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UO$_2$ PORE MIGRATION AND GRAIN GROWTH KINETICS

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Summary

A mathematical model for determining the UO_2 grain growth rate was developed in order to evaluate UO_2 steady-state creep rates and fracture strengths. This model may also be applied in the postirradiation examination of UO_2 nuclear fuel rods to estimate fuel temperatures experienced during experiments performed in the Loss-of-Fluid Test (LOFT) facility at the Idaho National Engineering Laboratory. The model was developed from a study of experimental data of UO_2 grain growth rates and of pore migration rates in UO_2 and effects of pore size and bubble pressure upon the migration rates. Because pores attached to UO_2 grain boundaries inhibit the rate of grain growth, a study of grain growth kinetics must consider the UO_2 pore migration rates.

Various theoretical models, depending on a particular mechanism of mass transfer such as surface diffusion, volume diffusion, or vaporization-condensation, may be used to describe pore migration rates. In principle, the mechanism controlling the pore migration can be determined from the effect of pore size upon the migration rate. Measurements of pore migration rates for pore sizes less than 0.1 μm indicate a surface diffusion mechanism. However, for pore sizes larger than about 0.1 μm, migration rates suggest a vapor transport mechanism with a constant pore pressure as the rate controlling mechanism.

Corresponding with these models for pore migration, different expressions result for grain growth dependencies on time. Grain growth varies with time (a) to the one-half power for cellular grain growth with no pore retardation, (b) to the one-third power for vapor transport with pore pressure in equilibrium with UO_2 surface tension, (c) to the one-fourth power for vapor transport with constant pore pressure or for lattice diffusion, and (d) to the one-fifth power for surface diffusion. Experimental grain growth data from different sources were fit to time to the one-fourth power dependency which is compatible with UO_2 pore migration rates. The resultant expression is

$$D^4 - D_0^4 = 1.72 \times 10^{10} \exp(-386800/RT)\ t$$

where D is the final grain size (μm), D_0 is the initial grain size (μm), T is the temperature (K), R is the gas constant (8.318 J/g-K), and t is the time (s).

This grain growth model was compared with out-of-pile grain growth measurements from

1. Introduction

Grain growth rates and pore size distribution must be known in order to evaluate mechanical properties of UO_2 such as steady-state creep and fracture strength. Because pores located at UO_2 grain boundaries retard the rate of grain growth, grain growth kinetics cannot be separated from UO_2 pore migration. Pore migration rates and the effects of pore size and bubble pressure upon the rates were reviewed, and with this knowledge, a mathematical model for UO_2 grain growth was developed based upon experimental grain growth data and theoretical considerations.

Analytical models for UO_2 grain growth are presented first. Then since pore migration cannot be directly separated from grain growth kinetics, pore migration rising from a temperature gradient is discussed in order to establish the mechanisms for pore migration during UO_2 grain growth. Experimental grain growth data are compared with appropriate analytical models to derive the best analytical representation for UO_2 grain growth kinetics.

2. Analytical Models for UO_2 Equiaxed Grain Growth

The driving force for equiaxed grain growth is the decrease in surface free energy brought about by the decrease in the number of grains and, correspondingly, the total grain boundary surface area. The grain boundaries move in the direction of the radius of curvature; the larger grains consuming the smaller grains or the grains with less than the equilibrium six sides. If the grain growth rate is assumed to be inversely proportional to the bubble radius, then upon integration using the Arrhenius equation for the diffusion coefficient and the boundary condition that at $t = 0$, the initial grain size is D_o and

$$D^2 - D_o^2 = k_o \exp(-Q/RT)t \qquad (1)$$

where Q is the activation energy, T is the temperature, R is the gas constant, D is the grain size, t is the time, and k_o is a proportionality constant.

Equation (1) has been successfully applied to metals at high temperatures, but with considerable deviations at low temperatures which are attributed to undissolved inclusions pinning the grain boundaries [1]. In ceramic materials such as UO_2, a large fraction of the porosity is located at the grain boundaries, and Speight and Greenwood [2] performed an analysis that showed bubbles could not prevent movement of grain boundaries, but their effect was to reduce the velocity of movement so long as they remain attached to the boundary. In this way, the effect of voids is markedly different from that of solid precipitates which remain relatively fixed in position and either permit only local boundary movement or allow complete breakaway. Small bubbles move rapidly and have a greater tendency to remain attached to the boundary, whereas larger bubbles move more slowly, and for a given spacing, have the greatest effect in retarding boundary movement.

Kingery and Francois [3] developed a model that considers the retarding affect of pores located on grain boundaries or more commonly at grain intersections. For grain boundary movement, the pores on these boundaries also have to migrate at a rate inversely proportional to the pore diameter. When, as usually found, the grain (and pore) growth is more rapid than other changes, the pore-grain geometry remains about the same and thus the pore size remains nearly proportional to the grain size, D. For the ideal case, eq. (1) is modified by the retardation of the pore and upon integration

$$D^3 - D_o^3, = kt\exp(-Q/RT) \tag{2}$$

Thus when pores restrict the grain boundary movement, the cube of grain size as a function of time results rather than the square of grain size as a function of time.

Nichols [1] extended the analysis of Kingery and Francois [3] and showed that their results implicitly assumed a vapor transport mechanism with the pressure in the pore remaining equal to the equilibrium pressure, $2\gamma/r$, where γ is the surface tension and r is the pore radius.

Nichols [1] also showed that for either volume diffusion or vaporization-condensation with constant pore pressure that equiaxed grain growth is expressed by

$$D^4 - D_o^4 = kt\exp(-Q/RT) \tag{3}$$

and surface diffusion is expressed by

$$D^5 - D_o^5 = kt\exp(-Q/RT) \tag{4}$$

The expressions for D^3, D^4, and D^5 versus t is examined in Section 3 based upon pore migration rates and experimental grain growth data to determine the appropriate expression to predict equiaxed grain growth in UO_2.

3. Pore Migration in UO_2

Various theoretical models [4,5] for the rates of pore migration when a temperature gradient exists have been proposed which depend upon a particular mechanism of mass transfer: surface diffusion, volume diffusion, or vaporization-condensation mechanisms with either constant pore pressure or pore pressure in equilibrium with the surface tension. These models are presented first, followed by an evaluation of the experimental data on UO_2 pore migration rates.

From irreversible thermodynamics, the motion of spherical pores along a thermal gradient, assuming that these spherical pores migrate as a sphere and without distortion, has been treated by various authors [4, 5] for the various mechanisms and may be written as

$$V = \frac{2\,D_s\,\nu\Omega\,Q_s^*}{r\,k\,T^2}\frac{dT}{dx} \qquad \text{(surface)} \tag{5}$$

$$V = \frac{2D_v\,Q_v^*}{f\,k\,T^2}\frac{dT}{dx} \qquad \text{(volume)} \tag{6}$$

$$V = A(T)\,P\,\Delta H_v\,\frac{dT}{dx} \qquad \text{vapor transport } P = \text{constant} \tag{7}$$

$$V = B(T)\,r\,P_v\,\Delta H_v\,\frac{dT}{dx} \qquad \text{vapor transport } P = \frac{2\gamma}{r} \tag{8}$$

where V is the velocity of pore migration, D_s is the surface diffusion coefficient, ν is the number of diffusing species per unit area, Ω is the atomic volume, Q_s* is the heat of transport for surface diffusion, r is the pore radius, $\frac{dT}{dx}$ is the thermal gradient in pore, D_v is the volume diffusion coefficient, Q_v* is the heat of transport for volume diffusion, f is the correlation factor, P_v is the matrix vapor pressure, ΔH_v is the heat of vaporization, P is the vapor pressure in pore, k is the Boltzman constant, and A(T), B(T) are constants.

The theoretical equations for different diffusion mechanisms predict certain relationships between core migration rates and pore size. For surface diffusion, the pore migration rate is inversely proportional to the pore radius. However, the migration rate is independent of pore size for volume diffusion or for vapor transport if the pressure in the pore is fixed. When the pore pressure is in equilibrium with the surface free energy, however, the pore migration velocity is directly proportional to the pore radius. In principle, the mechanism controlling the pore migration can be determined from the effect of pore size upon the migration rate.

The relative importance of the various mechanisms of mass transport depends upon the pore size and temperature. Surface diffusion dominates at small pore sizes for all temperatures and its relative importance increases with lower temperature. The critical radius, which distinguishes the surface diffusion and vapor transport ($P = 2\gamma/r$) mechanisms, has been evaluated by Speight [6] to be about 1 μm at 2000 K. Bubbles with radii larger the 1 μm would migrate by vapor transport with $P = \frac{2\gamma}{r}$ and surface diffusion would dominate at smaller radii. Volume diffusion or vapor transport with constant pore pressure also become more important at larger pore sizes, and which mechanism dominates depends upon the particular material.

Williamson and Cornell [7] measured the pore migration rates of pores less than 0.1 μm in UO_2 single crystals at temperatures between 1523 and 1723 K. These authors attributed the pore migration to surface diffusion since small bubbles were observed to move faster than larger ones.

Gulden [8] measured the migration of fission gas bubbles in UO_2 at temperatures between 1673 and 1773 K and for pore sizes between 2.5 pm and 14.0 pm. From the effect of migration rates upon the bubble radius, a volume diffusion mechanism was selected to be the rate controlling mechanism for small pores between 3.7 and 14.0 pm. This result contradicts the expectation of volume diffusion at very large pore sizes.

Oldfield and Brown [9] measured the migration rate of bubbles in UO_2 located at columnar grain boundaries. The measured rates were much lower than corresponding values predicted by a vapor transport mechanism. This experimental result supports the theoretical contention that the migration rates of pores located at grain boundaries should be different than the migration rates of pores located within grains. Migration rates of columnar grains ranged between 0.01 and 1 μm/s for temperatures between 2173 and 2723 K.

Michels and Poeppel [10] measured the migration rates of fission-gas bubbles in UO_2-PuO_2 mixed oxide fuel for pore sizes ranging from 2.5 to 6.5 μm. Much scatter existed in the pore migration rates and precluded a determination of the effect of pore size upon the migration rate. However, they selected the surface diffusion mechanism because it gave more reasonable predicted values than a vapor transport mechanism with pore pressure in equilibrium with surface free energy. Because of the large scatter in experimental data, however, they did not preclude the vapor transport mechanisms with pore pressure in equilibrium with surface free energy or constant pore pressure.

Ronchi and Sari [11] performed out-of-pile measurements of the migration rates for pores located at the columnar grain boundaries in UO_2. On the basis of a measured activation energy of 485600 J/mol slightly below the evaporation enthalpy of UO_2 and using a constant pore pressure, they deduced that these pores migrated by the vapor transport mechanism with a constant pore pressure. These migration rates were higher than those of Oldfield and Brown [9], but values were in agreement with values predicted by the vapor transport model. They concluded that the pore pressure could not be in equilibrium with the surface tension.

Buescher and Meyer [12] measured pore migration rates in single crystal UO_2 for pore radii between 0.01 and 1.0 μm. The migration velocities were found to be independent of pore size. The observed values were found to be substantially larger than those predicted by mechanisms of volume diffusion and vapor transport ($P = 2\gamma/r$) but smaller than those predicted from surface diffusion. They proposed a model based upon nonlocalized surface diffusion that is affected by collisions between diffusing species and gas atoms within the bubble. In ruling out the vapor transport mechanism, they ignored the case for constant pore pressure which predicts the migration rates to be independent of the pore size. Their results are entirely consistent with the vapor transport mechanism with constant pore pressure. The absolute values for pore migration rates, of course, depend upon the pore pressure assumed in the pores.

The results from experimental measurements of pore migration rates are summarized in Table I. The measurements of Williamson and Cornell [7] indicate a surface diffusion mechanism when the pore sizes are less than 0.1 μm. However, for pore sizes larger than about 0.1 m, Ronchi and Sari [11] and Beuscher and Meyer [12] demonstrate a vapor transport mechanism with a constant pore pressure as the rate controlling mechanism, and the results from Michels and Poeppel [10] do not preclude this mechanism. Pore size distributions shown in Figure 1 and obtained from LOFT fuel pellets show that the total pore volume is accounted for in pore sizes greater than 0.1 μm, and therefore, vapor transport mechanism with constant pore pressure is the applicable mechanism for pores in UO_2 fuel pellets.

4. Experimental Grain Growth Data

Lyons et al [13] compared available grain growth data from references [18 - 23] with the cubic model represented by eq.(2). They obtained a reasonable fit of the data with this equation except for the Padden data [15] at 1773 K and the data at 1973 K in the initial grain growth period and most of the Hausner data [17]. The differences with the Hausner data were attributed to UO_2 evaporation during annealing in an open system. A rerun of Hausners experiments with encapsulation of UO_2 specimens resulted in a constant time dependency for all temperatures and equal to that obtained at 2223 K, but still different than the third-order time dependency predicted by using eq. (2). This behavior, as well as Padden's data [15] in the initial period, may represent discontinuous grain growth where the pores are not in the grain boundaries and are not hindering the rate of boundary migration.

Nichols [1] reevaluated MacEwan data [14] and calculated an activation energy of 519100 J/mol which compares favorably with the value of 577700 J/mol for the heat of vaporization of UO_2. Using the value of 519000 J/mol rather than the 498150 J/mol value from Lyons et al [13] and the constant k of 2.38 x 10^{11} from Lyons et al, the grain growth equation for cubic relation becomes

$$D^3 - D_o^3 = 2.38 \times 10^{11} \exp(519100/RT) \quad (9)$$

where t is the time (s), R is the gas constant (8.318 J/g-K), and T is the temperature (K).

Equation (9) was compared with experimental data from references [14 - 16, 18, 20]. The experimental data from Padden [15], Hausner [17], and Runfors et al [19] that was questioned by Lyons [13] was not compared. A standard deviation of ±10.5 μm results from this comparison.

Ainscough et al [20] performed measurements of equiaxial grain growth at temperatures between 1573 to 1773 K and for fairly long times (up to 24 weeks). They rejected the cubic relationship given by eq. (2), claiming that their data did not follow the cubic relationship. In its place, Ainscough et al proposed for UO_2 a limiting grain size, D_m, which is a function only of temperature. The grain growth kinetics then become

$$D_m (D_o - D) + D_m^2 \ln \frac{(D_M - D_o)}{(D_m - D)} = kt . \quad (10)$$

Burke [21] successfully used eq. (10) to correlate grain growth data for α-brass specimens containing a stable array of inclusions. Although this equation was used for materials with inclusions retarding the grain growth, Ainscough et al [20] applied it to UO_2 grain growth with the inhibiting effect of pores. A comparison of this model with higher-temperature grain-growth studies reported by other investigators showed the rate constants calculated in terms of eq. (10) to be, in general, higher than those calculated by extrapolating the results of Ainscough et al. However, most of the measurements made on UO_2 where the O/U ratio is close to 2.000 gave rate constants within a factor of four of the predicted values.

A comparison of the Ainscough et al correlation with experimental data results in a standard deviation of ±5.5 μm.

Equation (3) was evaluated using experimental data from references [14-17] for UO_2 grain growth to determine the constants k and Q. The average value of Q was 386800 J/mol and the resultant expression is

$$D^4 - D_o^4 = 1.72 \times 10^{13} \, t \exp(-386800/RT). \quad (11)$$

The value of 386800 J/mol for the activation energy is much less than 577700 J/mol expected for the heat of vaporization. A reevaluation of the activation energy using the cubic relation of eq. (2) resulted in an even slightly lower value of about 364200 J/mol. Even though the activation energies do not compare with the expected value, eq. (12) is the best representation of the experimental grain growth data with the lowest standard deviation of 4.8 μm. A comparison of calculated values from eq. (11) with expermental values is presented in Figure 2.

In Table II, eq. (11) is compared with UO_2 grain growth data obtained from out-of-pile densification studies of UO_2 pellets [22]. Good agreement is obtained for about one-half of the data except for the material with initial grain sizes of 3 and 4 m. All of these data were reported not to correlate well with the cubic eq. (9) or eq. (10).

Additional grain growth data were obtained from LOFT fuel pellets heated out-of-pile at 1973 K for 14 and 24 hours. Measured grain growth after 14 hours was 12.2 μm and after 24 hours it was 17.6 μm. Good agreement is obtained with respective calculated values of 15.0 and 17.1 m, calculated from eq. (11).

5. Conclusion

A number of theoretical models were proposed for equiaxed grain growth in UO_2. An examination of pore migration rates as a function of pore size shows the rates to be independent of pore size and this result suggests that the vaporization-condensation mechanism operates with a constant pore pressure. Therefore, a D^4 versus t relationship for equiaxed grain growth in UO_2 is consistent with pore migration rates, and experimental UO_2 grain growth is well represented by this relationship.

TABLE I

SUMMARY OF PORE MIGRATION EXPERIMENTS

Investigator	Temperature (K)	Pore Size	Comments on Mechanism
Williamson and Cornell[7]	1523 to 1723	0.1 μm	Surface diffusion mechanism
Gulden[8]	1673 to 1773	2.5 to 14.0 pm	Volume diffusion for r 3.7 pm
Oldfield and Brown[9]	2228 to 2683	0.2 to 2 μm	Ledge nucleation impeded motion
Michels and Poeppel[10]	1858 to 2123	1 to 10 μm	Size dependence undetermined, but surface diffusion indicated with a possibility of vapor transport
Ronchi and Sari[11]	1873 to 2873	Not given	Vapor transport mechanism
Buescher and Meyer[12]	2213 to 2293	0.01 to 1.0 μm	Authors proposed an impeded surface diffusion mechanism, but results fit vapor transport with constant pore pressure

TABLE II

COMPARISON OF CALCULATED AND MEASURED UO_2 GRAIN GROWTHS DURING UO_2 DENSIFICATION [22]

Temperature (K)	Initial Grain Size (μm)	Time (hr)	Calculated Grain Size (μm)	Measured Grain Size (μm)
1573	3	1500	10.8	7
1573	4	1500	10.8	6
1573	5	1500	10.9	10
1873	3	14	11.0	17
1873	4	14	11.0	21
1873	5	14	11.1	10
1873	3	48	14.9	22
1873	4	48	14.9	21
1873	5	48	14.9	21
1973	3	48	20.4	33
1973	4	48	20.4	23
1973	14	48	21.4	18
1973	5	48	20.4	35
1973	22	48	25.3	23

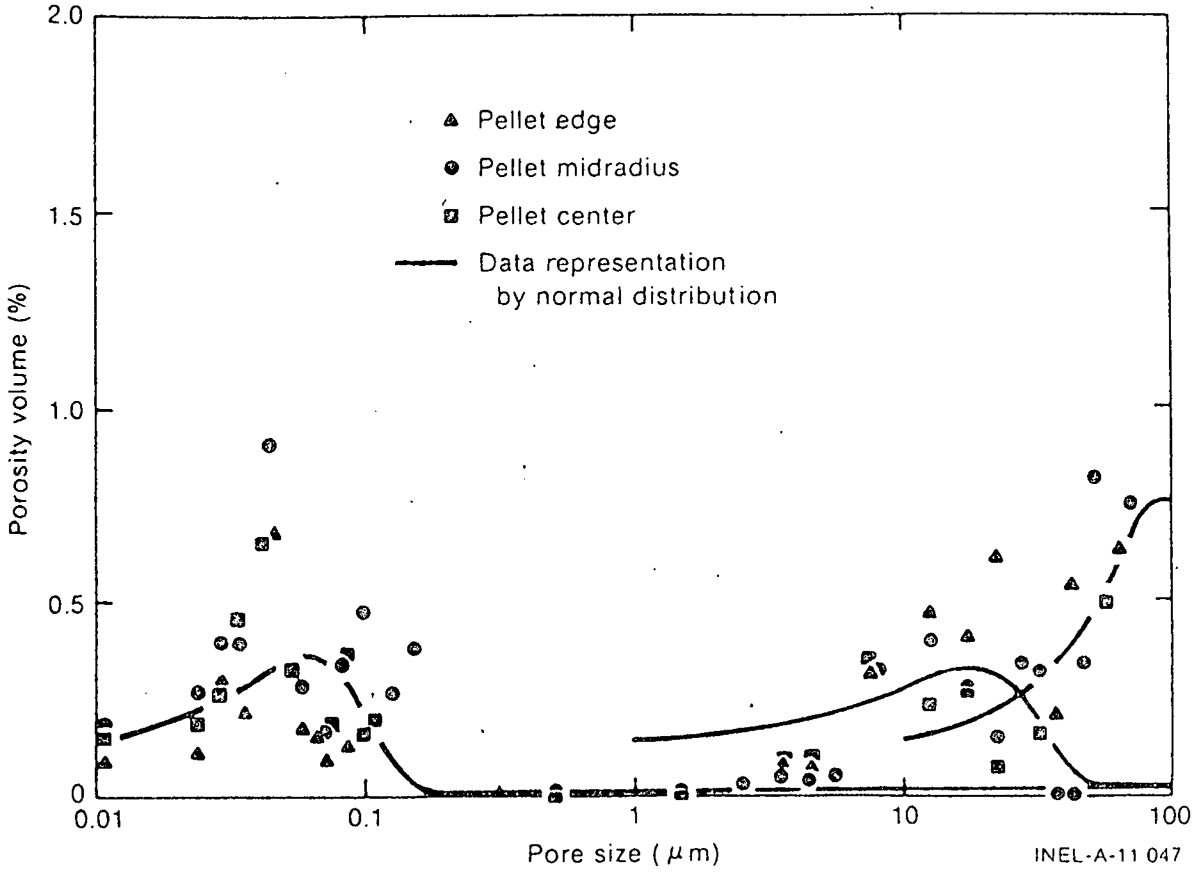

Fig. 1 Pore volume distribution for LOFT UO_2 pellets.

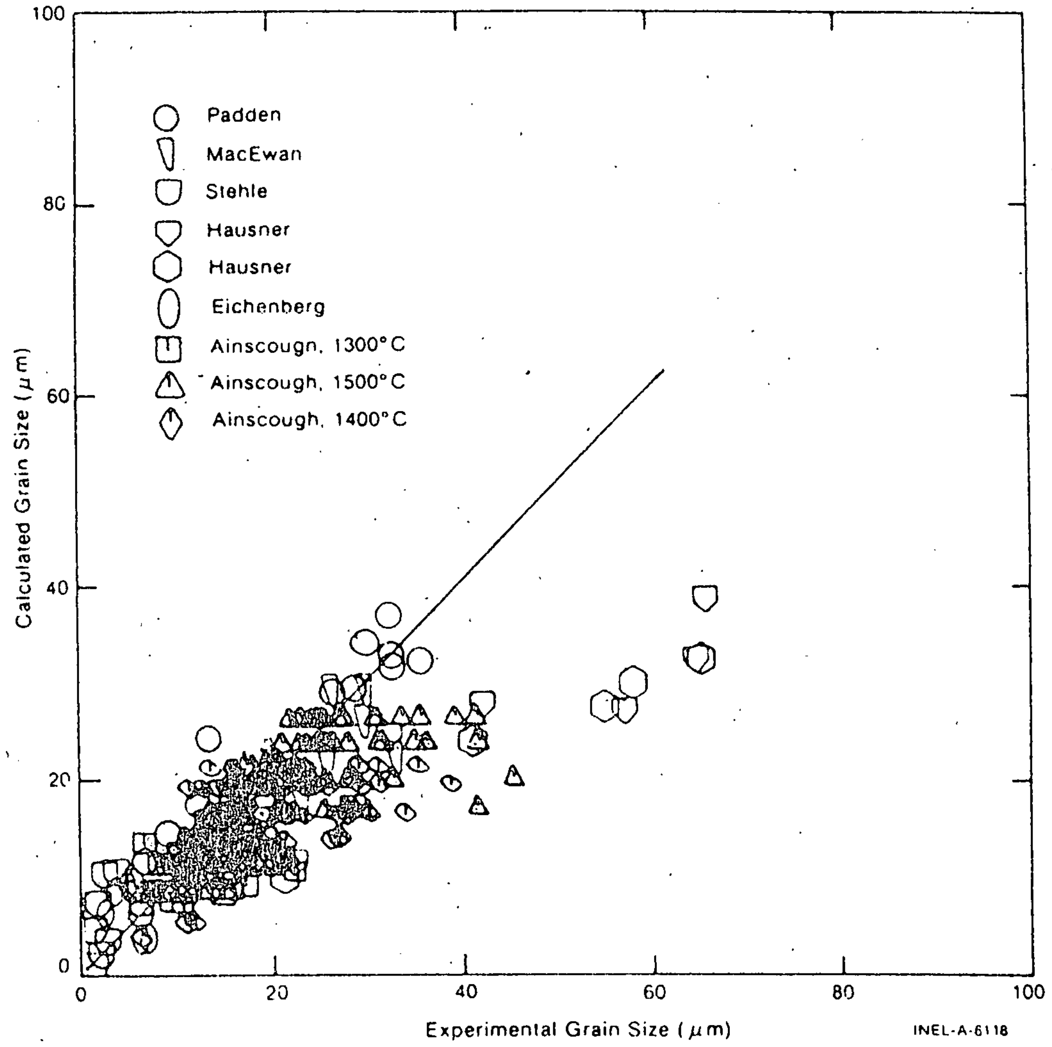

Fig. 2 Comparison of eq. (12) with experimental data for UO_2 grain growth.

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