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DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

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Mines Branch Research Report No. R 2

ABSTRACT

The properties of compressed uranium dioxide shapes have been examined after sintering in atmospheres of hydrogen, nitrogen + hydrogen, argon, wet argon, argon + oxygen, nitrogen, wet nitrogen, nitrogen + oxygen, and steam over the temperature range 1200° to 1500°C. Attention has been given particularly to the control of the non-stoichiometric oxygen in the oxide before, during, and at the completion of the sintering. It has been shown that the presence of non-stoichiometric oxygen up to a certain limit is desirable in the oxide to be sintered, and that it is also desirable that this non-stoichiometric oxygen should remain in the oxide while the sintering is taking place if it is desired to achieve good sintering at relatively low temperatures. However, the excess oxygen should be removed to yield an essentially stoichiometric oxide on cooling

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in order that the product may have satisfactory characteristics when used as a fuel element. The atmospheres listed above have been examined with a view to achieving control of the non-stoichiometric oxygen at the various stages, and a recommended procedure to achieve the desired result has been outlined. Use has been made of the published thermodynamic data for the uranium dioxide/oxygen system in interpreting the results and in forecasting suitable sintering conditions.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

This investigation of the effects of variations of furnace atmosphere on the sintering behaviour of compressed uranium dioxide shapes was undertaken as part of a series of studies on factors influencing the fabrication of high-density shapes of ceramic-grade material by the cold pressing and sintering method. This high-density material is of interest for possible use in nuclear reactor fuel elements. Previously reported investigations have dealt with the characteristics desirable in a UO_2 powder which is to be used for this purpose, employing the cold pressing and sintering technique(1), and with the effects on the sintering process associated with the presence of small quantities of foreign substances in the UO_2(2, 3), either as accidental impurities or as deliberate additions.

The object of these investigations, which were undertaken in conjunction with the Chemistry and Metallurgy Division of A.E.C.L., Chalk River, has been to determine the general conditions which affect the sintering behaviour of UO_2. A knowledge of these conditions is important in order that an economical method may be chosen for producing uranium dioxide compacts of the desired characteristics. The investigations made at the Mines Branch have been concerned principally with the factors affecting the fired densities of UO_2 compacts. It should be realized, however, that other properties such as thermal shock resistance, thermal conductivity, mechanical properties, resistance to corrosion, and general irradiation behaviour are also important characteristics of oxide fuel elements.

One of the desirable characteristics of a powder to be fabricated by compacting and then sintering in hydrogen at 1700°C, was shown(1) to be the presence of a moderate amount of non-stoichiometric oxygen in the oxide. The presence of this non-stoichiometric oxygen arises from the atmospheric oxidation of the freshly reduced UO_2 to an extent which will increase with increasing fineness of particle size. A material which attained an equilibrium oxygen/uranium atomic ratio of about 2.20 appeared to represent the optimum condition, and corresponded to an oxide having a particle size in the range 0.1μ to 1.0μ. A still finer material was generally pyrophoric in air and subject to uncontrollable oxidation and was thus not desirable from a practical standpoint. An oxide of composition $UO_{2.20}$ would, under the above conditions, sinter to densities always in excess of 10 g/cm^3 and often in excess of 10.5 g/cm^3. An oxide of approaching stoichiometric composition, e.g., Mallinckrodt oxide having a composition of about $UO_{2.03-2.04}$, gave sintered densities of about 8.0 g/cm^3 under similar conditions. The sintered product in both cases was strictly stoichiometric. The questions therefore arise as to the role of this non-stoichiometric oxygen in the sintering process, as to how long it should be retained during the process, when and how it should be removed if such removal appears either desirable or essential, and, in general, how its extent can be controlled throughout the sintering process.

The atmosphere in which the sintering of a refractory material is performed may have an effect on the course of the densification process. For example, it has been reported that Al_2O_3 sintering rates are higher in hydrogen atmospheres than in air, in vacuum, or in helium(4); chlorine, on the other hand, has been reported to retard the sintering of Al_2O_3(5). The sintering behaviour of UO_2 is known to be affected by the furnace atmosphere, which must not be strongly oxidizing, since UO_2 is quite easily oxidized to U_3O_8 at temperatures below 1000°C. This oxidation is accompanied by a large volume increase which causes disintegration of the fired body. In normal practice in the Mines Branch laboratories, the sintering has been done in a hydrogen atmosphere at temperatures in the region of 1700°C. A similar set of conditions has been used on an industrial scale(6). Lower sintering temperatures than 1700°C, however, would present certain advantages, such as savings in energy consumption and in less stringent requirements for high-temperature materials for furnace construction. The use of steam or wet inert gas atmospheres has been investigated by Arenberg and Jahn(7), who recommend the following firing schedule, involving a maximum temperature of only 1500°C:-

(a) Hydrogen to 1400°C

(b) Steam or wet inert gas, 1400°C to 1500°C and for a 1-hour soak at 1500°C

(c) Hydrogen from 1500°C to room temperature

A similar procedure has been recommended by Vasilos and Slaughter(8) The introduction of oxygen into the UO_2 by the steam to form UO_{2+x}, was given as the reason for the densification at temperatures lower than those required when a hydrogen atmosphere was used. Argon atmospheres have been reported to give good densification of UO_2 at 1400°C(9).

Although the introduction of non-stoichiometric oxygen by sintering in the presence of steam was reported to lead to a marked densification at temperatures lower than those required in the case of hydrogen sintering, nevertheless, the presence of this non-stoichiometric oxygen in the final sintered body may well be an undesirable factor. If a non-stoichiometric sintered oxide is used in a sealed unit in the reactor, it is highly likely that the non-stoichiometric oxygen will be released at the very high temperatures encountered in a pile while in operation. On cooling of the unit when shut down, this oxygen would react with the UO_2 to give significant amounts of U_3O_8 which, having a much lower density than UO_2, might lead to disruption of the fuel element. There is also the point that the presence of the non-stoichiometric oxygen represents additional non-fissile material, and, if the same density could be achieved with a stoichiometric sintered body, then the population of fissile atoms would be more favourable. These considerations lead one to the conclusion that a stoichiometric sintered body is to be preferred to a non-stoichiometric one.

The present work was done to extend and amplify these previous investigations, particularly with regard to the following factors:-

(a) the use of a wider range of atmospheres, including reducing, neutral and slightly oxidizing atmospheres;

(b) the study of the variation of sintered density with temperature for a number of different atmospheres;

(c) the study of the effects of non-stoichiometric oxygen on the sintering process;

(d) the study of means of control of the non-stoichiometric oxygen content during UO_2 sintering.

The results should indicate which atmosphere or combination of atmospheres would give a high degree of densification at temperatures low enough to effect significant savings in energy consumption and refractory material costs. A further desirable property of the <u>final</u> material has been stated to be an oxygen/uranium atomic ratio as close as possible to 2.00.

It has been found that sintered material of high O/U atomic ratio (two-phase material consisting of α-UO_2 and U_4O_9[A]) possesses poor mechanical properties(9). No attempt has been made to study the kinetics of the sintering process; the comparisons among the atmospheres in the current work have been made solely on the basis of firings involving a standard half-hour soaking period.

The work has been divided into sections dealing with reducing, neutral, and oxidizing atmospheres; each is dealt with in turn, and the general conclusions to be drawn from a consideration of the whole problem follow.

THERMODYNAMICS OF NON-STOICHIOMETRIC UO_{2+x}

The following is a list of the symbols and terms which will be used in the thermodynamic discussions in this report:-

R = gas constant (1.987 cal./deg.-mole)

T = temperature in ° Kelvin

P_{O_2} = partial pressure of oxygen in atmospheres

ΔF^o = standard molar free energy change. It will be recalled that $\Delta F^o = -RT\ln K$, where K = equilibrium constant for the reaction

---

[A] Note:- The oxide U_4O_9 is sometimes erroneously referred to as "β-UO_2" and occasionally also by the formula β-U_4O_9. The formula U_4O_9 will be used throughout in this report to indicate the oxide having this stoichiometry and a cubic crystal structure with a unit cell edge of 5.44A.

$\overline{F_{O_2}}$ = partial molar free energy of solution of oxygen in UO_{2+x}; thus, $\overline{F_{O_2}} = RT\ln P_{O_2}$

$\overline{S_{O_2}}$ = partial molar entropy of solution of oxygen in UO_{2+x}; $\overline{S_{O_2}} = -\left(\frac{\partial \overline{F_{O_2}}}{\partial T}\right)_{P,x}$

x = (O/U ratio — 2), i.e., the extent of the non-stoichiometry of the oxide under discussion.

The free energy of solution of oxygen in UO_{2+x}, for a range of values of x has been determined by Aronson and Belle(10) by means of EMF measurements using cells of the type:

$$Fe, FeO \,\|\, ZrO_2, CaO \,\|\, UO_{2+x}$$

Some of the results of this investigation have been plotted in Figure 1 as $\overline{F_{O_2}}$ against T; extrapolations have been made on the assumption of the constancy of $\overline{S_{O_2}}$. The UO_2 data on which Figure 1 is based are given in the Appendix (see end of report). Also plotted in Figure 1 are the values of ΔF^o for other reactions of interest in this investigation. The CO/CO_2 or H_2/H_2O ratios in equilibrium with UO_{2+x} at any temperature may be determined by joining the point C or H respectively, to the appropriate point on the chart and extrapolating to the corresponding scale on the right hand side of the chart. The oxygen partial pressure may be determined similarly using the point O and the P_{O_2} scale.

FIGURE 1

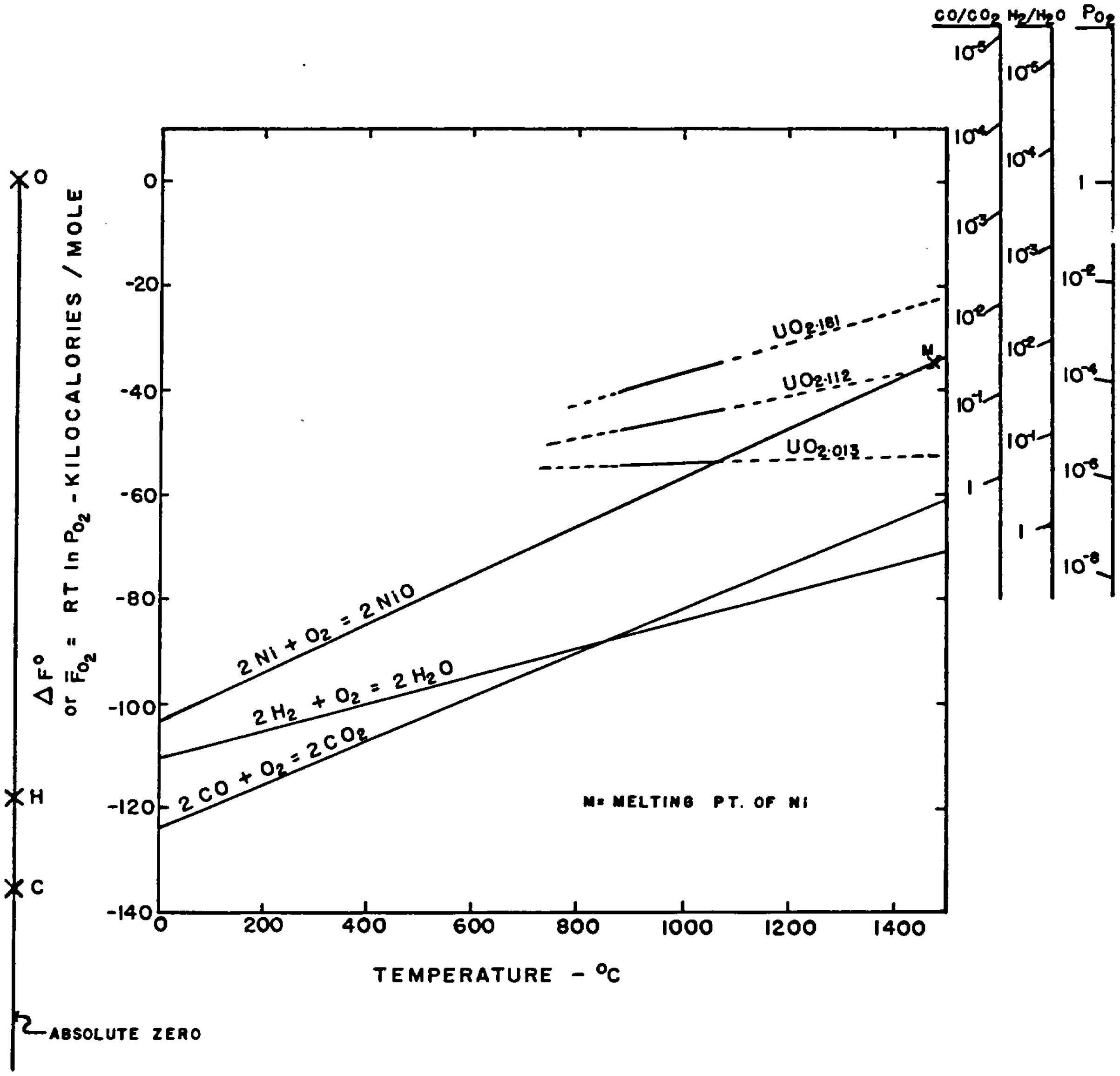

FIGURE 1. Free energy chart showing partial molar free energies of oxygen in non-stoichiometric UO$_{2+x}$. Broken lines indicate extrapolations of $\bar{F}_{O_2}$ data. (See Darken and Gurry, Ref. 13, for details of use of free energy charts.)

The solid lines on the graph for the reactions.

$$2CO + O_2 \leftrightarrows 2CO_2,$$

$$2H_2 + O_2 \leftrightarrows 2H_2O,$$

$$\text{and} \quad 2Ni + O_2 \leftrightarrows 2NiO$$

indicate the standard free energy changes for these reactions. The lines which can be drawn joining the points H and C to the appropriate scales represent partial molar free energies of oxygen in equilibrium with the appropriate gas ratios. The UO_{2+x} lines represent the partial molar free energies of oxygen in equilibrium with non-stoichiometric uranium dioxide of the indicated compositions.

Aronson and Belle summarized their data in the following equation:-

$$P_{O_2} \text{ (in atmospheres)} = 76 \exp\left[\frac{-33,000}{T°K}\right] \exp\left[\frac{31x}{1-x}\right] \quad .....(1)$$

where x = (O/U ratio —2), that is, the atomic proportion of the non-stoichiometric oxygen. Data for systems other than uranium dioxide / oxygen were taken from the compilation of Kubaschewski and Evans$^{(11)}$.

If the oxygen partial pressure in the sintering atmosphere is known, then equation (1) may be used to calculate the extent of the non-stoichiometry in the sintered oxide after equilibrium between the atmosphere and the oxide has been reached. In many cases, the oxygen partial pressures can be calculated from gas equilibrium data. For example, the known equilibrium constant for the reaction,

$$2H_2O + O_2 \rightleftharpoons 2H_2O, \text{ namely } K = \frac{\left[P_{H_2O}\right]^2}{\left[P_{O_2}\right]\left[P_{H_2}\right]^2}$$

may be used to calculate the oxygen partial pressures in atmospheres containing known P_{H_2O}/P_{H_2} ratios, or the oxygen partial pressures produced by the high-temperature dissociation of steam.

When using the thermodynamic data in the interpretation of the experimental results, it must be remembered that there may not have been time in the current work for the attainment of equilibrium and that, on slow cooling, the equilibrium obtaining at the peak soaking temperature may have been shifted to that appropriate to some lower (and undefined) temperature. However, the thermodynamic data do give, at least, qualitative information regarding the behaviour to be expected on firing under given conditions.

The stable phases in the uranium/oxygen system in the region UO_2 to U_3O_8 are shown in Figure 2; unstable phases formed by the low-temperature oxidation of UO_2 have been omitted. This diagram is based on that of Grönvold(12). It will be noted that at room temperature two distinct compounds, UO_2 and U_4O_9, exist, while at 900 °C a solid solution region extends from the composition $UO_{2.00}$ to the composition $UO_{2.18}$. It is probable that the range of

FIGURE 2

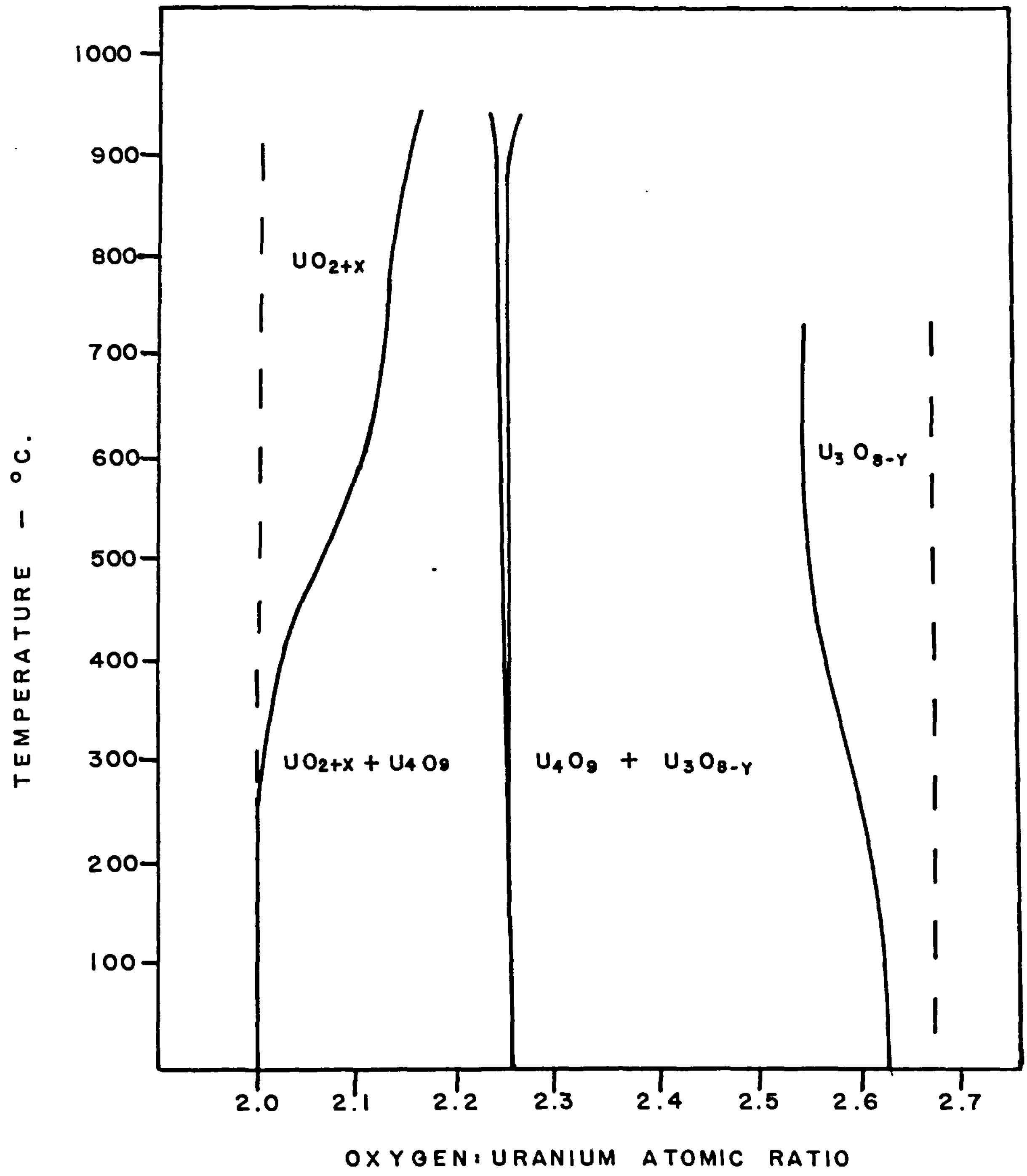

FIGURE 2. $UO_2 - U_3O_8$ Phase Diagram. Modified from Gronvald, ref. 12.

solid solution is even wider at higher temperatures, extending to $UO_{2.20}$ (10) or even further. It will be noted that equation (1) cannot be extrapolated to apply beyond the single phase region.

EXPERIMENTAL

A. Materials

The uranium dioxide used during the greater portion of this investigation is designated as Batch No. 9-2. It had been produced at the Carboloy Division of Canadian General Electric, Limited, Toronto, by the hydrogen reduction of ammonium diuranate made at Eldorado Mining and Refining Limited, Port Hope, Ontario. This material had an oxygen/uranium atomic ratio of 2.19 and sintered to a density of 9.47 g/cm^3 on firing in a hydrogen atmosphere under the "standard" conditions of heating to 1700°C and soaking at this temperature for thirty minutes(1). Other uranium dioxide samples used were reactor-grade material received from Mallinckrodt Chemical Works in 1955, and also material produced by the hydrogen reduction of ammonium diuranate prepared at the Mines Branch, the latter being designated as Batch No. B-2. The characteristics of the last two materials have been described previously(1).

The gases used were drawn from high pressure cylinders and were Canadian Liquid Air products. All gases (except hydrogen) were purified by passing over copper turnings at 500°C to remove oxygen and through calcium chloride and silica gel to remove moisture. This purification train was not employed when deliberate additions of oxygen or steam were used.

B. Procedures

Uranium dioxide compacts of 5 g weight and $\frac{1}{2}$ in. diameter were prepared by cold pressing at 40,000 psi using kerosene as binder and stearic acid as mould lubricant. The green and sintered densities of the compacts were obtained from weights and dimensional measurements.

The reported densities are mean values taken on five compacts unless otherwise indicated. Experimental errors in the determination of the sintered densities were generally not greater than ± 0.1 g/cm^3.

The sintering experiments were generally done in a platinum-wound alumina muffle furnace, containing a mullite tube holding the specimens. The desired gas atmosphere or mixture of gases passed through this tube, as required. Steam was produced by boiling water in a side-arm flask. The steam pressure (and hence the flow rate) was adjusted by controlling a release valve to the atmosphere in the gas line leading to the furnace. Temperatures were measured by means of a platinum-platinum:10% rhodium thermocouple. A few experiments were done in a platinum-wound mullite tube furnace through which the required atmospheres could be passed. The sinterings in undiluted hydrogen were performed in a molybdenum-wound alumina tube furnace, temperature measurements being made in these cases with a Leeds and Northrup optical pyrometer.

The firing cycle used involved heating to the desired peak temperature at rates of 90 to 150 deg. C per hour, soaking at this temperature for thirty minutes, and cooling at rates of 400 to 900 deg. C per hour. The slower heating and faster cooling rates were generally associated with the high-temperature experiments. Whenever a steam atmosphere was used, heating to 750°C and cooling below 750°C were done in an argon atmosphere to avoid difficulties in handling steam under conditions where condensation might take place in the cooler parts of the furnace.

C. Analyses

Oxygen/uranium atomic ratios were determined by the reduction of the non-stoichiometric UO_{2+x} to $UO_{2.00}$ with hydrogen, followed by weighing the resultant water, collected in an "Anhydrone" absorption tower(14). Alternatively, some of the oxygen/uranium ratios were determined from the weight change associated with the oxidation of a known quantity of UO_{2+x} to stoichiometric U_3O_8(14).

The phases present in the fired compacts were determined from X-ray diffraction powder patterns, obtained by using CuK_α radiation.

RESULTS AND DISCUSSION

A. Reducing Atmospheres

A hydrogen atmosphere has been widely used in these laboratories and elsewhere for the sintering of UO_2. The material used in most of the present investigation, (Batch No. 9-2), fired to 1700°C in hydrogen, produced a final density of 9.47 g/cm^3 (see Table 1). This represents rather poor sinterability(1); changes in final density with changes in sintering conditions will, however, tend to be larger for such a material than for material which sinters more nearly to the theoretical density of 10.97 g/cm^3 on firing under the "standard" conditions. Thus, Batch No. 9-2 is a suitable material to study for the detection of any significant improvement in sintering behaviour.

The results obtained for hydrogen sintering in the temperature range considered in this investigation (1200° to 1500°C) are given in Table 1 and are plotted in Figure 3 (see page 17). The densification obtained was much less than that obtained on firing to 1700°C, and there was no evidence of an approach to a constant sintered density with increasing temperature. The residual non-stoichiometric oxygen generally decreased with increasing peak sintering temperature.

The use of hydrogen diluted with nitrogen gave sintered densities no better than those obtained with hydrogen alone. Indeed, the 1200°C results indicated a somewhat lower density. This

TABLE 1

Sintering in Undiluted Hydrogen Atmospheres

UO_2 used:- Batch No. 9-2

Furnace used:- Molybdenum-wound alumina tube furnace

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content[**] of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.50	6.95	2.034	6.92[**]
1300	5.48	7.22[*]	2.043	7.20
1400	5.56	8.06	2.012	8.05
1500	5.55	8.81	2.003	8.81
1700	5.55	9.47	1.999	9.47

[*] Mean for 3 compacts.

[**] In this and the succeeding Tables, this final column of data gives the amount of uranium dioxide that would be present, in grams per cubic centimetre, if all the non-stoichiometric oxygen were removed without any concurrent crystallographic changes. These figures are given in all Tables in order to provide a basis for comparison with this and earlier work involving hydrogen sintering at 1700°C, where the final product is essentially stoichiometric UO_2. The actual uranium contents can thus be more directly compared.

FIGURE 3

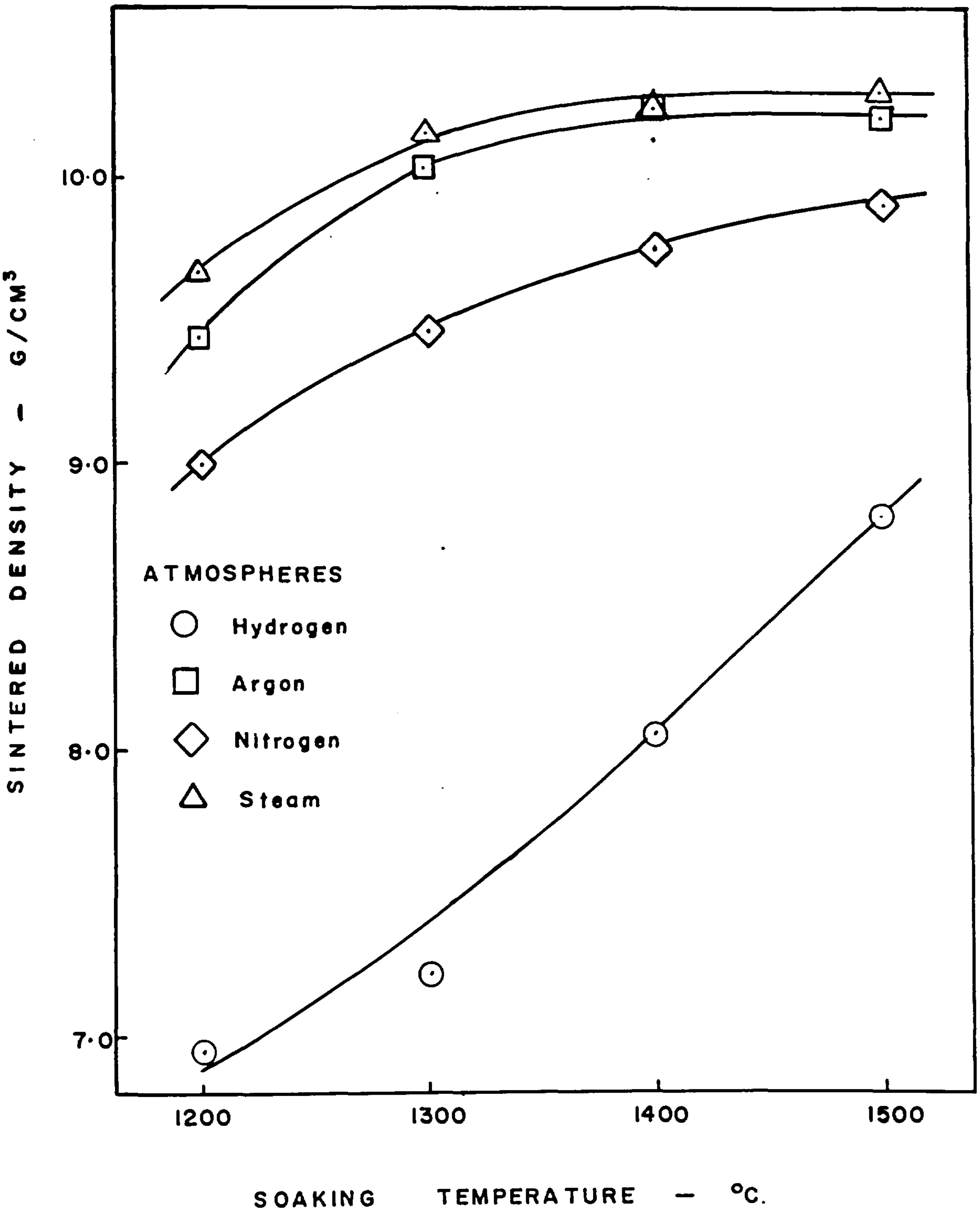

FIGURE 3. Variation of sintered density with soaking temperature for different atmospheres.

atmosphere, at 1400 °C, attacked the platinum thermocouple and the platinum foil upon which the compacts were placed; further use of this atmosphere was therefore discontinued. This attack is attributed to catalytic action of the platinum metals on the ammonia synthesis reaction. The few results obtained using this 4:1, N_2:H_2 atmosphere, are given in Table 2.

TABLE 2

Sintering in Nitrogen:Hydrogen Atmospheres
(N_2:H_2 = 4:1 by volume)

UO_2 used:- Batch No. 9-2

Furnace used:- Mullite tube furnace

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.45	6.45	2.080	6.42[A]
1400	5.45	8.15	2.016	8.14

[A] Phase present: α-UO_2.

Reference to Figure 1 (see page 8) shows that, in the presence of H_2, with no substantial concentration of H_2O available, the oxygen/uranium ratio should be reduced to well below 2.01. The results given in Table 1 indicate that at the higher temperatures, this is indeed so; at lower temperatures the removal of oxygen is probably too slow to approach completion during the firing cycle employed in this investigation.

B. Neutral and Slightly Oxidizing Atmospheres

(i) Argon Atmospheres

The results obtained on sintering in an argon atmosphere are presented in Table 3 and are plotted in Figure 3 (see page 17). The sintered densities are much higher than those attained in the hydrogen atmospheres, but the oxygen/uranium ratios are also higher and a considerable proportion of U_4O_9 was found by X-ray diffraction to be present in the final material.

TABLE 3

Sintering in Undiluted Argon Atmospheres

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.56	9.44	2.070	9.40
1300	5.52	10.04	2.189[AA]	9.93
1400	5.52	10.24	2.182[AA]	10.13
1500	5.46	10.21	2.167[AA]	10.11[A]

[A] Phases present after firing: α-UO_2 + U_4O_9.

[AA] This retention of non-stoichiometric oxygen at increasing temperatures is probably due to a small partial pressure of oxygen impurity in the argon supply. (See also page 33.)

When about 0.6% (by volume) of water vapour was added to the argon by passing the gas through water at 0°C, somewhat lower sintered densities were generally obtained (see Table 4), and correspondingly lower oxygen/uranium atomic ratios were found.

TABLE 4

Sintering in Argon + 0.6% Water Vapour Atmospheres

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.47	9.83	2.163	9.74
	5.66	9.32	2.068	9.28
	5.45	8.77	2.030	8.75
1300	5.67	9.61	2.053	9.58
1400	5.46	9.61	2.090	9.56
	5.60	9.68	2.062	9.64
1500	5.58	9.69	2.071	9.65[A]

[A] Phases present after firing: $\alpha\text{-}UO_2 + U_4O_9$.

These lower oxygen/uranium ratios may have been caused by a more efficient scavenging from the argon by the use of freshly reduced heated copper turnings of any oxygen impurity, since, as may be seen from Figure 1 (see page 8), a very small partial pressure of oxygen will prevent the loss of oxygen from UO_{2+x}. The oxygen loss will also be dependent on the gas flow-rate, which was not measured accurately. The three replicate experiments performed at 1200°C illustrate the variation in the oxygen/uranium ratio and also in the sintered densities obtained under conditions which were supposedly similar.

Firing in argon with soaking at the peak temperature in a 76% Ar:24% O_2 (by volume) mixture gave the results recorded in Table 5. The relatively high sintered densities again appear to be associated with high O/U ratios. Figure 1 indicates that at equilibrium the O/U ratios at all temperatures should be well above 2.18. The observed ratios were below this value at the lower temperatures, indicating that the oxidation did not proceed to completion during the half-hour exposure to the oxygen partial pressure. Some oxygen may have been lost during the cooling portion of the cycle, but this loss would have been greatest for the samples fired to the highest temperatures.

(ii) Nitrogen Atmospheres

The use of a nitrogen atmosphere gave the results shown in Table 6, and plotted in Figure 3 (see page 17). The sintered densities are lower than those obtained using the argon atmosphere; these lower densities are associated with lower O/U ratios. This difference in O/U ratios is probably due, as indicated before, to the difficulties in controlling oxygen losses from the compacts into the gas stream.

TABLE 5

Sintering in Argon:Oxygen Atmospheres

UO$_2$ used:- Batch No. 9-2

Furnace used:- Muffle furnace

Firing cycle:- Heat to peak temperature in undiluted argon.
Soaking at peak temperature for 30 min. in 76% argon:24% oxygen, by volume.
Cooling in undiluted argon.

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as UO$_{2.00}$ g/cm^3
1200	5.56	9.54[**]	2.089	9.49[*]
1300	5.68	9.88[**]	2.177	9.78
1400	5.68	9.60	2.151	9.51
	5.48	10.00	2.184	9.89
1500	5.63	10.22	2.212	10.09[*]

[*] Phases present after firing α-UO$_2$ + U$_4$O$_9$.

[**] Out of 5 compacts fired to 1200°C, 1 disintegrated.
Out of 5 compacts fired to 1300°C, 2 disintegrated.

TABLE 6

Sintering in Undiluted Nitrogen Atmospheres

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.50	8.99	2.049	8.96[A]
1300	5.59	9.57	2.076	9.53
1400	5.65	9.75	2.053	9.72
1500	5.58	9.90	2.074	9.86

[A] Phase present after firing : α-UO_2

The addition of 0.6% water vapour into the nitrogen stream gave the results listed in Table 7. Some differences from the corresponding results obtained with pure nitrogen may be noted. Where these differences occur, the higher sintered densities are associated with high O/U ratios.

On soaking at the peak sintering temperature in a stream of air, with heating and cooling in an inert gas (either nitrogen or argon), the results recorded in Table 8 were obtained. It was found that a considerable number of the compacts disintegrated during this firing cycle. This may have been due to strains produced by volume changes associated with oxidation of the outer portions of the compacts. The very high O/U atomic ratios indicate that oxidation in the air atmosphere (20% O_2, by volume) proceeded faster than it

TABLE 7

Sintering in Nitrogen + 0.6% Water Vapour Atmospheres

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Heating, soaking, and cooling in N_2 containing 0.6% water vapour.

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.46	9.37	2.099	9.32[*]
1300	5.58	9.47	2.054	9.44
1400	5.57	9.69	2.070	9.65
1500	5.57	10.00	2.093	9.95

[*] Phases present after firing: α-UO_2 + U_4O_9.

TABLE 8

Sintering in Nitrogen : Oxygen Atmospheres

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Firing cycle:- Heating to peak sintering temperature in inert gas.
Soaking at peak temperature for 30 min. in air.
Cooling in inert gas.

Soaking Temp. (°C)	Green Density g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.47	9.44(2 compacts)	2.292	9.28
1300*	5.48	9.95(2 ")	2.241	9.81
1400	5.57	8.69(5 ")	2.369	8.50**
1500	5.51	10.26(4 ")	2.268	10.10***

* Heating and cooling in argon in this case, in nitrogen in other cases.

** Phases present: $U_4O_9 + U_3O_8$.

*** Phases present: U_4O_9 + trace U_3O_8.

Note: Many compacts disintegrated. Of those which did not disintegrate, many were cracked and bloated.

- -

did in the argon/oxygen atmosphere. On soaking at 1400°C, a low sintered density was found to be associated with a high O/U atomic ratio; this apparently anomalous result is probably due to expansion of the compacts because of the presence of U_3O_8 in the sintered bodies, as indicated by the X-ray diffraction results.

(iii) Steam Atmospheres

The results obtained on sintering in a steam atmosphere (with argon used below 750 °C) are shown in Table 9; the sintered densities are plotted in Figure 3 (see page 17). Relatively good sintered densities were obtained, associated, as usual, with high O/U ratios. The O/U ratios of UO_{2+x} in equilibrium with a dynamic steam atmosphere may be calculated from the equilibrium constant, K, of the reaction

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2$$

$$\text{thus,} \qquad K = \frac{\left[P_{H_2}\right]\left[P_{O_2}\right]^{\frac{1}{2}}}{\left[P_{H_2O}\right]} \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

The value of P_{H_2O} may be taken as 1 atmosphere, and $P_{H_2} = 2P_{O_2}$.

Using equation (1), (see page 9), and equation (2) (above), the values of x, the non-stoichiometric oxygen, given in Table 10 may be calculated. It should be noted that this calculation involves extrapolation of the UO_{2+x} thermodynamic data both in regard to temperature and to values of x. The observed O/U ratios are lower than the calculated values. Some non-stoichiometric oxygen may have been lost during the period of heating in argon; also the reaction with the steam may not have been rapid enough to reach the equilibrium O/U ratio during the steam portion of the firing cycle.

TABLE 9

Sintering in Steam Atmospheres

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Firing cycle:- Heating to 750 °C in argon.
Heating from 750 °C to soaking temp., soaking for 30 min, and cooling to 750 °C in steam.
Cooling from 750 °C to room temperature in argon.

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U atomic ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1200	5.54	9.67	2.153	9.58
1300	5.62	10.17	2.180	10.06
1400	5.57	10.24	2.173	10.14
1500	5.52	10.30	2.173	10.20 ☆

☆ Phases present: α-UO_2 + U_4O_9.

TABLE 10

Comparison of Observed and Calculated Oxygen/Uranium Atomic Ratios Obtained on Firing in Steam of U_3O_8 or $UO_{2.19}$

Soaking Temp. (°C)	$K = \frac{\left[P_{H_2}\right]\left[P_{O_2}\right]^{\frac{1}{2}}}{\left[P_{H_2O}\right]}$ in $(atm)^{\frac{1}{2}}$	Calculated O/U Ratio	Experimental O/U Ratio after Firing		Phases Present after Firing of U_3O_8
			$UO_{2.19}$	U_3O_8 $(UO_{2.67})$	
1200	1.34×10^{-6}	2.217	2.153	--	--
1300	4.91×10^{-6}	2.206	2.180	2.208	$U_4O_9 + \alpha\text{-}UO_2$
1400	15.7×10^{-6}	2.196	2.173	2.177	$U_4O_9 + \alpha\text{-}UO_2$
1500	$43.6\ x^{10-6}$	2.187	2.173	--	--

The oxygen/uranium ratios obtained on firing U_3O_8 in steam (using the normal argon-steam-argon cycle) were somewhat closer to the calculated ratios. This tends to support the assumption that the pellets made from the uranium dioxide had not attained equilibrium during the cycle employed.

(iv) Discussion of Neutral and Slightly Oxidizing Atmospheres

In the presentation of the results obtained using neutral and oxidizing atmospheres, it was noted that there appeared to be some correlation between the sintered densities and the oxygen/uranium atomic ratios of the fired compacts. This relationship is shown explicitly in Figure 4 in which the sintered densities are plotted against O/U ratios for the various atmospheres at the four temperatures considered in this investigation. The results obtained on soaking in an air atmosphere have been omitted since the low density U_3O_8 oxide was present in at least some of the compacts after firing. If the final O/U ratios can be taken as roughly indicative of the O/U ratios at the temperature of sintering, it would appear that the attainment of a high sintered density, with any of the atmospheres used, depends principally on the amount of non-stoichiometric oxygen present in the crystal lattice at the sintering temperature. There is no single atmosphere which consistently gives densities either higher or lower than the densities "expected" on the basis of O/U ratios. The deviations of the points from a smooth curve may be attributed to changes in O/U ratios during the

FIGURE 4

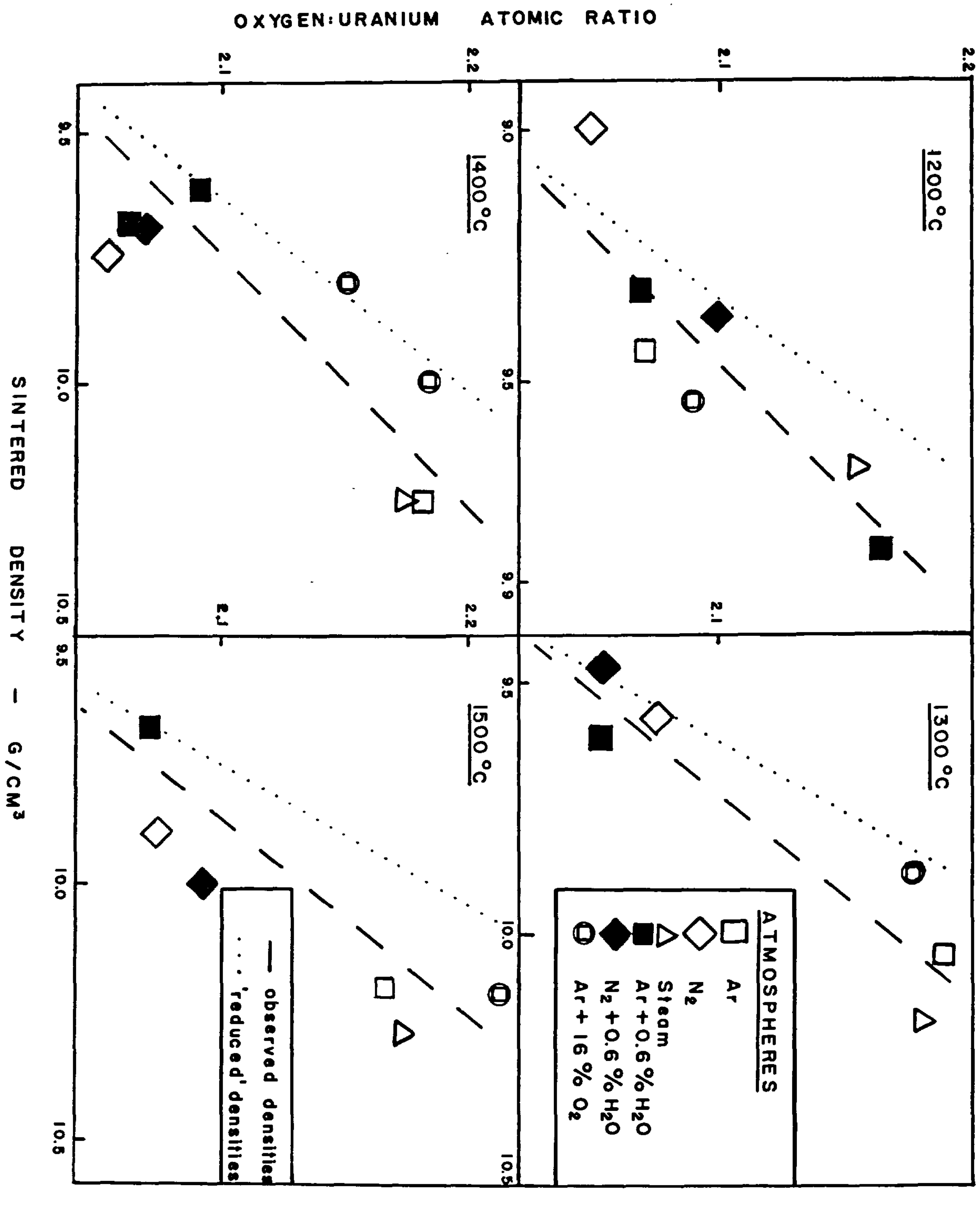

FIGURE 4. Variation of UO_{2+x} sintered densities with oxygen:uranium atomic ratios in sintered compacts.

cooling portion of the firing cycle, as well as to inherent experimental errors.

With regard to the observed sintered densities of the UO_{2+x} samples, it should be noted that if the excess oxygen were removed as, for example, by hydrogen reduction after sintering was complete, then the densities of the samples would be lowered to some extent because of two effects:-

(a) removal of oxygen, which would decrease the weight of a given sample—the magnitude of this effect is indicated by the calculated $UO_{2.00}$ contents reported in the tables of results; and

(b) expansion of the fluorite-type lattice in going from U_4O_9 (a_o = 5.441 A), to $UO_{2.00}$ (a_o = 5.470 A).

The dotted plots shown in Figure 4 were determined by correcting the observed (dashed) plots for these two effects. It is seen, however, that the beneficial effects derived from the presence of excess oxygen during the sintering process largely persist, even though this excess oxygen is removed after sintering has been completed.

The oxygen content of compacts fired in a neutral atmosphere will depend on any small partial pressure of oxygen that may be present in the gaseous phase. This, in turn, will depend on the amount of residual oxygen present in the gas supplied to the furnace; a mol. fraction as low as 10^{-7} may be significant. The rate at which any oxygen released from the compacts is removed by the gas stream is also an operative factor. It is apparent, therefore, that efficient control of the O/U ratio by a "neutral" atmosphere would be extremely difficult experimentally.

The use of a small proportion of water vapour in the inert gas appeared to be ineffective, while the addition of oxygen at high temperatures produced considerable disruption of the compacts, probably due to strains induced by uneven oxidation throughout the compacts. The use of a 100% steam atmosphere is probably the best method of maintaining the O/U ratio at a suitable level for good sintering.

The plots shown in Figure 3 (see page 17) indicate that, with increasing soaking temperature, a limiting sintered density is approached in the region 1400-1500°C for material having a O/U ratio of about 2.18.

C. Effects of Non-Stoichiometric Oxygen on the Sintering of UO_{2+x}

(i) Controlled Oxidation of Uranium Dioxide Before Sintering

In the previous section of this report (see page 29), it was shown that the sintered density of non-stoichiometric uranium oxide increases with increasing final O/U ratio up to the point where U_3O_8 begins to be formed as a significant constituent. It was assumed that the final ratio is indicative of the ratio obtaining at the sintering temperature, and hence, that the sintered density is dependent on the O/U ratio of the material during sintering. More direct evidence of the effect of non-stoichiometric oxygen may be obtained by sintering, under identical conditions, material which has been air-oxidized to various predetermined O/U ratios.

Uranium dioxide powder (Batch No. 9-2) was air-oxidized at 170°C from its original O/U ratio of 2.185 to three different higher O/U ratios. The final densities obtained on the firing of compacts made from these materials are listed in Table 11. The compacts (for each separate atmosphere) were all fired together and hence had exactly the same firing cycle.

Sintering in the argon atmosphere led to an increase in sintered density with increasing initial O/U ratio, and hence, it may be assumed, with increasing O/U ratio at the sintering temperatures. Since the samples were all present together in the furnace, the oxygen released from the material with a higher O/U ratio would increase the oxygen partial pressure in the sintering atmosphere and suppress the decomposition of the material with the lower O/U ratio. Thus all compacts should tend to approach the same O/U ratio, that is, to approach equilibrium with the same atmosphere. The equilibrium value of this O/U ratio may also be dependent on the presence of a partial pressure of oxygen impurity in the argon gas stream (cf. Table 3 and Discussion on page 31). The ratios would be different, however, during the critical first portion of the sintering process.

TABLE 11

Sintering of Non-Stoichiometric Uranium Dioxide Samples Oxidized to Different O/U Ratios

(a) UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

O/U Ratio before Sintering	Green Density g/cm^3	Sintered Densities		Final O/U Ratio of Ar-fired Compacts	Uranium Content of Ar-fired Compacts Calculated as $UO_{2.00}$ g/cm^3
		H_2 fired to 1700°C for 1 hour* g/cm^3	Ar-fired to 1400°C for 1 $\frac{3}{4}$ hour, g/cm^3		
2.185	5.56	9.37	10.11	2.168	10.01
2.241	5.57	9.41	10.27	2.171	10.17
2.340	5.60	9.30	10.39	2.168	10.29
2.363	5.74	9.26	10.51	2.179	10.40

* Mean values for 3 compacts

Phases present after sintering in argon: α-UO_2 + U_4O_9, in all cases.

Phase present after sintering in hydrogen: α-UO_2 only.

(b) UO_2 used:- Mallinckrodt

Furnace used:- Muffle furnace

O/U Ratio before firing	Green Density, g/cm^3	Sintered Density Ar-fired to 1400°C for 1 hour, g/cm^3	Final O/U Ratio of Fired Compacts	Uranium Content of Fired Compacts Calculated as $UO_{2.00}$ g/cm^3
2.034	6.29	7.30	2.023	7.29
2.078	6.31	7.48	2.038	7.46
2.107	6.36	7.66	2.056	7.63

The results of firing similar compacts in a hydrogen atmosphere indicate that there was no improvement in the inherent sinterability of the uranium oxide due to the air pre-oxidation procedure[A]. The non-stoichiometric oxygen would be removed from the UO_{2+x} before any significant degree of sintering could take place, and hence it would have no effect on the densification of the compacts.

A similar experiment was carried out using "Mallinckrodt" UO_2, air-oxidized at 185 °C to two different oxygen contents. The results obtained (quoted in Table 11b) exhibit the same trends as those noted for Batch No. 9-2.

(ii) Reduction of Non-Stoichiometric Uranium Dioxide Before Sintering

The results reported in Section B (see page 26) appear to indicate that a steam atmosphere provided a convenient method for controlling oxygen/uranium ratios during sintering. The starting material used in the experiments reported previously had an O/U ratio about the same as the final ratio in the sintered compacts. It would appear desirable, therefore, to show directly that the steam will bring the O/U ratio up to the desired level.

Compacts were pressed from Batch No. 9-2 oxide and were then fired in hydrogen to 1000 °C for 30 min. to remove most of the non-stoichiometric oxygen without producing significant sintering.

[A] Such a change might conceivably be produced by an increase in specific surface of the powder.

Of these compacts, half were subsequently fired in argon and the other half were fired in steam. The results, given in Table 12, indicate that the steam-fired compacts picked up considerable oxygen and sintered to a density about 0.5 g/cc higher than the argon-fired compacts, which retained a lower oxygen content.

D. Control of Non-Stoichiometric Oxygen

In the previous sections, it has been shown that the presence of non-stoichiometric oxygen in uranium dioxide, during firing, aids very markedly in attaining high sintered densities at relatively low temperatures. Non-stoichiometric UO_2 as the final material, however, is undesirable because of poor mechanical properties as discussed earlier (see page 5) and also because of a tendency for uranium to volatilize as oxides from the compacts[A].

The release at high temperatures of the non-stoichiometric oxygen itself has also been considered to be disadvantageous. Investigations were therefore undertaken to determine methods of control or removal of the excess oxygen <u>after</u> the sintering has been completed, i.e., after the benefit derived by its presence has already been achieved.

[A] For example, a very thin film of black sublimate gradually accumulated inside the furnace used in this work. Quantitatively this was not serious at the temperatures involved, but might become objectionable if the material were subjected to much higher temperatures for prolonged periods, as might occur in fuel rods of a nuclear reactor. (See also ref. 9.)

TABLE 12

Sintering of Uranium Dioxide Compacts Previously Reduced by Firing in Hydrogen to 1000°C for 30 Minutes

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Density after H_2 Firing at 1000°C, g/cm^3	Sintering Atmosphere (fired to 1400°C for 30 min.)	Sintered Density, g/cm^3	O/U Ratio of Sintered Compacts	Phases Present	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
5.98	Argon	9.53	2.045[A]	$\alpha\text{-}UO_2$	9.50
5.94	Steam	10.10	2.173	$\alpha\text{-}UO_2 + U_4O_9$	10.00

[A] Note:- This non-stoichiometric oxygen may have arisen either from oxygen impurity in the argon or from incomplete reduction in the original hydrogen firing to 1000°C.

(i) Maintenance of a Small Controlled H_2/H_2O Ratio

Examination of Figure 1 (see page 8) indicates that, in the presence of metallic nickel, hydrogen should be introduced into steam to the extent of about 1 mol. % according to the equation,

$$Ni + H_2O \rightleftarrows NiO + H_2 \quad \ldots\ldots\ldots\ldots (3)$$

This will apply over the whole temperature range with which this investigation is concerned. Nickel powder was placed in a boat in front of the compacts in the furnace, and steam was first passed over the nickel and then over the compacts during sintering. The results of experiments performed with soaking at 1300 °C and at 1400 °C are presented in Table 13. It will be observed that the O/U ratio are lower than were obtained in pure steam, and that the sintered densities were correspondingly lower. The calculated O/U ratios for equilibrium at the soaking temperature are also listed in Table 13 for comparison purposes. These results illustrate the great difficulty in choosing a single atmosphere which would give an O/U ratio low enough for an acceptable final material, and still high enough to facilitate sintering at an economically satisfactory low temperature.

(ii) Cooling in a Reducing Atmosphere

Since the attainment of compacts with the desired O/U ratio by low temperature sintering appears to be impossible when one single atmosphere is used throughout the whole firing cycle, investigations were undertaken on combinations of atmospheres

TABLE 13

Sintering of UO_2 in Steam Containing a Small Proportion of Hydrogen

Hydrogen introduced by passing steam over Ni metal. Soaking at temperature for 30 minutes.

UO_2 used:- Batch No. 9-2

Furnace used:- Muffle furnace

Soaking Temp. (°C)	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U Ratio	Calculated O/U Ratio	Uranium Content of Sintered Compacts Calculated as $UO_{2.00}$ g/cm^3
1300	5.46	9.43	2.093	2.087	9.38
1400	5.54	9.70	2.102	2.113	9.64

Phases present: α-UO_2 + U_4O_9, in compacts fired to both temperatures.

which would be neutral or slightly oxidizing during the heating and soaking portions of the cycle and reducing during the cooling portion. One such combination which has been reported to be satisfactory(7)(8) is sintering in steam followed by cooling in hydrogen. The results obtained in these laboratories,using this and other combinations of atmospheres are presented in Table 14. These various atmospheres were chosen so that the cooling atmosphere would be an experimentally convenient modification of the heating atmosphere.

The introduction of hydrogen into a carbon dioxide stream during the cooling cycle should give a reducing atmosphere in which carbon monoxide is produced by the reaction[A],

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$

However, the results appear to indicate that the reaction between carbon monoxide and the non-stoichiometric oxygen in the sintered compacts is too slow to give any significant reduction. Reference to Figure 1 (see page 8) indicates that, if equilibrium were reached, the O/U ratio should be below 2.01.

[A] The P_{H_2}/P_{CO} equilibrium ratios, after the addition of 13% H_2 to CO_2, are calculated to be 0.047 and 0.08 at 1400°C and 1100°C, respectively. The corresponding P_{CO}/P_{CO_2} ratios are 0.167 and 0.16,respectively.

TABLE 14

Sintering of UO_2 Compacts Cooled in Reducing Atmospheres

UO_2 compacts heated and soaked in atmospheres neutral or slightly oxidizing to $UO_{2.00}$, and cooled in reducing atmospheres. Soaking at 1400°C for 30 minutes.

Furnace used:- Muffle furnace

Type of UO_2	Heating and Soaking Atmosphere	Cooling Atmosphere	Green Density, g/cm^3	Sintered Density, g/cm^3	O/U Ratio of Fired Compacts	Uranium Content of Fired Compacts Calculated as $UO_{2.00}$ g/cm^3
Batch No. 9-2	CO_2	CO_2+ca. 13% H_2	5.52	10.04	2.186	9.93(2)
	Argon	Ar+ca. 13% H_2	5.47	9.73	2.104	9.67(2)
	Steam	Steam + H_2	5.46	9.92	2.011	9.91(3)
Batch No. B-2(1)	Steam	Steam + H_2	5.59	10.57	2.058	10.53
	Steam	H_2(4)	5.48	10.52	2.002	10.52
Oxidized Batch No. B-2(5)	Steam	H_2(4)	5.57	10.48	1.999	10.48

Notes:-

(1) Sinters to 10.62 g/cm^3 on firing in hydrogen to 1700°C for 30 minutes, and to 10.29 g/cm^3 on firing in hydrogen to 1400°C for 30 minutes.

(2) Phases present after firing:- α-UO_2 + U_4O_9

(3) Phases present after firing:- α-UO_2 only.

(4) Soaked for 15 minutes at 1400°C in hydrogen before cooling.

(5) Batch No. B-2 powder oxidized in air at 165°C for 1 hour, to an O/U ratio of 2.362, from an original value of 2.242.

The addition of about 13% hydrogen during the cooling portion of the argon firing was also tried. Reference to Figure 4 shows, however, that the sintered density is close to that expected on the basis of the final O/U ratio. It is doubtful, therefore, whether the addition of the hydrogen produced any significant reduction in this ratio from its normally expected value.

The addition of H_2 during the cooling portion (1400 to 750 °C) of a steam cycle produced an O/U ratio of 2.011, compared to the value 2.13 which might be expected on the basis of the sintered density (see Figure 4). An even higher O/U ratio might be expected on the basis of previously obtained results (see Tables 9 and 12). It would appear, therefore, that a significant removal of non-stoichiometric oxygen had taken place. Unfortunately, the experimental arrangement did not permit an accurate estimation of the H_2/H_2O ratio, which may have varied in the range 0.3 to 0.6.

A similar cycle was used to sinter compacts of the Batch No. B-2 UO_2, which sinters under standard conditions to a density of 10.62 g/cm^3, much higher than the 9.47 g/cm^3 obtained using Batch No. 9-2 UO_2. The final density obtained on firing in the steam:H_2 cycle, with soaking at 1400 °C, compared very favourably with the "standard" sintered density. The O/U ratio, however, was considerably higher than that obtained using the Batch No. 9-2 compacts (see Table 14, page 41); this may possibly have been due to the slower diffusion of H_2 into the denser material. The use of a higher H_2/H_2O ratio (or perhaps undiluted H_2) for cooling, combined with soaking in this atmosphere before cooling, might reduce the O/U ratio to a more acceptable level. This behaviour is illustrated by the last two experiments detailed in Table 14; here, the use of undiluted hydrogen for cooling, combined with soaking in this atmosphere before cooling, reduced the O/U ratio to 2.002. The air-oxidation of the Batch No. B-2 oxide powder from its original O/U ratio of 2.242 to 2.362 before use did not produce any appreciable change in the sintered densities of compacts made from this material and sintered in the steam: hydrogen cycle.

GENERAL DISCUSSION

It has been found that uranium dioxide sintered densities which are as good or better than those attained on sintering in hydrogen at 1700°C may be attained at 1500°C or even at 1400°C if the oxygen/uranium atomic ratio of the material is in the range 2.1 to 2.2 at the sintering temperature. The sintered density increases with increasing O/U ratio and with increasing soaking temperature until a limit is reached in the region 1400-1500°C for material with O/U ratios in the region of 2.18. Such O/U ratios in a final product give, however, a two phase (α-UO_2 + U_4O_9) material with undesirable properties.

A recommended method of obtaining high densities by a cold-pressing and sintering method at relatively low soaking temperatures would be as follows:

(a) Start with a UO_2 powder of inherently good sintering properties(1).

(b) Fire in a steam atmosphere to 1400 °C for about 30 minutes.

(c) Cool in a H_2-H_2O or H_2 atmosphere. The use of hydrogen, after steam, while still maintaining the soaking temperature, may be necessary for very high density material because of the slow diffusion rates of hydrogen into the sintered mass.

This cycle differs from that recommended by Vasilos and Slaughter(8) in that, in our recommendation, heating is not carried out in hydrogen, since a high initial O/U ratio, maintained up to the peak temperature, seems desirable in the light of the results obtained in this investigation.

The mechanism by which the uranium dioxide containing excess oxygen sinters to relatively high densities at low temperatures is not apparent. Two very general suggestions may be advanced: (1) increased diffusion rates in the non-stoichiometric material, reflecting a lower Tammann temperature which in turn reflects a lower melting point, and (2) vapour phase transfer of the material may take place, since a certain volatility of the non-stoichiometric oxides is apparent. Further investigation of the structure and physical properties of the UO_{2+x} phase(s), however, would be necessary before any conclusions could be reached.

In particular, investigations of the diffusion mechanisms of uranium and of oxygen in the non-stoichiometric UO_{2+x} might indicate the reasons for enhanced sintering behaviour. Such experiments could involve the use of isotopic tracers and might indicate whether entities such as UO_2^{++} ions were involved in the diffusion process. If the UO_{2+x} were shown to be an ionic semi-conductor, then transport number experiments might shed light on the nature of the mobile ion present; if, however, UO_{2+x} is an electronic semi-conductor (as it may well be), such experiments could not be carried out.

The study of the mechanism whereby the enhanced sintering behaviour is associated with non-stoichiometric oxygen was considered to be beyond the scope of the present work, which was aimed primarily at determining the effects accompanying the use of a variety of atmospheres in the sintering process, and at discovering, if possible, a more attractive firing cycle than the use of hydrogen at 1650-1700°C.

It is possible that the steam in the recommended steam: hydrogen firing cycle could be replaced by carbon dioxide with equally satisfactory results.

This would be probably an unfavourable change economically as CO_2 is more expensive than steam. However, it is not itself an expensive material and may be more easily manipulated than steam. It may, also, possibly give rise to less difficulty from corrosion of equipment, provided it is kept dry.

These factors would have to be taken into consideration in the lay-out of a final manufacturing flow-sheet for reactor grade UO_2 compacts prepared by the cold pressing and sintering technique.

In any case, however, it is highly likely that the use of either the steam-hydrogen or the CO_2-hydrogen cycle at a peak temperature at 1400 °C would be more attractive economically, both from the point of view of power requirements and of usage of refractory equipment, than the use of a hydrogen cycle with a peak temperature of 1650-1700 °C.

CONCLUSIONS

(1) The sintering of uranium dioxide pellets is greatly aided by the presence of excess oxygen in the UO_2 lattice. This excess oxygen is removed by hydrogen firing. Control of the excess oxygen is difficult experimentally in predominantly inert atmospheres, owing to the extremely low equilibrium pressure of oxygen in this system. Steam appears to maintain the O/U ratio at a level suitable for sintering. Introduction of excess oxygen into the uranium oxide before sintering has been shown to be beneficial.

(2) The control of the O/U ratio can be guided to a certain extent by the use of published thermodynamic data. It must be realized, however, that, in a number of systems such as $CO/O_2/CO_2$ and $Ni/O_2/NiO$ which develop a partial pressure of

oxygen, equilibrium may not be attained during the course of a convenient time-cycle for the sintering process.

(3) The non-stoichiometric oxygen, which is beneficial in promoting sintering but undesirable in the final material, may be removed by hydrogen at moderately high temperatures after sintering has taken place.

(4) A firing procedure for fabricating UO_2, suitable for use in fuel rods, has been suggested.

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(Appendix follows on)
(page 50.)

APPENDIX

Partial Molar Free Energies and Entropies of Solution of Oxygen in UO_{2+x}

O/U Ratio	$-\bar{F}_{O_2}$ (kcal/mole)			$-\bar{S}_{O_2}$ in Entropy Units	$-\bar{H}^{o}_{O_2}$ k.cal/mole
	1150°K	1250°K	1350°K		
2.013	54.8	54.2	53.6	6.3	62.1
2.018	53.8	53.2	52.6	6.4	61.2
2.044	51.8	51.1	50.4	6.8	--
2.051	51.5	50.3	49.0	12.2	--
2.075	50.9	49.5	48.1	13.6	--
2.087	48.9	47.3	45.6	16.7	67.2
2.112	47.6	45.8	44.0	18.3	68.7
2.128	46.3	44.0	41.8	22.5	72.0
2.142	44.6	42.1	39.6	25.3	73.7
2.160	42.5	39.8	37.1	27.1	73.6
2.181	40.4	37.6	34.7	28.0	--
2.198	--	35.1	32.3	27.9	70.0
2.203	--	35.2	32.2	29.4	71.9
2.035	52.4	51.2	49.9	12.8	67.2
2.038	51.5	50.3	49.1	12.2	65.5
2.164	42.8	40.1	37.4	27.1	74.0
2.295[a]	(31.8)	(28.7)	(25.0)	--	--
2.504[a]	(31.6)	(28.8)	(25.2)	--	--

[a] Values in parentheses are for 2-phase regions.

Note:- The data in the lower portion of the Table are taken from Progress Reports of the Bettis Field Establishment of the Westinghouse Electric Corporation, Pittsburgh. The data in the upper portion of the Table were obtained from a private communication from Dr. Seymour Aronson of the Westinghouse Electric Corporation, Pittsburgh, dated October 4, 1957.
