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PERFORMANCE OF HIGHLY LOADED FUEL OPERATING AT HIGHER
TEMPERATURES AND FISSION RATES***

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ALUMINUM- U_3Si_2 INTERDIFFUSION AND ITS IMPLICATIONS FOR THE PERFORMANCE OF HIGHLY LOADED FUEL OPERATING AT HIGHER TEMPERATURES AND FISSION RATES

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ABSTRACT

Recent irradiation tests of U_3Si -Al dispersion fuel have shown performance limitations of this fuel when high volume fractions of U_3Si_2 operate at high temperatures and high fission rates. This potential problem is associated with high rates of Al- U_3Si_2 interdiffusion that may lead to complete consumption of matrix aluminum and the formation of excessive porosity.

INTRODUCTION

Aluminum- U_3Si_2 interdiffusion manifests itself by the formation of a single intermetallic compound, $U(AlSi)_3$, in the diffusion zone at the U_3Si_2 -Al interface -- the solubility of Al in U_3Si_2 itself being very small ($\ll 1$ at.%). $U(AlSi)_3$ has a composition intermediate between UAl_3 and USi_3 -- two cubic compounds that are mutually soluble. The Al-to-Si ratio is approximately 3.5 and the composition of the compound lies on the tieline between U_3Si_2 and Al, as shown in the isothermal section of the ternary equilibrium diagram^[1], (Fig. 1). The compound has a density of ~ 7.1 g cm^{-3} and approximately equal volumes of U_3Si_2 and Al are used in its formation. Consequently, there is only a small volume change, $\sim 4\%$, involved in the transformation of Al and U_3Si_2 to $U(AlSi)_3$.

Annealing experiments^[2,3,4] with dispersion fuel samples have shown that the growth of the $U(AlSi)_3$ layer at the U_3Si_2 -Al interface obeys classical diffusion kinetics, i.e., the width of the layer "Y" is described by $Y = \{K^{th}[\exp(-Q^{th}/RT)]t\}^{1/2}$ where Q^{th} is the activation energy for interdiffusion in $U(AlSi)_3$. K_0 is a reaction constant, t is time in seconds, T is the absolute temperature, and R is the gas constant.

Measurable layer formation occurs after several hundreds of hours at a temperature of around 400°C and at much shorter times at higher temperatures; however, at 300°C no

interaction is observed after more than 1000 hours. Although the thermal by activated diffusivity of aluminum in $U(AlSi)_3$ per se is rather high, as has been found in similar compounds such as UAl_3 ^[5] and $ZrAl_3$ ^[6], it is still extremely low at aluminum-dispersion-fuel operating temperatures in current research reactors (normally well below 300°C).

Postirradiation examinations of U_3Si_2 -Al, however, do show a substantial and well-defined $U(AlSi)_3$ layer in fuel samples irradiated in ORR and HFIR at, respectively, ~100°C and ~200°C, as shown in Fig. 2. It is a well-documented fact that at temperatures below approximately 1/2 the absolute melting temperature of a solid (in the case of $U(AlSi)_3$ this is 835 K or 562°C), diffusion can be enhanced by irradiation. The postirradiation microstructure of a U_3Si_2 -Al dispersion sample made with depleted U, and irradiated alongside similar LEU samples (see Fig. 3) shows that the $U(AlSi)_3$ formation is clearly due to fission damage, since it is not measurably present in the DU sample.

Al- U_3Si_2 INTERDIFFUSION DURING IRRADIATION

Experimental Data

Postirradiation data from two U_3Si_2 -Al dispersion fuel irradiation test programs were used from the RERTR miniplate program carried out in the Oak Ridge Research Reactor (ORR) and the ANS fuel development program performed in the High Flux Isotope Reactor (HFIR). The fuel temperature (i.e., the temperature of the dispersion or fuel meatThe bulk in all the ORR samples was normally ~100°C or less while the fission rate of the samples varied somewhat depending on irradiation position, but more so depending on the enrichment of the fuel used, i.e., LEU, MEU, or HEU. Most of the samples, however, consisted of LEU. The fuel temperatures in the HFIR tests spanned a range from 100°C to 425°C; the fission rate also varied with enrichment but was on the whole one-to-two orders of magnitude higher in this high-flux reactor. The extent of interdiffusion was measured by optical metallography and scanning electron microscopy (SEM). Compositional information was obtained by SEM-EDX.

Examples of ORR and HFIR LEU samples are shown in Fig. 2. In both cases the interdiffusion zone at the fuel particle periphery is clearly distinguishable -- it is substantially wider in the HFIR sample, which ran at a higher temperature and a much higher fission rate. The data used in this study are collected in Table I.

Analysis

Enhanced diffusion during irradiation is the result of point defects (vacancies and interstitials) created in excess of the thermal equilibrium concentration by, in the case of fuel, fission fragments. The magnitude of the enhancement depends, therefore, on the damage rate -- fission rate in this case. The behavior of the point defects upon formation determines the functional relationship between fission rate and diffusivity. Annihilation of the created vacancies and interstitials by mutual recombination results in a square root fission rate dependence while a linear dependence prevails when annihilation occurs at sinks. The temperature dependence of radiation-enhanced diffusivity varies from athermal for the latter

case to an Arrhenius dependence for the former with an activation energy of one-half the migration energy for vacancies -- roughly one quarter of the activation for thermal diffusivity.

TABLE I DATA OF SAMPLES USED FOR U ₃ Si ₂ -Al INTERDIFFUSION CORRELATION						
Sample	Enrichment	U-235 Depletion, %	Temp., °C	t, 10 ⁶ s	Fission Rate, 10 ¹⁵ cm ³ s ⁻¹	Zone Width, 10 ⁻⁴ cm
ORR-100	LEU	45	100	15.1	0.13	2.0
ORR-92	LEU	85	100	21.9	0.21	4.0
ORR-93	LEU	93	100	34.7	0.14	4.4
ORR-34	LEU	90	100	25.9	0.18	3.4
ORR-123	MEU	44	100	11.0	0.38	2.2
ORR-124	MEU	69*	100	23.8	0.26	2.8
ORR-121	HEU	44*	100	11.2	0.84	3.2
ORR-122	HEU	69*	100	23.5	0.61	4.4
ORR-125	LEU	34	100	12.3	0.32	2.2
ORR-99	LEU	79	100	30.8	0.14	4.0
ORR-36	LEU	97	100	33.3	0.13	3.6
HFIR 3-1	HEU	74*	100	1.98	8.1	5.0
HFIR 3-14	HEU	88*	200	1.98	10.1	18.0
HFIR 3-10	LEU	91	200	1.98	2.5	10.0

*High total U burnup samples.

To define the process of U₃Si₂-Al interdiffusion in such fundamental terms would require very controlled experiments. The present analysis, instead, attempts to use the available postirradiation data to derive a useful correlation that is consistent with the physics of radiation damage.

The fission-enhanced formation of the U(AlSi)₃ interdiffusion zone "Y" between U₃Si₂

$$Y^{irr} = [K^{irr} F^n \exp(-Q^{irr}/RT)(t-t_0)]^{1/2} \quad (1)$$

and aluminum may be expressed by:

where K_r is a materials constant, T is the dispersion temperature in K, Q is the activation energy, (t - t₀) is the irradiation time minus an incubation time allowing for the establishment of a sound

U_3Si_2 -Al bond, and F is the fission rate in the U_3Si_2 particles.

The best fit through the LEU and MEU data was obtained with the following parameters:

$$Q^{irr} = 5870 \text{ cal/mole}$$

$$K^{irr} = 1.1 \times 10^{-25}$$

$$n = 1$$

$$t_0 = 3.9 \times 10^6 \text{ s}$$

The linear fission rate dependence permits the data to be expressed in terms of

$$Y^2/\langle F \rangle \text{ vs } t$$

where $\langle F \rangle$ is the time-average fission rate or, in effect, the final fission density, FD, divided by irradiation time. All the LEU and the low-burnup MEU data fit the correlation rather well, as shown for the 100°C data in Fig. 4. A variation in irradiation temperature of $\pm 12^\circ\text{C}$ is reasonable considering flux variations and microstructural changes during the long irradiation history of the samples. The temperature dependence (shown in Fig. 5) was derived from data at only two temperatures and is, therefore, a bit tenuous; however both the fission rate and temperature dependences are consistent with models of radiation enhanced diffusion and do represent the LEU data rather well.

It proved not possible to include the high-burnup MEU and HEU samples in the correlation with any reasonable fission rate dependence. The reason for this can be found in the morphology of the interdiffusion zone. As shown in Fig. 6, the interdiffusion zone for the high-burnup MEU sample contains globular features while the zone for the LEU sample has a very smooth appearance. It is reasoned that the features in the MEU sample impede the interdiffusion; indeed, a change in the K^{irr} from 1.1 to 0.4×10^{-25} results in a good fit of all the MEU and HEU data, as shown in Fig. 7. Since the RERTR program is concerned with LEU, the different behavior of fuels that are burned to uranium depletion that pass that well beyond full LEU burnup is at this point primarily of academic interest.

For the purpose of evaluating LEU behavior over a wide range of operating temperatures and fission rates Eq. (1) can be combined with a separate thermal diffusion equation derived from out-of-reactor annealing tests on U_3Si_2 -Al dispersion fuel plates

$$Y^{irr} = [K^{th} \exp(-Q^{th}/RT)(t-t_0)]^{1/2} \quad (2)$$

where $K^{th} = 9.3 \times 10^{12}$ and $Q^{th} = 4200$ cal/mole.

The composite (sum) of these two equations is shown in Fig. 8. In addition to some of the data from Table I, a few data points from other experiments are included for comparison. Depending on the fission rate, thermal diffusion dominates from about 400°C upwards but the interdiffusion is controlled by fission at the lower temperatures that prevail in most research reactor applications.

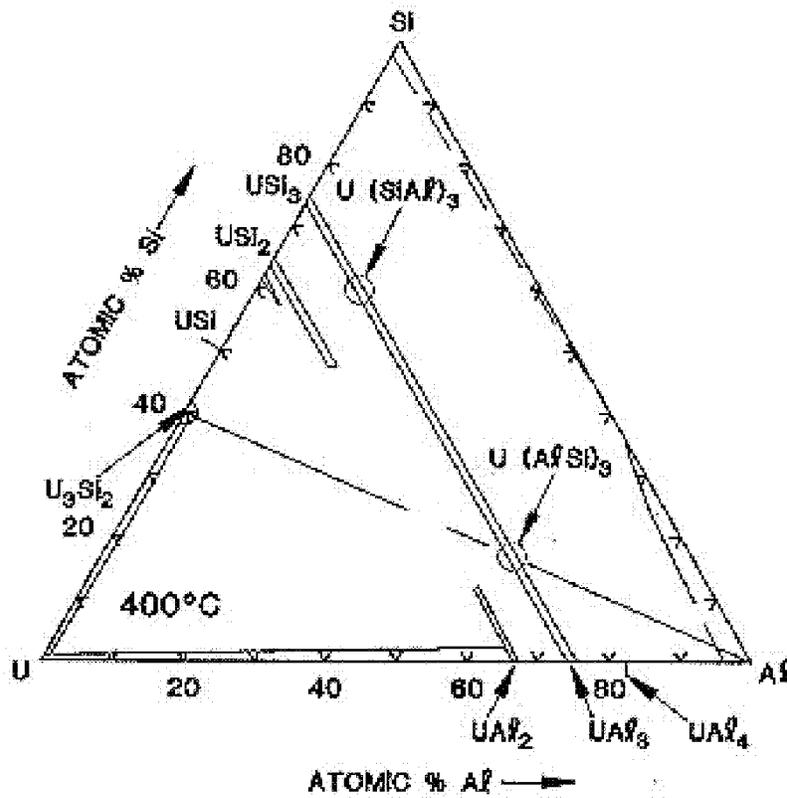
DISCUSSION AND CONCLUSIONS

What, then, does this rate of interdiffusion mean in terms of U_3Si_2 -Al dispersion fuel behavior? Clearly at the low temperatures and moderate fission rates that exist in most research reactors the formation of thin interaction zones at the fuel particle surfaces has no discernable effect. However, as the latest HFIR tests have shown, the effects can be dramatic at higher operating temperatures and fission rates. This is shown in Figs. 2 and 9 for nominally 4.8 gU cm⁻³ (43 vol.% U_3Si_2) LEU dispersion samples irradiated at temperatures currently estimated to be 200°C, 300°C, and 400°C, respectively. In the 200°C sample the interdiffusion zone width is substantial but the overall fuel meat microstructure is essentially similar to that of the ORR samples. At 300°C, however, the interdiffusion process has virtually consumed all matrix aluminum and crack-like voids have developed at the erstwhile fuel particle surfaces. In the 400°C sample these voids have developed to occupy approximately 50% of the meat volume, clearly, any fuel plate would have pillowed under these conditions. It appears that this phenomenon is associated with the disappearance (through interdiffusion) of the matrix aluminum. It is therefore sensitive to the amount of aluminum available i.e., to the fuel loading as well as the interdiffusion rate. This is parametrically illustrated in Figs. 10 and Fig. 11 where the calculated change in aluminum matrix volume is plotted versus fission density. No fission rate effects appear in these calculations because, as mentioned earlier, the diffusivity depends linearly on the fission rate, which allows the product of time and fission rate, i.e., fission density, to be used as a parameter.

As the curves in Figs. 10 and 11 show it is the combination of high loading and temperature that lead to conditions where matrix aluminum may be fully consumed at realistic maximum burnup levels. With the present data it is not possible to state whether complete aluminum consumption alone is a sufficient condition to trigger excessive void formation or whether a second condition, high fission rate, is also required. A test at high temperature but low fission rate may resolve this question. Since excessive void formation has never been observed prior to aluminum depletion, even at the high fission rates in the HFIR test, we are confident that this phenomenon can be avoided by placing appropriate limits on burnup (fission density).

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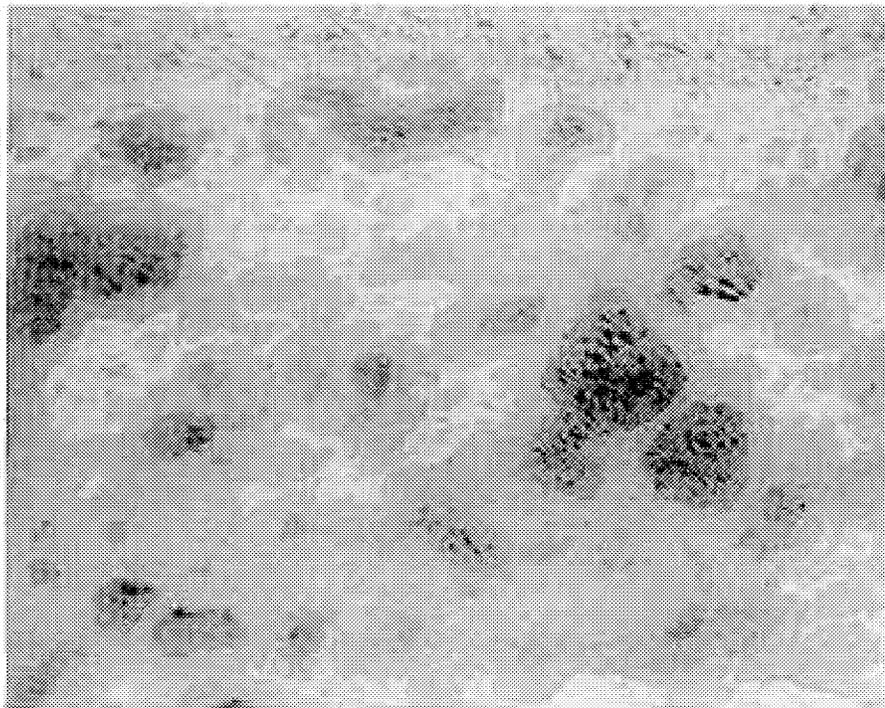
PARTIAL TERNARY DIAGRAM

Fig. 1. Isothermal Section of U-Si-Al Equilibrium Diagram Showing Solubility Ranges of Ternary Compounds.



Plate A54, ORR, 300 Days at -100°C
 3.7 g cm^{-2} LEU, -90% Bu

(300x)



HANS-3-10, HFIR, 24 Days at -200°C
 4.6 g cm^{-2} LEU, -90% Bu

(250x)

Fig. 2. $\text{U}(\text{AlSi})_3$ Interaction Layer (Light Grey) in U_2Si_7 -Al Dispersion Fuel Irradiated in ORR and HFIR

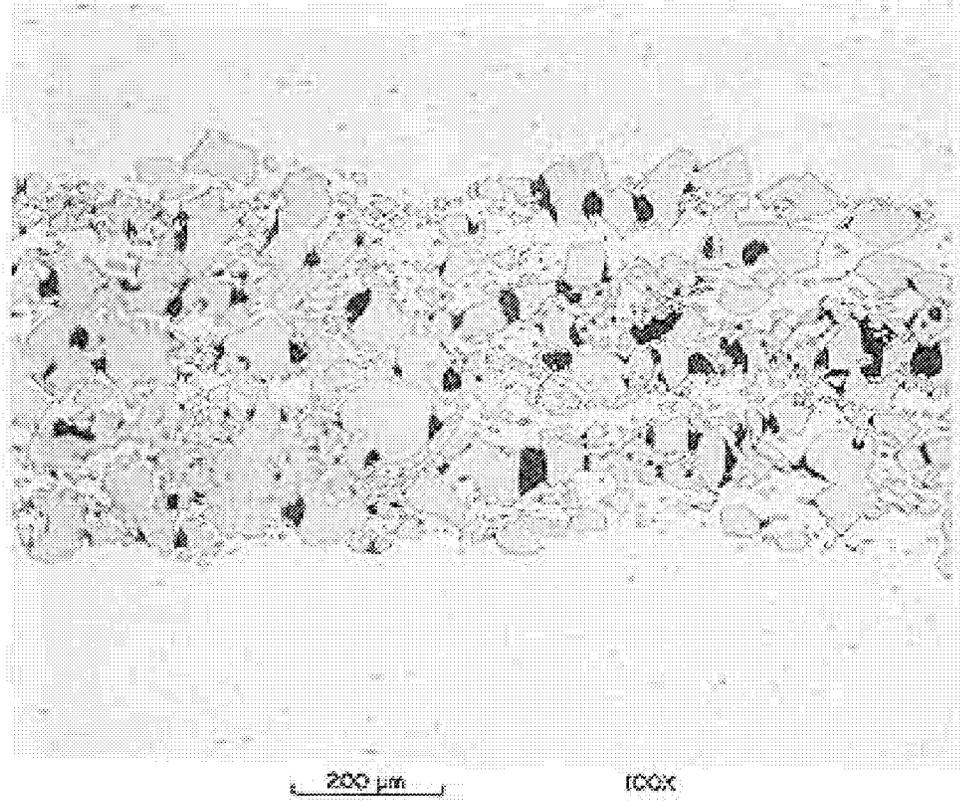
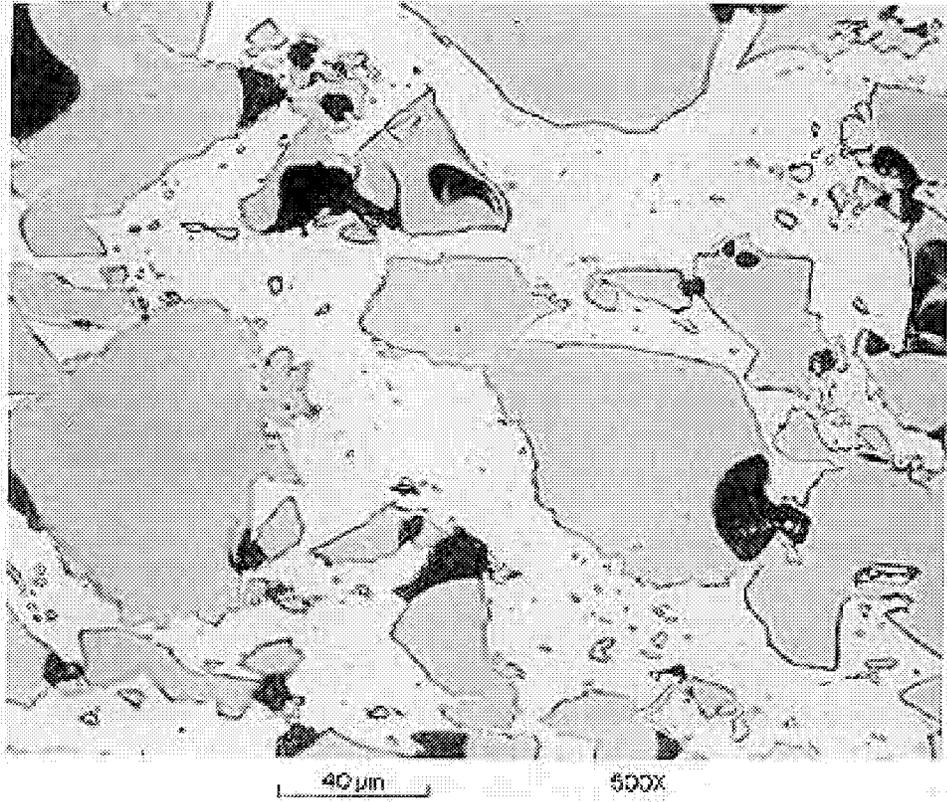


Fig. 3. U_3Si_2 -Al Dispersion with DU Irradiated in ORR for 250 Days, Showing No $(AlSi)_3$ Layer

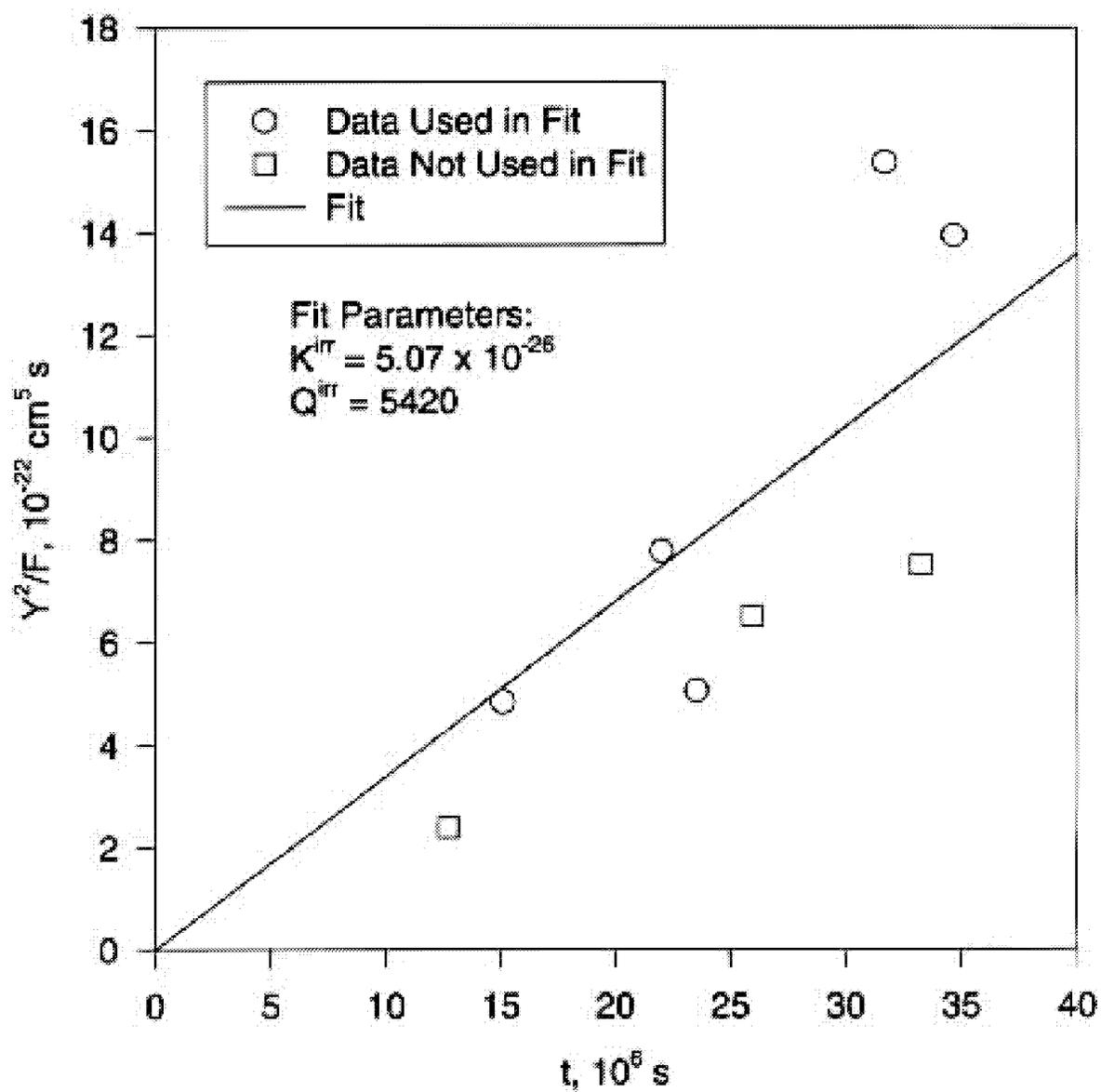


Fig. 4. Interdiffusion Correlation and Measured Interaction Widths for LEU Samples Irradiated in ORR at ~100°C

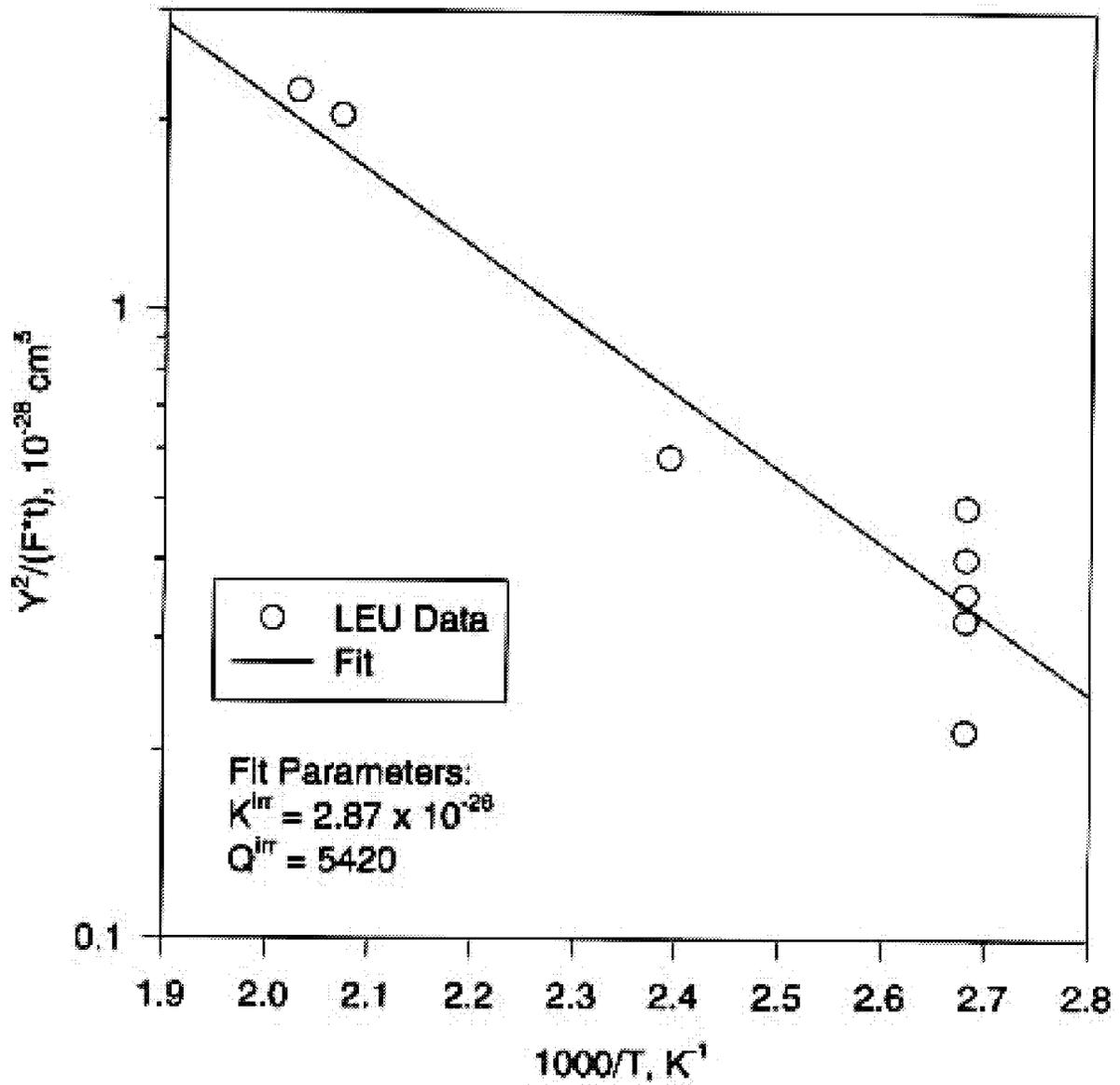


Fig. 5. Calculated and Measured Interaction Widths for LEU Samples Irradiated in ORR and HFIR at 100°C and 200°C

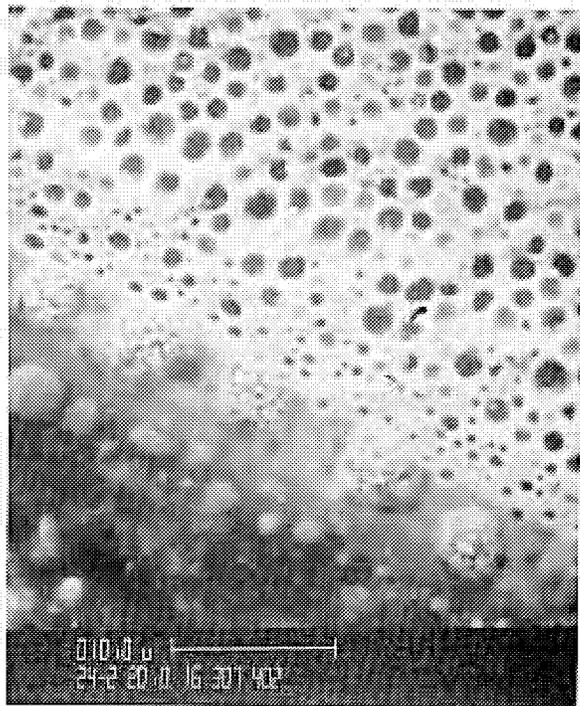


Fig. 6. Comparison of Interaction Zone Structure
Upper: LBU (70% Bu), Lower: HEU (70% Bu)

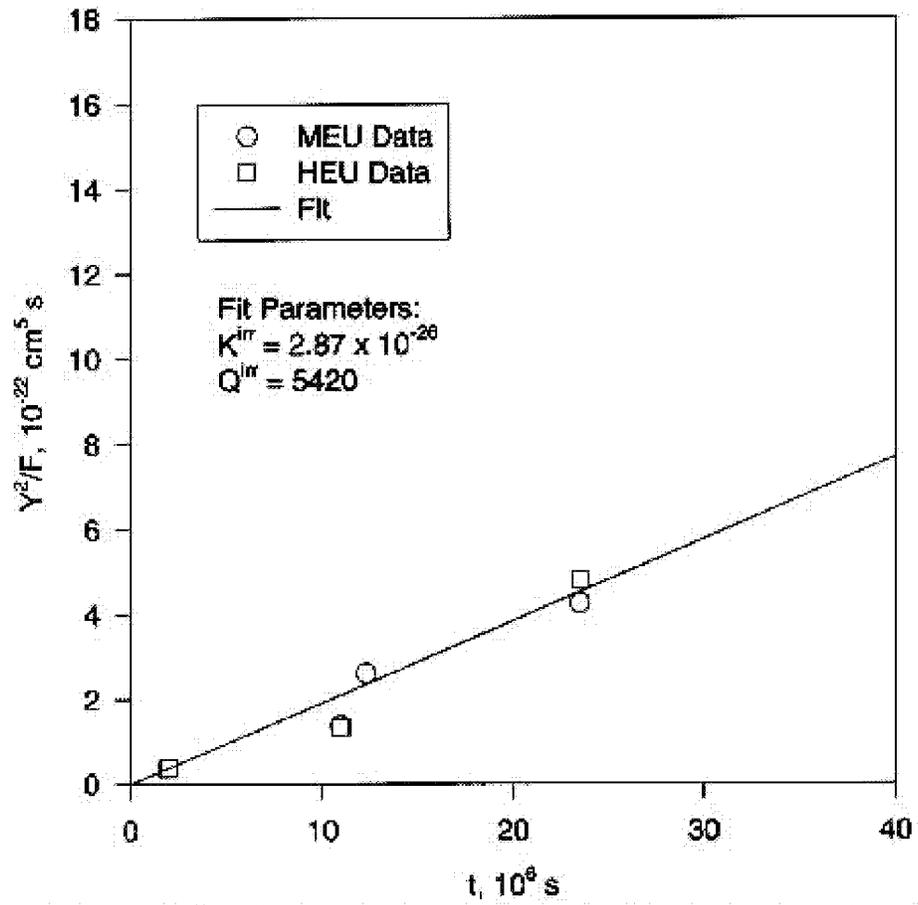


Fig. 7. Correlation and Measured Interaction Widths for High Uranium Burnup (MEU and HEU) Samples Irradiated in ORR and HFIR at 100°C

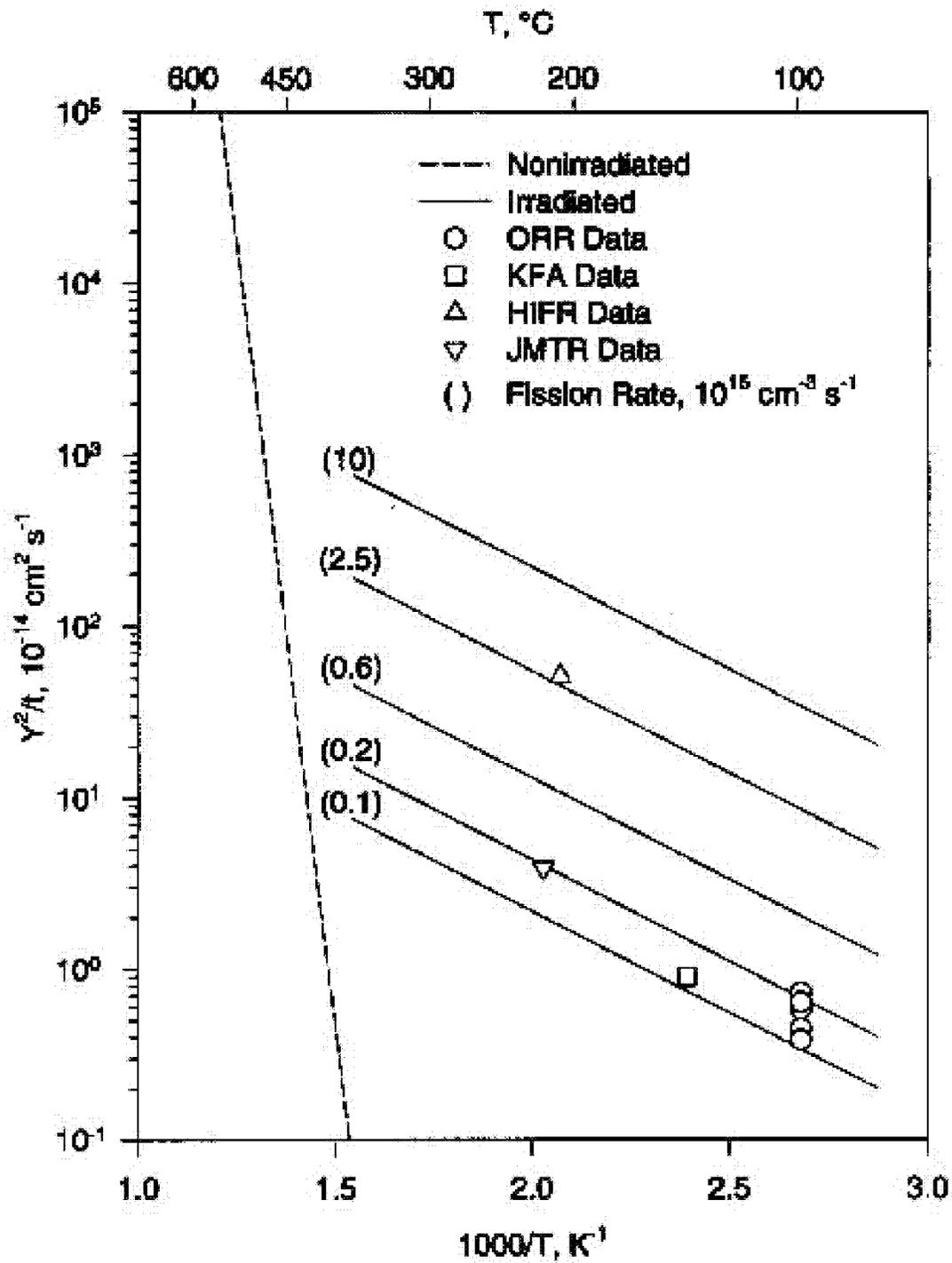
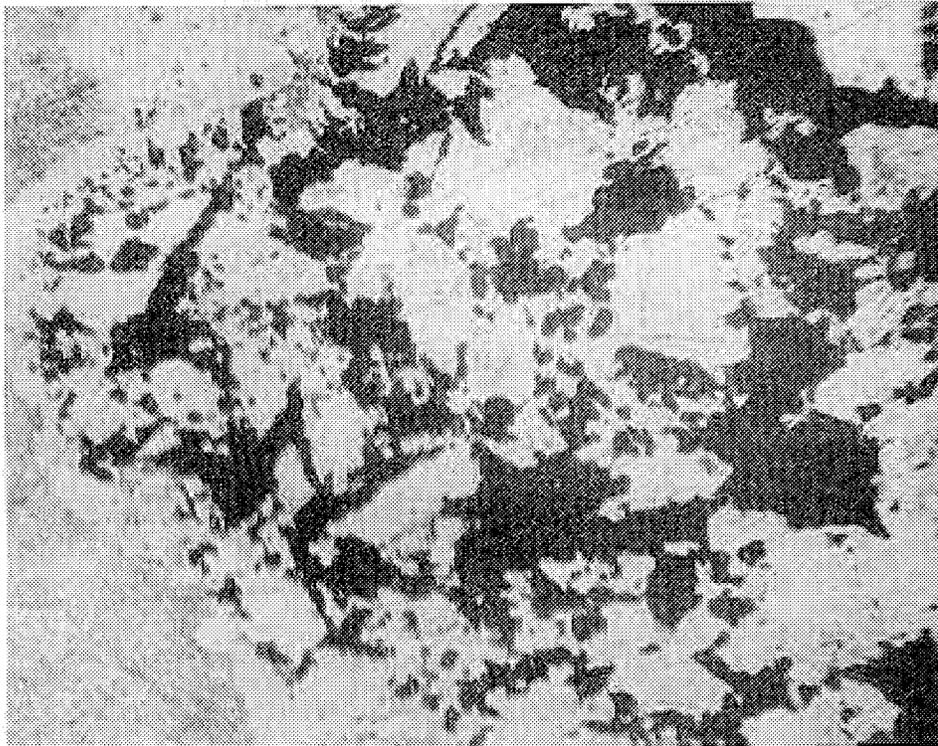


Fig. 8. Rate of U(AISI)₃ Layer Formation as a Function of Temperature and Fission Rate



HANS 3-18, 24 Days at ~300°C, LEU, ~75% Bu

(250x)



HANS 3-17, 24 Days at ~400°C, LEU, ~75% Bu

(250x)

Fig. 9. Meat Microstructure of 4.6 g cm^{-3} U_3Si_2 LEU Fuel Irradiated in HFIR at High Burnup and High Temperature

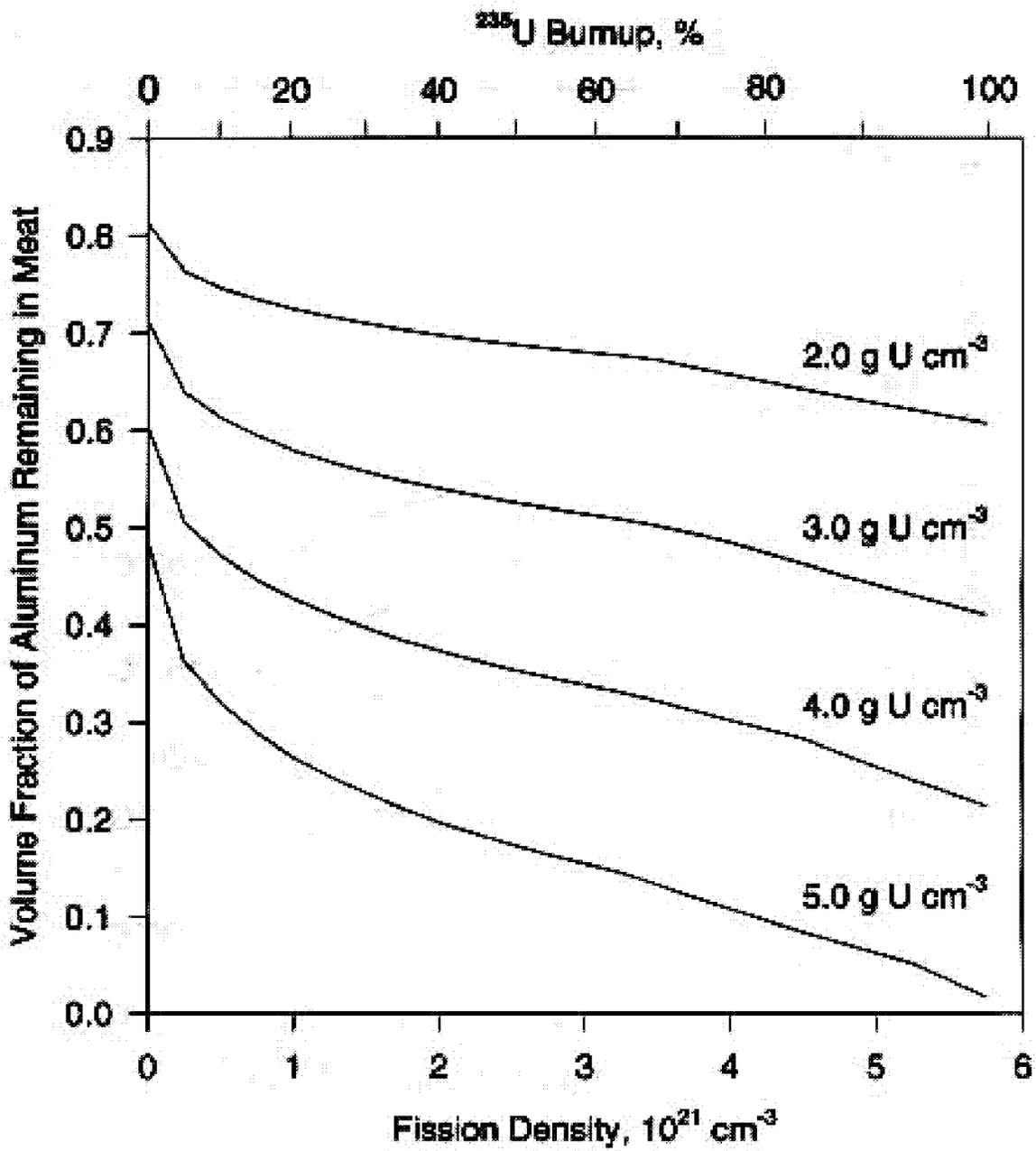


Fig. 10. Diminution of Aluminum in the Fuel Meat as a Function of Fission Density in the Fuel Particles for Various Fuel Loadings for $T = 200^\circ\text{C}$

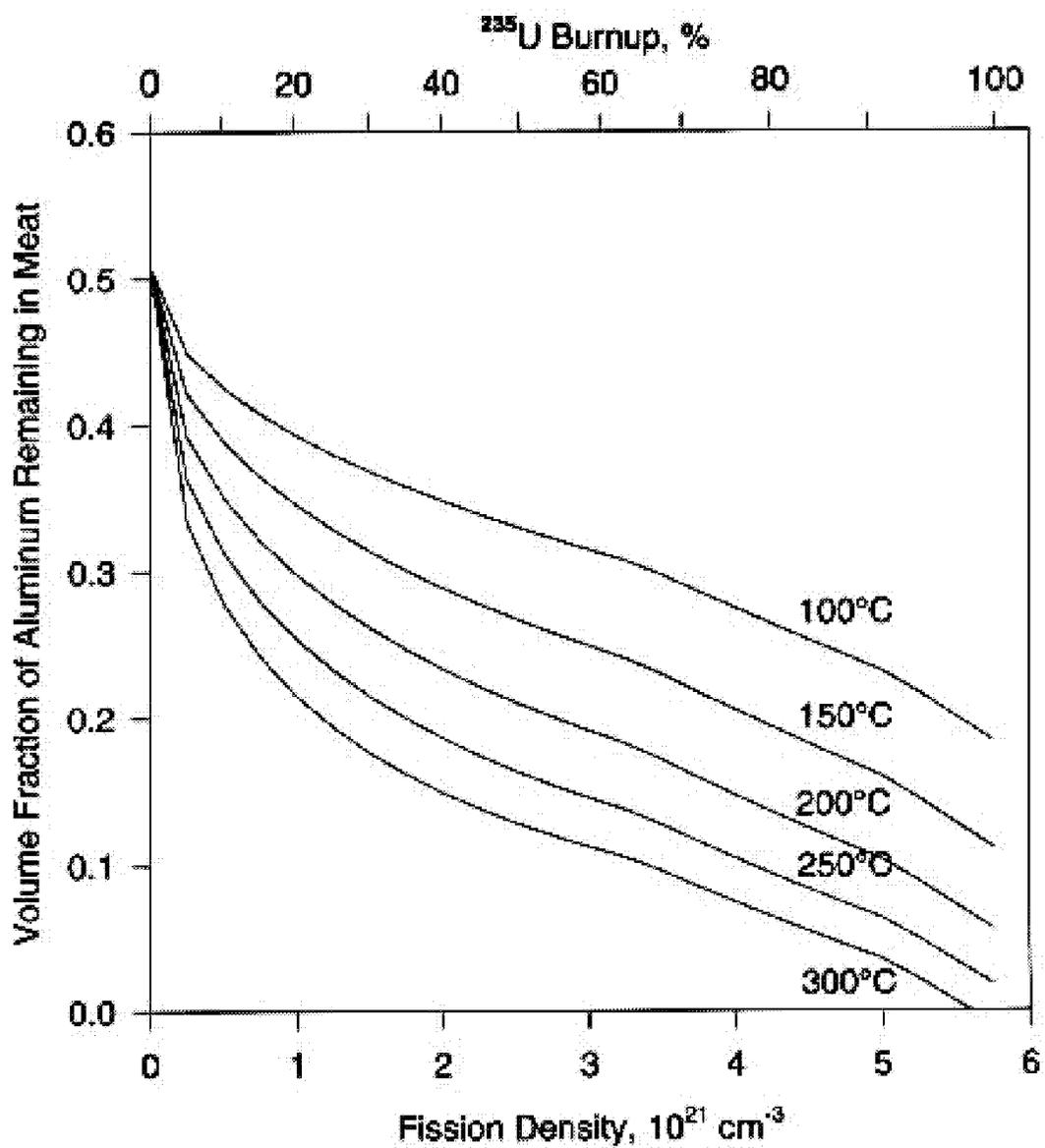


Fig. 11. Diminution of Aluminum in the Fuel Meat as a Function of Fission Density in the Fuel Particles for Various Fuel Meat Temperatures for $\rho_u = 4.8 \text{ g cm}^{-3}$