Sintered density of carbon monoxide-reduced $UO_2$ pellets sintered in atmospheres of carbon monoxide in part or overall. (1): Sintered in CO, (2): in $H_2+2CO$, (3): in $H_2+CO$, (4): in $2H_2+CO$, and (5): in $H_2$, at 1400°C.

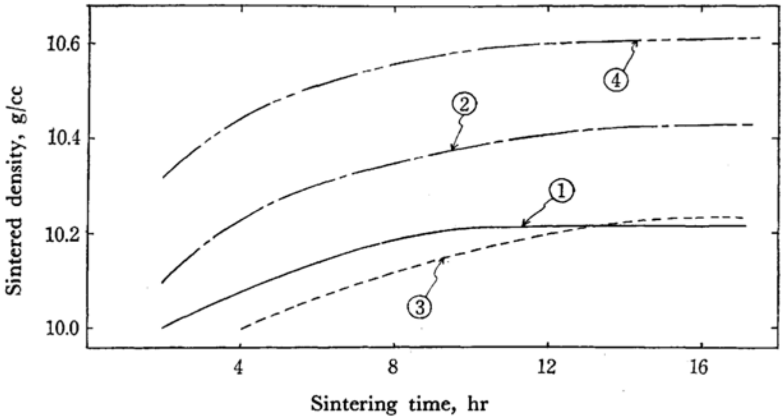

Fig 2. Sintered density of hydrogen-reduced $UO_2$ pellets sintered in atmospheres of carbon monoxide in part or overall. (1): Sintered in CO, (2): in $H_2+2CO$, (3): in $2H_2+CO$, and (4): in $H_2$, at 1400°C.

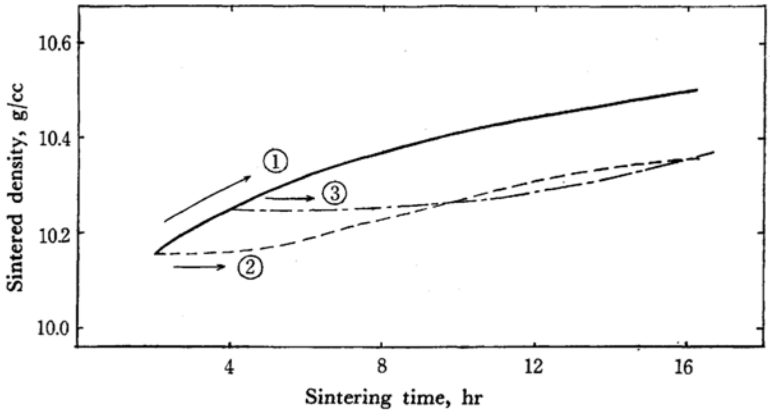

Fig. 3. Two-stage sintering in nitrogen followed by hydrogen atmosphere *versus* sintering time at 1400°C, with the use of hydrogen-reduced $UO_2$ pellets. (1): Sintered in $N_2$ only, (2): Sintering in $H_2$ after 2 hr sintering in $N_2$, and (3): Sintering in $H_2$ after 4 hr sintering in $N_2$.

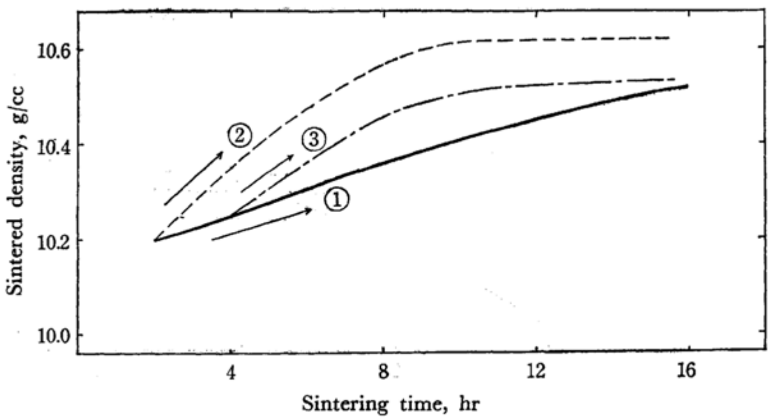

Fig. 4. Two-stage sintering in nitrogen followed by carbon monoxide atmosphere *versus* sintering time at 1400°C, with the use of hydrogen-reduced $UO_2$ pellets. (1): Sintered in $N_2$ only, (2): Sintering in CO after 2 hr sintering in $N_2$, and (3): Sintering in CO after 4 hr sintering in $N_2$.

hindered the densification of the pellets; *i. e.*, the density of the product, which would otherwise be increased along with the initial sintering atmosphere, was considerably decreased by admitting the hydrogen gas.

It is worth noting, on the other hand, that the nitrogen firing, followed by carbon monoxide-introduction, was remarkably effective in the densification of the product, as is shown in Fig. 4, where a density of 10.6 g/cc is obtained by a 2-hr nitrogen sintering plus a 7-hr carbon monoxide sintering. It is also interesting to observe in this case that the pellet which is treated longer with nitrogen (*e. g.*, 4 hr) emerges with a lower sintered density than that described above in spite of the successive carbon monoxide treatment.

The dissolution process into nitric acid as regards sintered pellets was undertaken by Taylor *et al.*10) in an attempt to provide data for the design of a plant for the continuous dissolution of uranium oxide fuel in nitric acid; the sintered pellets exhibited activation energies of about 15 kcal/mol for much higher nitric acid concentrations.

However, the raw-material $UO_2$ has not yet been dissolved as a measure for describing the densification behavior. An examination of the Arrhenius plots for the nitric acid dissolution rates of the raw-material $UO_2$ powders has shown that the values of the activation energy vary from sample to sample, ranging from 12 to 24 kcal/mol; typical examples are illustrated in Fig. 5. Accordingly, it is clear from Fig. 6 that, with an increase in the activation energy up to about 20 kcal/mol, the pellet density sintered in carbon monoxide also increases up to a maximum of about 10.6 g/cc, while that with the higher activation energies, beyond 20 kcal/mol, shows an inferior densification behavior.

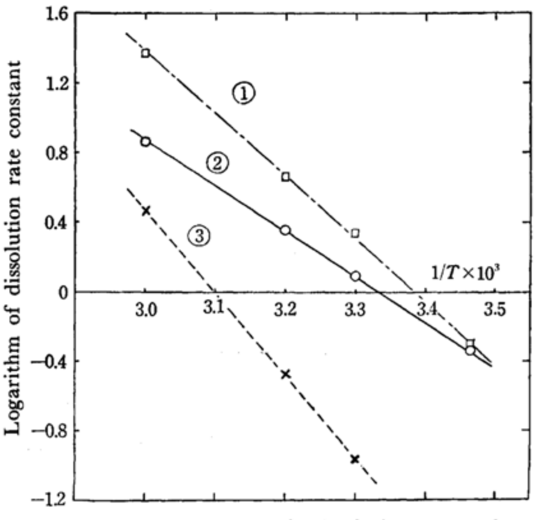

Fig. 5. Arrhenius plot of dissolution rates for typical $UO_2$ samples. (1): 10 g U/*l*, no-washed ADU, simultaneous decomposition and reduction by $H_2$; $E=16$ kcal/mol, (2): 100 g U/*l*, washed ADU, decomposition before reduction by $H_2$, $E=12$ kcal/mol, (3) 100 g U/*l*, no-washed ADU, with decomposition before reduction by $H_2$, $E=22$ kcal/mol.

It is also of interest to survey several values of the activation energies for the diffusion of oxygen in uranium oxides investigated elsewhere and to compare these values with the value of 20 kcal/mol obtained for the maximum sinterability in terms of nitric acid dissolution. Ristic and Kostic11) obtained 20.2 kcal/mol for the sintering of $UO_2$. Stamenkovic and Ristic12) obtained 24.5

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10) R. F. Taylor, E. W. Sharratt, L. E. M. de Chazal and D. H. Logsdail, *J. Appl. Chem.*, **13**, 32 (1963).

11) M. M. Ristic and E. Kostic, *Nucl. Sci. Abstr.*, **17** (19), Abstr. No. 32658 (1963).

12) I. Stamenkovic and M. M. Ristic, *Keram. Z.*, **16** (9), 561 (1964).

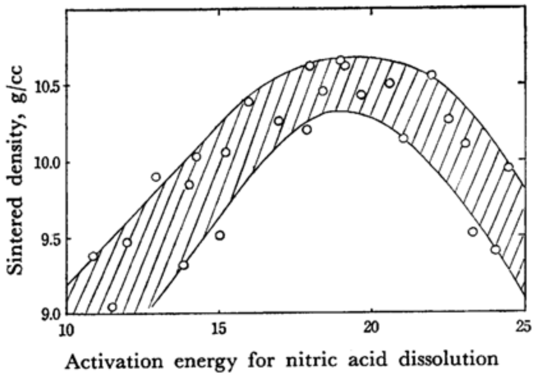

Fig. 6. Nitric acid dissolution activation energies of $UO_2$ powders *versus* sintered densities of the $UO_2$ pellets at 1400°C with carbon monoxide.

kcal/mol for the oxidation of $UO_2$ powders at 172—220°C. Walder[13] determined the value of activation energies for the oxidation of $UO_2$ at 120—360°C to be 20—27 kcal/mol. Therefore, it appears possible to say that the activation energies exhibited by the two independent phenomena, the dissolution of $UO_2$ into nitric acid and the self-diffusion of oxygen in solid $UO_2$, come very close to each other in magnitude, suggesting that the mechanism of the self-diffusion of oxygen which takes place in oxidation and the sintering of $UO_2$ powders can possibly be described by analogy with the behavior in the nitric acid dissolution of the material. At this early stage of investigation, however, it is impossible to extend say anything further about this problem.

Most importantly, however, it may be pointed out that the value of the activation energy for nitric acid dissolution will provide an approximate measure for judging the sinterability of a given $UO_2$ powder, being one of the outstanding characteristics inherited from the foregoing powder production process.

In parallel with this, the X-ray diffraction patterns of the prepared $UO_2$ samples were examined in order to obtain another convenient characteristic measure for dealing with their low-temperature sinterability. Figure 7 plots the deviations of the relative intensities of the (220) peak against the sintered densities at 1400°C obtained in an atmosphere of carbon monoxide. As a standard reference of the relative intensity of the (220) peak, the ASTM Card gives the value of 49 as the fraction of the intensity of (111), which is taken as 100.

The plots in Fig. 7 have been distributed around a well-defined convexity to the above; it may be seen that the sintered density rises to a maximum at the point where the relative intensity of (220) is slightly stronger than the standard value of 49, and then decreases. It can not yet be decided whether this slight shift from neutral is substantially significant or whether it is a mere experimental discrepancy. Figure 7 implies, however, that a lattice disorder, if any, present in the $UO_2$ crystalline phase will possibly act as a resistance to the sound composition of $UO_2$ grains when sintered at a minimum sintering temperature such as 1400°C. At the same time, it is of interest to note that a $UO_2$ sample with a stronger intensity for the (220) peak was much less frequently encountered among the laboratory-produced $UO_2$ powders in comparison with one with a weaker intensity of the peak.

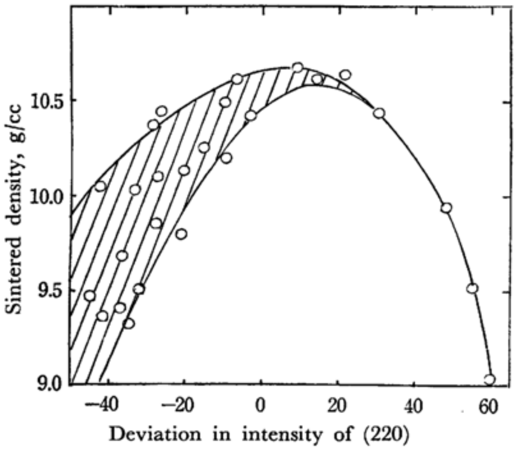

Fig. 7. Deviations in relative intensity of (220) X-ray diffraction peak of $UO_2$ powders *versus* the sintered densities at 1400°C with carbon monoxide.

It should be noted that the examination of the relative intensity for a specific X-ray peak of $UO_2$ powder seems, particularly with an industrial point of view, to be a quite feasible criterion for making a quick estimation regarding the low-temperature sinterability.

## Summary

The effect of carbon monoxide on the densification of $UO_2$ pellets was examined at around 1400°C instead of in the conventional 1600—1800°C range. A high density (above 95% of the theoretical level) was obtained using carbon monoxide as the sintering atmosphere.

The densities of the sintered $UO_2$ pellets were related to the activation energy of the dissolution rate for a nitric acid solution and a specific X-ray diffraction peak of $UO_2$ powder. The density showed a maximum for the $UO_2$ samples with an activation energy of about 20 kcal/mol. The densification behavior was inferior in a $UO_2$ powder with much deviations from the standard relative intensity of the (220) peak. The above two characteristics furnish experimental criteria for judging the low-temperature sinterability of $UO_2$ samples.

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[13] D. B. Y. Walker, *J. Appl. Chem.*, **15**, 128 (1965).