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The sintering of non-stoichiometric UO_2 under non-isothermal conditions

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The sintering kinetics of non-stoichiometric uranium dioxide powders have been studied in the temperature range 700 to 950° C. The results of the relative linear shrinkage during the stepwise heating of samples, were analysed as a function of sintering temperature and time. It has been shown that it is impossible to explain the exceptionally large shrinkage of UO_{2+x} compacts in the temperature range 0.3 to 0.4 T_m by means of a single sintering mechanism.

1. Introduction

Uranium dioxide belongs to the very complex U – O system where polymorphism, metastability and solid solution frequently occur. The existence of U^{4+} and U^{6+} ions leads to the typical non-stoichiometry of uranium dioxide [1]; the explanation that had originally been proposed was that disorder in the UO_2 structure resulted from random occupation of holes in the fluorite structure by interstitial oxygen. However, Willis's investigations [2, 3] using neutron diffraction of $UO_{2.13}$ single crystals to determine the oxygen positions, indicated a quite different model (Fig. 1), where the oxygen atoms occupy three different positions which are clearly defined.

The sintering mechanism, as well as the influence of non-stoichiometric oxygen on mass-transfer in non-stoichiometric UO_2, are subjects of contradictory opinions. While a number of authors consider volume diffusion to be the sintering mechanism [4-7], others think that it is plastic flow [8]. The role of non-stoichiometric oxygen, too, is interpreted differently; some authors think that non-stoichiometric oxygen makes diffusion quicker, others believe that it increases material plasticity and therefore initiates a plastic-flow mechanism, while some think that non-stoichiometry does not affect the mass-transfer at all [9].

Our paper is a contribution to the study of the kinetics and mechanism of sintering in non-stoichiometric uranium dioxide powder.

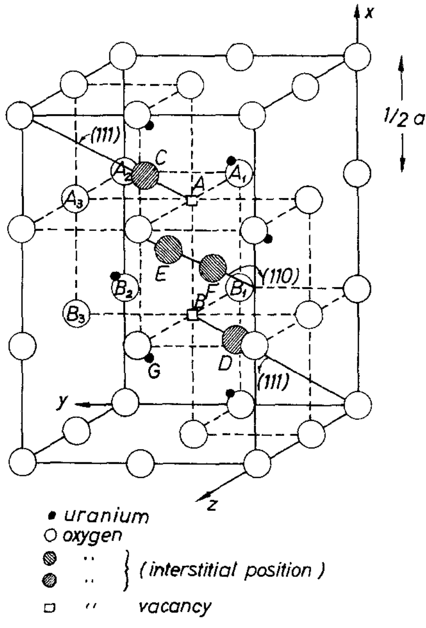

Figure 1 Willis's model of UO_2.

2. Experimental work and results

The uranium dioxide powder used in the experimental work was obtained by the calcination of ammonium diuranate, and reduction of the UO_3 so formed.

The specific surface area was determined by the BET method and found to be 3.60 m²/g. The particle size distribution was established by sedimentation analysis on an automatic sedimentation balance; distilled water was used as the fluid with 2.8 g/l Na_3PO_4 activator. The cumulative sedimentation curve was treated by Oden's technique, and from the particle size distribution the agglomerate average diameter was determined as 11.3 μm.

The O/U ratio of the UO_2 powder was determined gravimetrically by oxidation to U_3O_8 [10], and found to be 2.15.

Dilatometric analysis of the sintering process was performed on a Netsch dilatometer (type 402E) using a step-wise heating technique. The samples used for dilatometric examination were prepared by pressing under a pressure of 2t/cm^2, with water as binder, and then drying in a vacuum-oven at 100° C. The experimental observations started from the temperature at which shrinkage began. The experiments were carried out in a stationary argon atmosphere with a heating rate of 100° C/min. The temperature steps had the same value of about 25° C in all experiments, while the time of isothermal heating was 5, 10, 20, 40 and 60 min. (Characteristic curves are given in Figs. 2 to 4.)

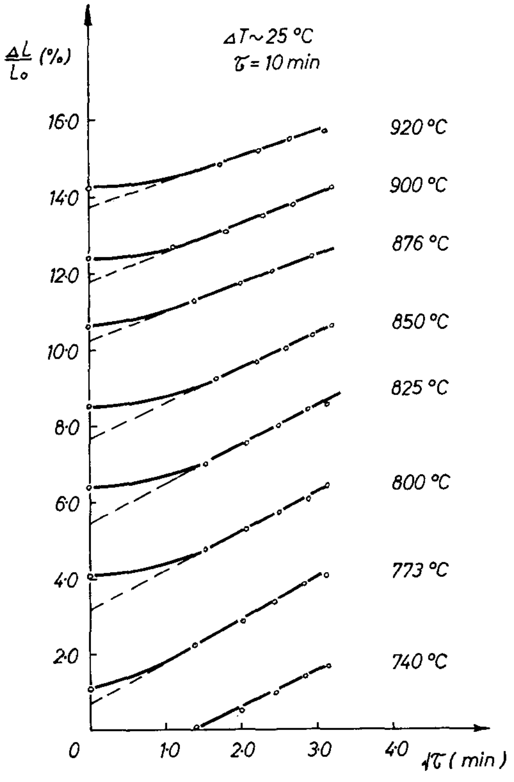

Figure 2 Relationship between the relative linear shrinkage and temperature and time of sintering ($\triangle T = 25°$ C, $\tau = 10$ min).

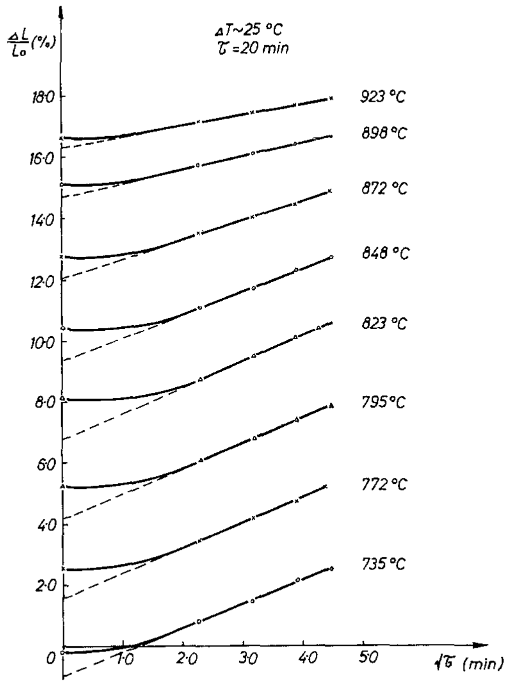

Figure 3 Relationship between the relative linear shrinkage and temperature and time of sintering ($\triangle T = 25°$ C, $\tau = 20$ min).

3. Discussion

Phenomenological analysis of porous body shrinkage during sintering, examined by Pines and Geguzin [11] in non-isothermal conditions by a step-wise heating technique, showed that in a general case the kinetics can be described by the following equation:

$$\Delta L/L_0 = m + n\sqrt{\tau} \qquad (1)$$

where $\Delta L/L_0$ = relative linear shrinkage; m = shrinkage for isothermal sintering time $\tau = 0$; n = isothermal shrinkage rate, and τ = time.

The values m and n are functions of the temperature and time of isothermal heating; while the value m increased monotonously with increasing temperature, the dependence of parameter n on the temperature has the form of a statistical distribution with a maximum. The maximum occurs in the temperature range where the greatest defect structure changes take place.

Our experimental results (Figs. 2 to 4), analysed on the basis of Equation 1, made it possible to determine n as a function of tem-

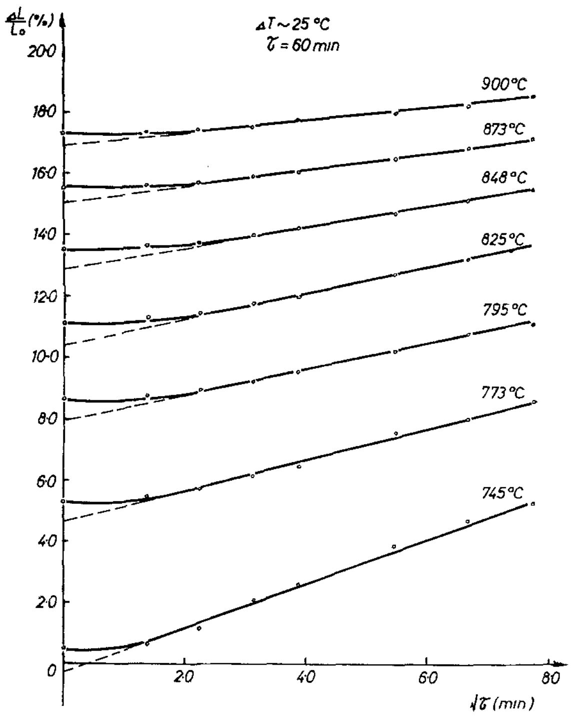

Figure 4 Relationship between the relative linear shrinkage and temperature and time of sintering ($\triangle T = 25°C$, $\tau = 60$ min).

perature and time of isothermal heating, by applying the least squares method (Fig. 5). It is observed that the change of n with temperature does not have the expected form of a normal distribution, but that it is only a part of this function. The continual decrease of the shrinkage rate during the sintering of non-stoichiometric UO_2 can be due to 1. decrease of the non-stoichiometric defect concentration during sintering, due to the decrease of the O/U ratio, or 2. decrease of the chemical potential gradient due to a change in the total defect concentration, or of a geometric change in particle/particle contact, up to the temperature at which the beginning of shrinkage was noticed.

One of the possible explanations for the decrease in defect concentration is the decomposition of UO_{2+x} at elevated temperatures according to the equation

$$UO_{2+x} \rightarrow UO_{2+x-a} + a/2\ O_2 \qquad (2)$$

However, thermodynamic considerations [12] indicate that this reaction will occur only above 1300°C, so that in our own case the defect concentration should remain practically constant, which was found experimentally; the O/U ratio after sintering was 2.145 ± 0.005 in all cases.

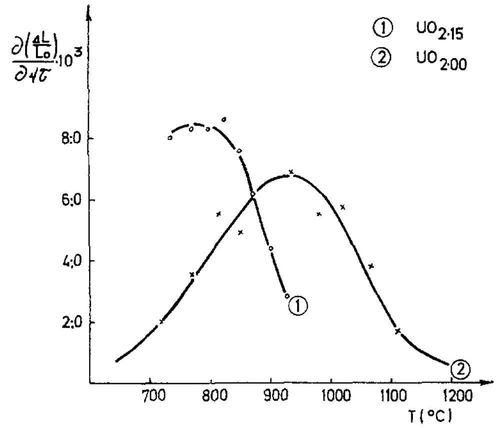

Figure 5 Relative linear shrinkage rate dependence $(\triangle L/L_0)_T/\partial\sqrt{\tau}$ on the sintering temperature.
(1 – $UO_{2.15}$; 2 – $UO_{2.0}$, $\tau = 20$ min).

On the other hand, because the flux of transferred material is proportional not only to the defect concentration but also to the chemical potential gradient, according to the relation [13]

$$J = -BC\nabla\mu \qquad (3)$$

where j = the flux of atoms or ions per unit surface, B = atom mobility, C = atom concentration in unit volume, and $\nabla\mu$ = total chemical potential gradient, it is possible for the transferred material flux to decrease with increasing sintering temperature, due to decrease in the chemical potential gradient, regardless of the fact that the defect concentration has remained constant.

It is known that, due to the decreasing free-surface energy, i.e. to the decreasing surface curvature, the chemical potential decreases while sintering takes place, the direct consequence of which is a decrease in the shrinkage rate. In this way, due to the existence of a large concentration of non-stoichiometric point defects, and of other structure defects in the initial powder as well, the shrinkage rate proves to be highest during the early stages of sintering. This is preceded, in any case, by a temperature range with a smaller shrinkage rate which, because of the existence of the high defect concentration, is very narrow (Fig. 5). For this reason it should be expected that the dependence of shrinkage rate on the sintering temperature in UO_2 powder of stoichiometric composition, will be shown by Equation 1 with a clear maximum. We have proved this experimentally using our original UO_{2+x} powder, which had previously been reduced at 500°C for one h in a hydrogen atmosphere to stoichiometric UO_2. Analysing these data, the dependence of the relative linear shrinkage rate on temperature was found (Fig. 5, curve 2). Probably due to the very small concentration of non-stoichiometric defects, the maximum on the function presented by Equation 1, has moved towards a higher temperature in relation to the starting material.

Supporting the above thesis on the role of non-stoichiometric and other structure defects in the sintering of UO_{2+x} one can add, also, the evidence of the activation energies obtained in the step-wise heating experiments [4, 14, 15] (Figs. 6 and 7). The continual increase in activation energy in UO_{2+x} during sintering may be the result of 1. a mass-transfer diffusion mechanism only, which proceeds more easily in the initial stages due to the existence of a greater number of defects in the powder compact (free surfaces, dislocations, micropores etc.) or 2. a change in the basic mass-transfer mechanism, from plastic flow controlled by dislocation motion to a diffusion mechanism.

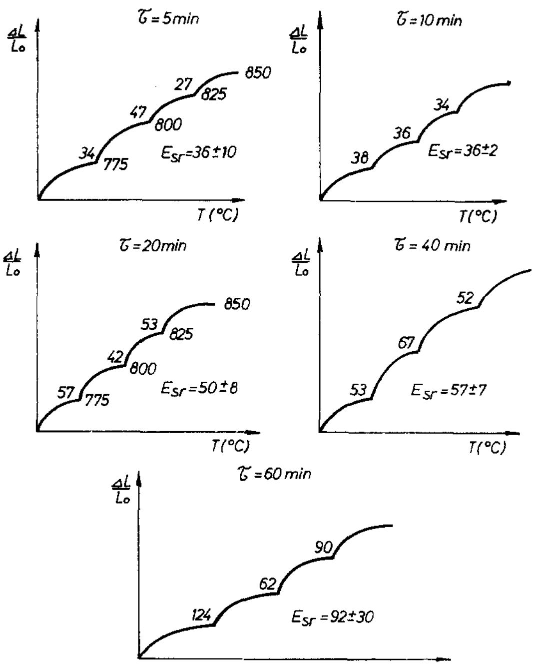

Figure 6 Relationship between activation energy of sintering and temperature and time of sintering.

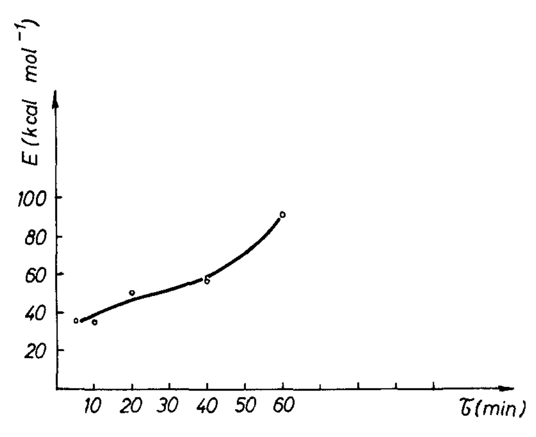

Figure 7 The average activation energy dependence on sintering time.

After examining the literature [4-10, 16-22], it can be concluded that considerable disagreement exists in the opinions of individual investigators regarding the influence of non-stoichiometric oxygen on the mass-transfer mechanism during the sintering of UO_{2+x}. While most of the authors agree with the fact that the non-stoichiometric oxygen excess can considerably enhance diffusion of the slower U^{4+} ion, their opinions on the change of the activation energy are contradictory.

While analysing these problems it is necessary to bear in mind the fact that the sintering process has been examined in the narrow temperature range of 750 to 920°C, that is 0.35 to 0.41 T_m, where the values of the diffusion coefficients are very low. In fact, diffusion coefficients of U^{4+} ions in UO_{2+x} for such a low temperature range are not given in the literature. However, if the value of the diffusion coefficients are estimated on the basis of the results obtained by Marin and Contamin [18], then $D_{1000K} \sim 10^{-25} - 10^{-30}$ cm^2 sec^{-1}. On the other hand, by applying some of the equations reported in the literature, for example, the Johnson-Cutler equation [23], the conclusion is reached that the diffusion coefficient calculated from the data on shrinkage is $\sim 10^{-8}$ cm^2 sec^{-1} for the first isotherm (T = 745°C). Accepting the fact that the effective diffusion coefficient, due to the existence of a large number of lattice defects, can be increased in relation to the equilibrium one by a factor of 10^5 or more [24, 25], then the enormous difference in values between the effective and equilibrium diffusion coefficients eliminates the possibility of volume diffusion as a mass-transfer mechanism during the early stages of the non-stoichiometric UO_2 powder sintering.

On the other hand, when a diffusion-viscous flow mechanism is considered, the macroscopic-viscous flow of material is connected by the self-diffusion of atoms or ions while the viscosity coefficient, η, is connected with the diffusion coefficient D by the relation [26-28]

$$\eta = \frac{K_B T L^2}{D\Omega} \qquad (4)$$

where L = mean particle size, or the mean distance between dislocations and grain boundaries, capable of acting as vacancy sources or sinks, K_B = Boltzmann's constant, T = temperature, and Ω = atomic volume.

Calculation shows that, according to Equation 4, an identical quantity of material could be transferred in the case that the diffusion coefficient is 10^{-25} cm^2 sec^{-1} as when it is 10^{-8} cm^2 sec^{-1}, under the condition that the value L in the first case is $\sim 10^8$ times smaller than in the second. The values L in the starting powder UO_2 is about 10^4 to 10^5 Å, but in order to show the shrinkage at 1000°C which we have found, it would be necessary for L to have a value of about 10^{-3} Å which is nonsense. This analysis shows that the diffusion-viscous flow mechanism cannot be the operative mechanism for mass transport.

A plastic-flow mechanism has been suggested by a number of investigators who were not able to explain high shrinkage rates in the initial sintering stages. Bearing in mind, however, the fact that it has been shown in a series of papers that local stresses in a porous body created by capillary forces cannot lead to stationary flow, the plastic flow mechanisms must also be excluded as a possible mechanism for causing the porous body densification during the sintering [29, 30]. At the same time, calculated values of the effective activation energy in the range of 35 to 92 kcal mol^{-1}, do not offer any possibility to predict with certainty the mechanism responsible for mass transfer during sintering. On the contrary, calculated values for the effective activation energy, support the view that mass-transfer is easier in the early stages and more difficult after a long soaking time during isothermal sintering [30, 31].

This analysis of the non-stoichiometric UO_2 sintering mechanism indicates that it is impossible to explain the exceptionally high shrinkage at a temperature $\sim 0.4\ T_m$ on the basis of a single mass-transfer mechanism.

Finally, taking into account all of these considerations, it must be concluded that no single particular mechanism is exclusively responsible for the sintering of non-stoichiometric UO_2 in the temperature range investigated. This is in full accordance with the latest ideas on the sintering of real systems where the conclusions from studies of model systems cannot be applied [32].

4. Conclusions

The examination of the sintering of non-stoichiometric UO_2 under non-isothermal conditions indicates that the change of the relative linear shrinkage rate

$$\partial(\Delta L/L_0)_T/\partial\sqrt{\tau}$$

as a function of the sintering temperature and time does not have the form of a statistical function with normal distribution, but it is only a part of that function. The existence of a large concentration of point defects, and of other structure defects governs the very narrow temperature range in which the shrinkage rate increases.

The activation energies of 35 to 92 kcal mol^{-1} cannot find their physical interpretation in attributing some of the basic transfer mechanisms to particular values: the values obtained are merely evidence of the easier mass-transfer at the beginning of the sintering process.

The analysis of the mass-transfer mechanism during the sintering of UO_2 indicates that it is impossible to explain the exceptionally high shrinkage at a temperature $\sim 0.4\ T_m$ on the basis of a single mass-transfer mechanism.

References

1. W. BILTZ and H. MÜLLER, *Z. Anorg. Chemie* **163** (1927) 257.
2. B. T. M. WILLIS, *Nature* **167** (1963) 755.
3. *Idem, Proc. Brit. Ceram. Soc.* **1** (1964) 9.
4. J. J. BACMANN and G. CIZERON, *J. Amer. Ceram. Soc.* **51** (1968) 209.
5. J. AMATO, R. L. COLOMBO, and A. M. PROTTI, *J. Nuclear Materials* **11** (1964) 229.
6. C. MAJANI, C. FERRO, M. FRANCIA, and I. STAMENKOVIĆ, *Physics of Sintering* **1** (1969) M11.
7. M. H. TIKKANEN and J. REKOLA, *ibid, Spec. Issue* (1971) 203.
8. R. SCOTT, A. R. HALL and J. WILLIAMS, *J. Nuclear Materials* **1** (1959) 39.
9. A. BEL *et al*, *ibid* **1** (1959) 259.
10. A. J. TAYLOR, TID 7637 (1961).

11. B. YA. PINES and YA. YE. GEGUZIN, *Zhur. Techn. Fiz.* **23** (1953) 2078 (in Russian).
12. M. H. RAND and O. KUBASCHEWSKI, "The Thermochemical Properties of Uranium Compounds" (Oliver and Boyd Ltd, Edinburgh and London, 1963).
13. D. L. JOHNSON, *Physics of Sintering* **1** (1969) B1.
14. J. E. DORN, "Activation energies for Creep and Recovery" (ASM Cleveland, 1957) p. 258.
15. T. ROKSANDIĆ, LJ. TRBOJEVIČ, D. USKOKOVIĆ, and B. ŽIVANOVIĆ, IBK-Report, No. 854 Beograd, 1969.
16. A. B. LIDIARD, *J. Nuclear Materials* **19** (1966) 106.
17. R. J. HAWKINS and C. B. ALCOCK, *ibid* **26** (1968) 112.
18. J. F. MARIN and P. CONTAMIN, *ibid* **30** (1969) 16.
19. H. J. MATZKE, *Trans. Amer. Nuclear Soc.* **8** (1965) 131.
20. G. CHRISTIE and J. WILLIAMS, *J. Nuclear Materials* **5** (1962) 1.
21. W. M. ARMSTRONG and W. R. IRVINE, *ibid* **12** (1964) 261.
22. R. A. WOLFE and S. F. KAUFMAN, Westinghouse (USA) Report, WAPD-TM 587 (1967).
23. D. L. JOHNSON and I. B. CUTLER, *J. Amer. Ceram. Soc.* **46** (1963) 541.
24. YA. YE. GEGUZIN, "Physics of Sintering" (Izd. Nauka, Moskva, 1967) (in Russian).
25. G. C. KUCZYNSKI, "Modern Development in Powder Metallurgy" (ed. H. Hausner), vol. I (Academic Press, New York, 1967) p. 332.
26. F. K. N. NABARRO, Rep. on Conf. Strength Solids, London (1948).
27. C. HERRING, *J. Appl. Phys.* **21** (1950) 437.
28. I. M. LIFSHIC, *Zhur. Eksp. Teor. Fiz.* **44** (1963) 1349 (in Russian).
29. C. HERRING, *J. Appl. Phys.* **21** (1950) 301.
30. V. A. IVENSEN, Kinetika Uplotneniya Metallicheskih Poroshkov pri Spekanii (Izd. "Metalurgija", Moscow, 1971) (in Russian).
31. M. ŽIVKOVIĆ, L. DJORDJEVIĆ, D. USKOKOVIČ, and M. M. RISTIĆ, *Porosh. Metal.* **1** (1972) 103 (in Russian).
32. G. V. SAMSONOV, R. L. COBLE, H. FISCHMEISTER and M. M. RISTIĆ, *et al*, "Discussion on II RTM on Sintering", Herceg-Novi, Yugoslavia 6-10 September (1971).

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