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Kinetics of surface smoothing in uranium monocarbide single crystals

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The relaxation of sinusoidal profiles to flatness on the (110) surfaces of nearly stoichiometric uranium monocarbide single crystals has been determined between 1800 and 2160°C in a helium atmosphere. From the wavelength dependence of the relaxation constants, it was established that the mass-transfer rate due to capillary forces is primarily controlled by volume diffusion in the lattice. The diffusion coefficient D_m associated with the relaxation process is given by the Arrhenius relation $D_m = D_o \exp(-Q/RT)$, with $D_o = (3.6 \pm 2.0) \times 10^{-3}$ cm^2/sec and the activation energy $Q = 72.2 \pm 2.9$ kcal/mole. These values are compared with the published tracer and mass-transfer diffusion data on uranium monocarbide. Faceting of profiles occurred after annealing in helium on the (100) and (111) surfaces indicating the presence of cusps in the surface-energy plot at these orientations.

1. Introduction

Carbides of uranium and plutonium are being considered as potential fuels for fast-breeder reactors because of their good thermal conductivity and large fissile atom density. Swelling of nuclear fuel due to the retention of insoluble gaseous fission products, mainly xenon and krypton, is of concern in fuel-element design. Swelling rates are influenced by the nucleation, coalescence, re-solution, and migration of inert gas bubbles caused by various driving forces and the interaction of the bubbles with grain boundaries and dislocations [1]. Bubbles may migrate by surface diffusion, volume diffusion in the lattice, or by diffusion in the gas phase (vapour transport). The theoretical velocities are, of course, extremely sensitive to the migration mechanism and to the values of the various diffusion parameters that describe the process. The sinusoidal profile technique has been successfully employed to establish the relative importance of various mass-transport mechanisms in uranium dioxide [2]. In the present paper we summarize experiments on uranium carbide that utilize the same technique to obtain information on transport properties which appropriately describe complex processes such as the behaviour of inert gas bubbles in a temperature gradient.

A previous attempt to identify the rate-controlling mechanism in the development of grain-boundary grooves on the surface of hyperstoichiometric uranium carbide at 1970 to 2185°C [3] did not establish the mechanism. However, the grain-boundary grooving experiments performed on hypostoichiometric uranium carbide in the temperature range of 1100 to 1600°C indicate that surface diffusion is the rate-controlling mass-transport mechanism [4]. The values of the diffusion coefficients obtained in the two published studies showed a discrepancy that appears too large to be explained by the differences in stoichiometry. Nicholas and Hodkin [4] established that the mechanism was surface diffusion and reported $D_S = 5.6 \times 10^{-4} \exp(-31\,400/RT)$ cm^2/sec (D_S = surface-diffusion coefficient). Based on the assumption that surface diffusion controlled the development of the grooves, Maiya and Routbort [3] calculated $D_S = 4.9 \exp(-70\,000/RT)$ cm^2/sec. It was decided that measurements of sinusoidal profile relaxation to flatness on uranium carbide single crystals would not only resolve the discrepancy, but would yield information on the anisotropy of surface energy in uranium carbide.

2. Theory

Relaxation of a sinusoidal surface profile on a crystalline solid occurs when the solid is annealed in a gaseous solution of its vapour in an inert gas. The relaxation process is driven by the tendency of the crystal to minimize the total surface free energy of the system. The theoretical description of these phenomena has been well developed by Mullins [5–7]. The time-dependent amplitude $a(t)$ of the sinusoidal profile is given by [6]

$$a(t) = a(0) \exp(-Kt) \ , \qquad (1)$$

where $a(0)$ = initial amplitude, $K = A'\omega^3 + C\omega^3 + B\omega^4$ = decay constant, and $\lambda = 2\pi/\omega$ = wavelength. The constants A', C, and B result from the contribution of vapour-phase diffusion, volume diffusion, and surface diffusion and are defined as follows:

$$A' = \frac{\rho D_g \gamma_s \Omega^2}{kT} \ ,$$

$$C = \frac{D_m \gamma_s \Omega}{kT} \ ,$$

and

$$B = \frac{D_s \gamma_s \Omega^2 N_s}{kT} \ ,$$

where ρ = equilibrium vapour density over a surface of zero curvature = p/kT, p = equilibrium vapour pressure of the solid, k = Boltzmann's constant, T = absolute temperature, γ_s = surface free energy, Ω = volume per molecule, N_s = molecular density of the surface, D_m = volume-diffusion coefficient in the lattice, D_s = surface-diffusion coefficient, and D_g = diffusion coefficient of vapour molecules in the inert gas.

Experimentally the predominant surface-relaxation mechanism can be identified from the wavelength dependence of the decay constant K. For example, a log–log plot of the decay constant versus wavelength yields a slope of -4 for surface diffusion, -3 for diffusion in the lattice and surrounding inert gas, and a slope intermediate between these values when the relaxation occurs by a combination of the various diffusion processes.

3. Experimental procedure

The zone-refining technique for the preparation of hypostoichiometric uranium carbide single crystals used in this experiment has been described previously [8]. The crystals contained $\simeq$ 90 ppm oxygen, $\simeq$ 450 ppm nitrogen, but less than 30 ppm of metallic impurities. Each crystal was oriented and polished parallel to the desired surface within ± 1°, as determined by the Laue back-reflection technique. Sinusoidal profiles with a periodicity ranging from 8 to 40 μm were produced by a photoetching technique described elsewhere [9]. In all specimens the profiles were produced along the same crystallographic direction (see fig. 1).

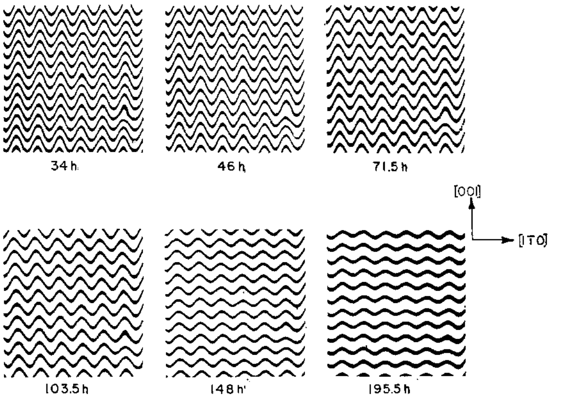

Figure 1 Interferograms of the (110) surface of uranium carbide after annealing at 2158°C in helium (λ = 20.43 μm).

Following etching and cleaning, the crystals were isothermally annealed for various times in a high-purity tungsten crucible under 1 atm of flowing helium to determine the smoothing kinetics. Temperature was measured by a calibrated optical pyrometer under black-body conditions and maintained constant to within ± 5°C. After annealing, interferograms of the surface profiles were photographed with a Zeiss interference microscope. The relaxation of a typical sinusoidal profile on the (110) surface at 2158°C is shown in fig. 1. Ten or more independent amplitude measurements were made for each annealing time and wavelength. The average value of the amplitude was used to construct plots of log amplitude versus time, as shown in figs. 2 and 3.

Before the diffusion anneals, the uranium carbide was hypostoichiometric (C/U ratio $\simeq$ 0.96) as determined by chemical analysis and verified by the observation of free uranium using optical metallography. During the initial high-temperature anneals, the plots of log amplitude versus time could not be fit to a straight line. This was due to the change in stoichiometry that occurred during the high-temperature anneals in flowing helium. Chemical analysis after annealing revealed that the samples had become slightly

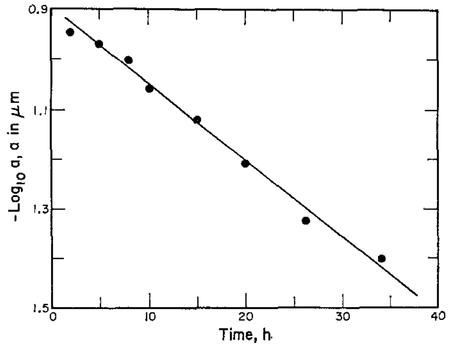

Figure 2 Sinusoidal profile-relaxation rate for (110) surface of uranium carbide at 2158°C (λ = 12.54 μm).

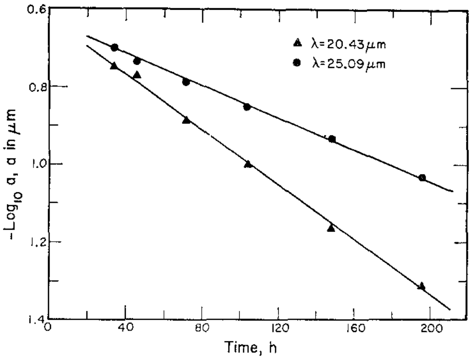

Figure 3 Sinusoidal profile-relaxation rate for the (110) surface of uranium carbide at 2158°C (λ = 20.43 and 25.09 μm).

hyperstoichiometric (C/U ratio = 1.02 ± 0.03), which corresponds to the congruent vaporization composition recently reported by Tetenbaum and Hunt [10]. Neither free uranium nor UC_2 could be detected by scanning-electron microscopy. Consequently, it was not possible to study the mass transport in UC_{1-x} as a function of x. It was also impossible to study surface smoothing of very hyperstoichiometric uranium carbide because of the distortion and faceting of the surface profiles caused by the presence of fine Widmanstätten-type UC_2 precipitates in the uranium carbide matrix. Therefore, all the measurements reported in the present paper refer to uranium carbide with the congruent vaporization composition.

4. Results and discussion

To establish the rate-controlling mass-transport mechanism in uranium carbide, the wavelength dependence of the decay constant was studied on the (110) surface of uranium carbide at 2158°C. The results, shown in fig. 4, indicate that the dominant mechanism of surface smoothing is volume diffusion; i.e., the slope of the plot of log K versus log λ is -3, which is the expected slope for a volume-diffusion mechanism. To determine whether volume diffusion in the lattice or diffusion in the gas phase is responsible for the surface smoothing, the contribution for vapour-phase transport was calculated using the published evaporation rates [11, 12]. The calculation is described in detail in ref. [2]. The largest value of published vapour pressures indicates that the vapour-phase contribution is less than volume diffusion in the lattice by two orders of magnitude even at the highest temperature. Hence the vapour-phase contribution to relaxation is negligible and may be ignored.

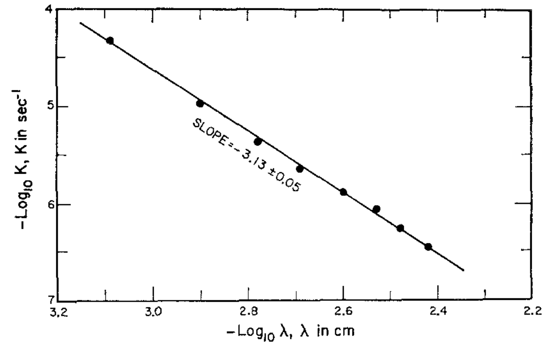

Figure 4 Wavelength dependence of the decay constant for the (110) surface of uranium carbide at 2158°C. The slope was determined from a least-squares fit.

It was not possible to investigate the surface-relaxation process on the (100) and (111) orientations because the sinusoidal profiles faceted at these low-index orientations. A typical example of a faceted profile near the (100) orientation is shown in fig. 5. The observations suggest that the variation of surface free energy γ_s with orientation displays cusps or singularities at the (100) and (111) orientations. The results are similar to the orientation dependence of the surface energy of gold [13]. For example, the surface free energy plot for gold at 1030°C was found to be cusped at the (111) and (100) orientations, but not on the (110) surface. Based on the work of Willertz and Shewmon [14] concerning bubble diffusion in gold, the above observations imply that inert gas-bubble move-

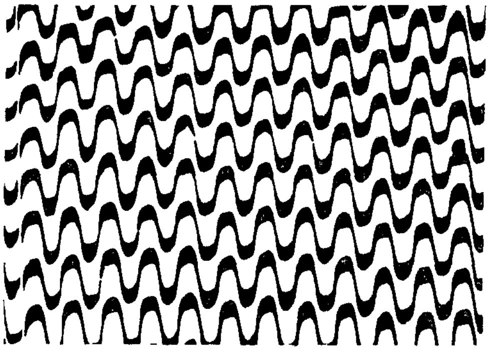

Figure 5 Interferogram of a faceted (100) uranium carbide surface after annealing at 2015°C in helium for 5.6 h ($\lambda = 8.24$ μm).

ment in uranium carbide cannot be described by a simple diffusion model.

TABLE I Mass-transfer diffusion constants measured on the (110) surface of uranium carbide at 2158°C*

λ (μm)	$C\omega^3 \times 10^5$ (sec^{-1})	$C \times 10^{17}$ (cm^3/sec)	$D_m \times 10^9$ (cm^2/sec)
8.24	4.625	10.43	1.47
12.54	1.045	8.30	1.17
16.67	0.425	7.93	1.12
20.43	0.226	7.76	1.09
25.09	0.127	8.06	1.14
29.51	0.086	8.88	1.25
33.21	0.054	8.03	1.13
37.99	0.034	7.60	1.07

*The surface free energy was assumed to be 780 ergs/cm².

If Mullins' theoretical description [6] applies to the relaxation process, then the mass-transfer diffusion constant D_m is independent of wavelength, provided the anisotropy of surface energy near the (110) surface is small. This is indeed the case, as shown in table I. Therefore, it may be concluded that Mullins' theoretical description is applicable to uranium carbide and that the rate of surface relaxation is solely due to volume diffusion in the lattice. Equation 1 may then be utilized to calculate the mass-transfer diffusion constant from the decay constant obtained at various temperatures. The constants used in this calculation are $\gamma_s = 780$ ergs/cm² [15] and $\Omega = 3.052 \times 10^{-23}$ cm³/molecule ($\Omega = a_0^3/4$, where a_0 = lattice parameter), and the results are plotted in fig. 6. Included in the Arrhenius plot are the results of our previous grain-boundary grooving study [3] calculated for $\gamma_s = 780$ ergs/cm². Shown for comparison are the tracer-diffusion coefficients for uranium, D^U_{UC}, and carbon, D^C_{UC}, [16–20], which have been divided by 0.78 to correct for the correlation effect [21] of vacancy diffusion.

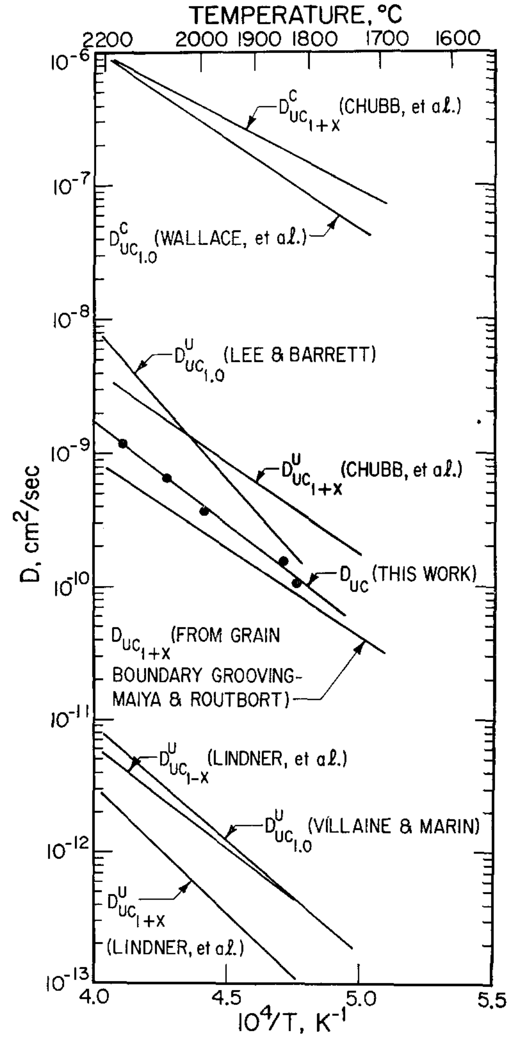

Figure 6 Temperature dependence of the mass-transfer (lattice) diffusion coefficients compared with previous results obtained using grain-boundary grooving techniques. The tracer-diffusion coefficients for uranium D^U_{UC} and carbon D^C_{UC} have been corrected for correlation effect.

The results of the sinusoidal profile relaxation in uranium carbide may be described by the equation $D_m = D_0 \exp(-Q/RT)$, where the pre-exponential term $D_0 = (3.6 \pm 2.0) \times 10^{-3}$ cm²/sec, and the activation energy $Q = 72.2 \pm 2.9$ kcal/mole. We conclude that the formation and growth of grain-boundary grooves in the high-temperature regime (1970 to 2185°C) in less pure uranium carbide [3], which resulted in $D_0 = (0.23 \pm 0.19) \times 10^{-3}$ cm^2/sec and $Q = 62.0 \pm 4.0$ kcal/mole, are also controlled by volume diffusion in the lattice. As mentioned previously, in the low-temperature regime (1100 to 1600°C), surface diffusion dominates the development of grain-boundary grooves [4]. Mass-transport techniques have been used to establish a similar change in the predominant transport mechanism from surface to vapour-phase diffusion in UO_2 [22] at approximately 1700°C.

The mass transport, which causes the surface-profile shape changes in uranium carbide, must involve migration of both uranium and carbon. However, the identification of the rate-controlling species is obscured because the tracer-diffusion data exhibit a wide variability. Although our results lie near the data of Lee and Barrett [18] and Chubb *et al* [20] for uranium self-diffusion in uranium carbide, their reported diffusion coefficients are $\simeq 10^3$ higher than the diffusion coefficients reported by Villaine and Marin [16] and Lindner *et al* [17].

The formation and migration energies of both the uranium and carbon vacancies in uranium carbide have been measured from changes in electrical resistivity on quenching and annealing [23]. The results of these studies indicate that the activation energy for self-diffusion of uranium vacancies in a uranium sublattice is between 83 and 90 kcal/mole, whereas the activation energy for the diffusion of carbon vacancies in the carbon sublattice is between 47 and 65 kcal/mole. To further complicate the analysis, the stoichiometry of the uranium carbide on which tracer diffusion measurements were made is not reliable unless the initial composition is near the congruent vaporization composition or the carbon potential is carefully controlled. Therefore it is impossible to identify the rate-controlling diffusing species on the basis of activation energy.

The pre-exponential factor obtained from this study is in closer agreement with the majority of the uranium tracer-diffusion data than with the carbon tracer-diffusion data. The pre-exponential is

$$D_0 = a_0^2\, \nu \exp\left(\frac{\Delta S_f + \Delta S_m}{R}\right), \tag{2}$$

where a_0 = lattice parameter, ν = frequency factor, ΔS_f = entropy of formation of a vacancy, and ΔS_m = entropy of migration of a vacancy.

Zener [24] has pointed out that a relationship exists between the diffusion rate in a solid and its elastic constants inasmuch as the shear modulus measures the lattice strain at the saddle point. Zener's model can be applied to a vacancy mechanism to calculate the total entropy ΔS ($\Delta S = \Delta S_f + \Delta S_m \simeq \lambda\beta Q/T_m$, where $\beta = -[d(\mu/\mu_0)]/d(T/T_m)$, λ is a constant $\simeq 1$, Q is the activation energy of self-diffusion, μ_0 = shear modulus at $T = 0$°K, and T_m = melting temperature). Hence D_0 may be estimated from the published values of the Debye temperature θ_D [25], T_m [26], and the temperature variation of the elastic constants [8]. Using these values, $D_0 \simeq 3 \times 10^{-5}$ cm^2/sec, which is in fair agreement with the results of Villaine and Marin [16] and Lindner *et al* [17], but which is lower than our experimental value by $\simeq 10^2$.

When more than one atomic species is present in a compound, the mass-transport methods yield an effective diffusion coefficient. For an ionic AB-type solid, the effective diffusion coefficient D_{eff} is related to D_A and D_B by [27]

$$D_{eff} = \frac{D_A D_B}{D_A + D_B}\,. \tag{3}$$

Generally this equation reduces to the self-diffusion coefficient of the slower moving species. Equation 3 is based on the assumption that the fluxes of two types of ions in the lattice are coupled, and electrical neutrality is maintained everywhere, which may not be valid for uranium carbide. For example, the coupling forces depend on whether the uranium atom is an electron donor or acceptor with respect to the carbon atom, and how much charge is transferred. This problem has not been investigated in uranium carbide. Furthermore, for the case of lattice diffusion determined from shape-change measurements, an additional factor must be considered [27] in the rate equation to account for the change in defect concentration at the surface, relative to the interior. Consequently, no firm conclusions can be drawn concerning the identification of the rate-controlling species in uranium carbide.

5. Summary

The relaxation of sinusoidal profiles with wavelengths between 8 and 40 μm occurs by volume diffusion in the lattice at temperatures of 1800 to 2160°C. The results may be described by $D_m = (3.6 \pm 2.0) \times 10^{-3} \exp(-72\,200 \pm 2900)/RT$ cm^2/sec. A comparison of the present measurements with the previously published mass-transport data suggests that a changeover in the predominant transport mechanism from surface to lattice diffusion occurs between 1700 and 1900° C, whereas surface diffusion dominates the shape changes in the low-temperature regime (1100 to 1600° C). The rate-controlling diffusing species cannot be identified because of the discrepancies in the published tracer self-diffusion data and because the mass-transport technique yields an effective diffusion coefficient. At temperatures of 1800 to 2160° C, in a helium atmosphere, the surface free energy plot (γ_S plot) for nearly stoichiometric uranium carbide appears to be cusped at the (100) and (111) orientations but not at the (110) orientation.

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