KERNFORSCHUNGSZENTRUM

KARLSRUHE

Juli 1970

KFK 1254
EUR 4318 e

Institut für Neutronenphysik und Reaktortechnik
Projekt Schneller Brüter

Some Considerations on Coated Particles, with Oxide Fuel, and Graphite and Silicon Carbide Coating, for Gas Cooled Fast Reactor Application

M. Dalle Donne, G. Schumacher

GESELLSCHAFT FÜR KERNFORSCHUNG M. B. H.
KARLSRUHE

KERNFORSCHUNGSZENTRUM KARLSRUHE

Juli 1970

KFK 1254
EUR 4318 e

Institut für Neutronenphysik und Reaktortechnik
Projekt Schneller Brüter

Some Considerations on Coated Particles, with Oxide Fuel, and Graphite and Silicon Carbide Coating, for Gas Cooled Fast Reactor Application.

by

M. Dalle Donne[x]
G. Schumacher

Gesellschaft für Kernforschung m.b.H., Karlsruhe

---

[x] Delegated by Euratom to the Karlsruhe Fast Breeder Project.

ABSTRACT

Recently, coated particles with a SiC outer coating layer have been proposed for Gas Cooled Fast Reactor application. SiC is a very fragile material. Although under fast irradiation it can creep at relatively low temperatures, a very low strain (>0.3%) can produce hairline cracks. A SiC coating layer can therefore withstand only moderate overpressures when subjected to large fast neutron exposures. In the present paper the pressure inside the particle due to gas fission products and $CO-CO_2$ is calculated. The operation temperature of the particle due to the condition strain ⩽0.3% is given as a function of SiC layer thickness in conditions typical for GCFR's application.

ZUSAMMENFASSUNG

In letzter Zeit wurden "coated particles" mit SiC-Umhüllung für die Anwendung in gasgekühlten schnellen Reaktoren vorgeschlagen. SiC ist ein sehr sprödes Material. Obwohl es unter Bestrahlung mit schnellen Neutronen schon bei relativ niedrigen Temperaturen zu Kriechen beginnt, entstehen schon bei einer sehr niedrigen Dehnung (>0,3%) Haarrisse. Eine SiC-Umhüllung kann deshalb nur mäßigen Überdrücken widerstehen, wenn sie hohen Dosen schneller Neutronen ausgesetzt ist. In der vorliegenden Arbeit wird der Druck, der im Inneren der "coated particles" durch die gasförmigen Spaltprodukte und die Bildung von $CO-CO_2$-Gas entsteht, berechnet. Die mögliche Betriebstemperatur der Partikel, die durch eine zulässige Dehnung von ⩽0,3% begrenzt ist, wird als Funktion der SiC Schichtdicke unter Bedingungen, die für einen GCFR typisch sind, errechnet.

1. INTRODUCTION

Recently Gratton et al. [1] [2] have proposed a Gas-cooled Fast Reactor having as fuel coated particles cooled by helium, which is flowing directly through a bed of loose particles. The elimination of the graphite matrix and graphite sleeves in respect of the thermal High Temperature Reactor, makes the neutron spectrum much harder, so that the reactor becomes a breeder, while the very large heat transfer surface per unit volume made available by direct cooling of the coated particles allows a very high power density in the core, required to minimize the fissile inventory. The coated particle proposed at present by Dragon for a low-enrichment thermal High Temperature Reactor has a kernel of (U, Th) O_2 with 20% porosity, 800μ diameter and a coating with an inner porous pyrocarbon layer roughly 50μ thick, an interlayer of Silicon carbide and an outer layer of dense pyrocarbon both 50μ thick [3]. The inner carbon porous layer protects the SiC layer from the recoil of fission fragments, the dense SiC layer acts as the main barrier against the diffusion of fission products while the dense outer pyrocarbon layer shrinks under irradiation and maintains the fragile SiC layer under compression. In a fast reactor, due to the very large neutron fast fluence, of the order 10^{23}nvt, almost two order of magnitude greater than in a thermal reactor, the outer pyrocarbon layer would surely crack and would not be able, toward the end of the coated particle life in core, to maintain the SiC under compression [4] [5] [6] [7] [8]. The dimensional stability of Silicon Carbide under fast neutron irradiation is much better expecially at high temperatures [9], therefore Gratton has proposed for the GCFR a coated particle where the outer pyrocarbon layer has been eliminated and the SiC layer made 100μ thick.

Released for printing, Juli 29, 1970

In this case however the SiC can, at the end of the particle life in the core, be under tension due to the internal gas pressure - gaseous fission products and CO-CO$_2$ pressure and possibly the swelling pressure of the inner pyrocarbon layer - when these pressures combined are greater than the outer pressure of the cooling gas. The data on tension rupture strength of pyrolitic SiC in the literature vary considerably, but they always lay substantially above 10^3 kg/cm^2 [10][11] [12] [13] so that the SiC can withstand the internal over-pressure without difficulty for a short time. However SiC is a very fragile material and although under irradiation it can creep at relatively low temperatures, it appears that hairline cracks are formed for relatively low amounts of creep strain (>0.3%) [14]. It seems therefore likely that this is the phenomenon limiting the pressure inside the SiC coated particle under fast irradiation. In the present paper we try to assess the pressure build-up of the gaseous fission products, the CO - CO$_2$ pressure inside the coated particle and the limitation in this pressure build-up given by a creep strain under irradiation of 0.3%. No attempt was made to assess the swelling pressure of the inner pyrocarbon layer upon the SiC, because no data are available for fast fluences typical of a fast reactor, furthermore this pressure depends very much upon the quality,density etc. of the pyrocarbon, indeed it might be even possible that, with a proper choice of the deposition parameters of the pyrocarbon this does'nt exertany swelling pressure at all on the SiC [15].

2. DESCRIPTION OF THE COATED PARTICLE

The coated Particle under consideration has a kernel of $(U_{0.8}Pu_{0.2})O_{2-y_o}$ with a 850μ diameter. This nucleus is surrounded by a pyrocarbon porous layer (buffer layer) 45μ thick and by a dense pyrocarbon layer (sealing layer) 5μ thick. This sealing layer protects the kernel from chemical attack during the deposition of the SiC layer, and should be as thin as possible to minimize the swelling pressure of the PyC against the SiC during irradiation. A 5μ thickness has been achieved in laboratory, while industrial production of the coated particles might require a thicker sealing layer. The density of the fuel is assumed to be 0.83 of the theoretical density, whilst that of the porous graphite layer is 1.1 gr/cm^3 (51.1% TD). The volume of fuel is therefore 2.669 x 10^{-4} cm^3 and the void volume in kernel and in the buffer layer is 1.126 x 10^{-4} cm^3.

With the most recent design of the Coated Particle Gas Cooled Fast Reactor /16/ the maximum fuel rating is 406 W/gr, the maximum burn-up ist 100 000 MWD/t (=11.1% Fima), the residence time of the fuel in core is 278.6 full days and the fast fluence ($E \geq 0.18$ Mev) of the particles in the region of the highest power density is 0.75 x 10^{23} nvt. The maximum hot spot temperature has been assessed to be in the fuel kernel about 950°C. The helium coolant pressure is 70 Atms.

3. CALCULATION OF GAS FISSION PRODUCTS PRESSURE

The power produced in the highest rated particles in the design mentioned above is 1W and the temperature drop in the kernel is about 40°C. The inside of the particle canbe, with good approximation for our purpose, assumed to be isothermal. This is a significant difference from the pin-type fuel where the temperature differences in the fuel are of the order of 1000-2000°C. The gas pressure build-up inside the particles is given mainly by the fission products xenon, kripton, rubidium, cesium, tellurium and cadmium.

Findlay et al. /¯17_7 have recently published their experimental data on the release of ^{85M}Kr and ^{133}Xe from uranium-plutonium dioxide. This release can be considered representative of all isotopes of Kr and Xe. Indeed Bagley and Donaldson have shown with their experiments that the fractional yields of Xe and Kr in a fast reactor are practically always the same in various conditions of burn-up and temperature /¯18_7. The data of Findlay et al.refer to stoichiometric uranium-plutonium dioxide irradiated up to 12.3% Fima, with heat ratings up to 580 W/gr. The temperature range was 550-1550°C. They found that the emission may be described by a diffusion model; the release of ^{85M}Kr and ^{133}Xe is defined between 800°C and 1550°C by the equations:

$$D^{85M}\mathrm{Kr} = 2.6 \times 10^{-9} \exp(-1.62/kT)\ \mathrm{cm}^2/\mathrm{sec} \qquad (1)$$

$$D^{133}\mathrm{Xe} = 9.2 \times 10^{-9} \exp(-1.89/kT)\ \mathrm{cm}^2/\mathrm{sec} \qquad (2)$$

Besides the diffusion coefficient, the other parameter governing the release of the gas is the surface area of the fuel per unit weight S_o. For sufficiently high burn-ups ($\geqslant$5%) and sintered fuel, all specimens attained a similar high surface area irrespective of initial characteristics. This surface area is practically independent of further increases of burn-up (up to 12.3%) and heat ratings (up to 580 W/gr). The temperature effect on this surface is given in Fig. 1 /¯17_7.

By the Fick's law of diffusion the number of atoms flowing in the unit time through a surface S is given by:

$$\frac{dn_p(t)}{dt} = SD\,\frac{dC}{dx} = \frac{SD}{X}\left[\frac{n_F(t)}{V_F} - \frac{n_p(t)}{V_p}\right] \tag{3}$$

Where the concentration gradient $\frac{dC}{dx}$ has been assumed equal to the difference of concentration in fuel and the pores divided by the average distance that the diffusing atom has to run to reach the surface of the fuel grain X. The equation of continuity is:

$$n_F(t) = Kt - n_p(t) \tag{4}$$

Where Kt is the number of atoms produced by fission at the time t of the element considered. From equations (3) and (4) one obtains:

$$\frac{dn_p(t)}{dt} = n_p(t)\,\frac{SD}{X}\left[\frac{1}{V_F} + \frac{1}{V_p}\right] + \frac{SD}{XV_F}\,Kt = -\,A\,n_p(t) + Bt \tag{5}$$

If one assumes that V_F and V_p are independent of time, than equation (5) can be analitically solved:

$$n_p(t) = \frac{B}{A}\left[t - \frac{1 - \exp(-At)}{A}\right] \tag{6}$$

(with the initial condition $n_p(0) = 0$)

However, under irradiation the kernel swells so that V_F increases and Vp decreases. We assume that this swelling is linear with time and with a rate of 1% ΔV per 1% Fima. Furthermore, in accordance with Findlay et al. suggestion, we assume S independent of time. This is, strictly speaking, only valid for large burn-ups (≥5%). Thus our solution is incorrect for low burn-ups. However we are particulary interested in the behaviour of the particle at the end of its core life, when the inside pressures are the highest and the burn-ups ≥5%. In this case our solution is correct.

Equation (5) can be written as:

$$\frac{dn_p(t)}{dt} = - n_p(t)\ \frac{SD}{X}\left(\frac{1}{V_{Fo}+at} + \frac{1}{V_{Po}-at}\right) + \frac{SDK\ t}{X(V_{Fo}+at)} \qquad (6)$$

The solution of equation (6) is:

$$n_p(t) = \frac{SDK}{X}\ f(t) \int_o^t \frac{t}{f(t)\ (V_{Fo}+ at)}\ dt$$

$$\text{with } f(t) = \left(\frac{V_{Po}\ -at}{V_{Fo}\ + at}\right)^{\frac{SD}{aX}} \qquad (7)$$

and the gas pressure inside the particle is given by:

$$p(t) = \frac{n_p(t)\ 2.2414 \times 10^4}{6.023 \times 10^{23}\ (V_{Po}-at)}\ \frac{T}{293}\ \left[\text{Atms}\right] \qquad (8)$$

The numerical constants in equations (7) and (8) are given by:

$$\left.\begin{aligned} V_{Fo} &= 2.669 \times 10^{-4}\text{cm}^3 \\ V_{Po} &= 1.126 \times 10^{-4}\text{cm}^3 \end{aligned}\right\}\ \text{see Section II}$$

$S = S_o\rho\ V_{Fo} = 11x1.126x10^{-4}xS_o=1.239x10^{-3}S_o\ cm^2$ and S_o is given by Fig. 1 as a function of irradiation temperature.

$X = \frac{2}{S_o\rho} = \frac{2}{11S_o}$. In case of a perfectly spheric fuel grain one has $X = 9/4\rho S_o$. For a cubic fuel grain: $X = 3/2\rho S_o$. In practice the form of the grain will be somewhat in between, therefore we assume $X = 2/\rho S_o$.

D is given by equations (1) and (2) for Kr and Xe as a function of irradiation temperature.

$$a = \frac{b_{max} \times V_{Fo}}{t_{max}} = \frac{0.111 \times 2.669 \times 10^{-4}}{278.6} = 1.063 \times 10^{-7} cm^3/d$$

$$\left[\frac{2.2414 \times 10^4}{6.023 \times 10^{23}} K \right] = \frac{V_{Fo} \times \rho \times \frac{238}{270} \times b_{max}}{t_{max}} Vg =$$

$$= \frac{1.126 \times 10^{-4} \times 11 \times \frac{238}{270} \times 0.111}{278.6} Vg = 1.036 \times 10^{-4} Vg\ cm^3/d$$

Vg is the volume of fission gas at 20°C and 1 Atm produced by 1 gr of metal after 1% burn-up. It is equal to 0.0155 cm^3/gr% for krypton and 0.22 cm^3/gr% for xenon [19].

Equations (7) and (8) have been solved by numerical computation. The results are given in Fig. 2 and 3. The calculated fission gas pressures are little affected by the variation of fuel volume due to swelling. Calculations performed with equation (6), where a = o, give fission gas pressures only 5 ÷ 15% lower than those of Fig. 2 and 3. Essentially this is due to the fact that, when one takes into account of fuel swelling, the less space available in the pores is partially compensated by the bigger volume of the fuel, which can then take more fission gas. The computed pressure are, however, strongly depedent on the assumed values of S_o and X. Calculations performed with other values of S_o and X show that the pressure is, in first approximation, proportional to S_o/X.
Other contributions to the fission products pressure are given by the vapour pressure of the metals cadmium, cesium, rubidium and tellurium. From equation (7) one can see that the number of atoms reaching the grain surface $n_p(t)$ is proportional to KD. The values of K for the above mentioned fission products in relation to the K of krypton have been obtained from Appendix I of [25].

The values of D for the same metals have been estimated by plotting the values of D given by equations (1) and (2) for krypton and xenon against the respective atom diameters. The diffusion coefficients of Cs, Rb and Te have been obtained by linear extrapolation at the corresponding ion diameter. This seems to be a reasonable approximation because all the atoms or ions considered have diameters greater than those of uranium or oxygen. Cd should have a much higher diffusion coefficient because it has a ion diameter equal to that of uranium, thus we can assume that the Cd vapour is evenly distributed in the whole of the particle(fuel volume and voidage) and the Cd pressure can be easily calculated once the value of K is known. For Cs and Te the pressure calculated by the Kr pressure corrected proportionally to KD would be much higher than the respective vapour pressure, this means that the vapour pressure is reached after a short time. Of course afterwards this pressure remains constant.

For temperatures below 1200°C the Rb pressure can be calculated with the proportionality factor KD. For $T \geq 1200°C$ however the pressure is limited by the amount of rubidium fission atoms available. The pressures thus calculated are always below the vapour pressure of rubidium.

The vapour pressure of the metals have been calculated by extrapolation of the equations given in /‾28_7. The calculated fission gases pressures are given in Table 2 for the temperature range 800 - 1400°C.

4. CO/CO_2 PRESSURE INSIDE THE COATED PARTICLES

1. Basic Thermodynamic Relations

Assuming the kernel of the coated particle, as an isothermal, closed system, the equilibrium pressure of the carbon oxide gas can be determined, provided that the free enthalpies for the reaction of the elements and oxides present in the system with oxygen are known. The equilibrium will be reached when the composition of the oxides is such that their oxygen partial pressures are identical.

The partial molar free enthalpies for the reaction with oxygen of the oxides of uranium-plutonium fuel $\overline{\Delta G}_{O2}$ (F) are known [20,21]. From these values the equilibrium partial pressure of the oxygen over the fuel, $[P_{O2}(F)]$, can be calculated as follows:

$$[\bar{P}_{O2}(F)] = \exp \frac{\overline{\Delta G}_{O2}(F)}{RT} \qquad (9)$$

The relation between the pressure of the carbon monoxide $[\bar{P}(CO)]$ and the equilibrium partial pressure of the oxygen in the carbon monoxide $[\bar{P}_{O2}(CO)]$ is derived from the reaction equation:

$$C + \frac{1}{2} O_2 = CO. \qquad (10)$$

This yields:

$$[\bar{P}(CO)] = [\bar{P}_{O2}(CO)]^{\frac{1}{2}} \exp \frac{-\Delta G(CO)}{RT}. \qquad (11)$$

Since at equilibrium the oxygen partial pressures must be indentical, the equilibrium pressure of carbon monoxide is:

$$[\bar{P}(CO)] = \exp \frac{\frac{1}{2}\overline{\Delta G}_{O2}(F) - \Delta G(CO)}{RT} \qquad (12)$$

The carbon dioxide content in the gas is evaluated by use of the reaction equation:

$$CO + \frac{1}{2} O_2 = CO_2 \qquad (13)$$

This yields:

$$[\bar{P}(CO_2)] = [\bar{P}(CO)] \exp \frac{\Delta G(CO) + \frac{1}{2}\overline{\Delta G}_{O2}(F) - \Delta G(CO_2)}{RT} \qquad (14)$$

The latter two relations are used to calculate the carbon oxide pressure. The ratio of equilibrium pressures of CO_2 and CO over slightly hyperstoichiometric fuel is given in Fig. 4, where y is equal to the oxygen/metal ratio minus 2.

2. Calculation of the Carbon Oxide Pressure as a Function of Burnup

At the beginning of irradiation the gas pressure in the fuel is formed in accordance with the free enthalpies. This pressure is dependent on the stoichiometry of the fuel and on temperature. The result of the computation is shown in Fig. 5 for the temperature range from 900 - 1400°C. It can be seen that for a slightly substoichiometric fuel the pressure remains below 5 atm. Stoichiometric fuel causes pressures between 3 and 120 atm. For hyperstoichiometric fuel the equilibrium pressure of the carbon oxide gases is very high. It amounts to as much as some 1000 atm. for a O-to-M ratio of 2.001 at 900°C.

Evidently, the pressure level attained in a coated particle is dependent on the pore volume and the oxygen supplied. Since oxygen is released from the plutonium oxide due to fission of plutonium, the amount of oxygen supplied is increased with burnup. The following calculations will yield the amount of oxygen which is available for the formation of carbon oxides as well as the resulting pressure level.

In the stoichiometric fuel the number Z_O of oxygen atoms released by fission is:

$$Z_O = 2bZ_f \tag{15}$$

where "b" is the burnup and Z_f the number of fuel atoms in the kernel.

A portion Z_O^{fp} of the oxygen atoms is consumed by the formation of stable fission product oxides.

$$Z_O^{fp} = b\ Z_f \cdot 10^{-2} \cdot \Sigma S_K\ Y_K \tag{16}$$

Y_k is the number of atoms of the fission product k related to 100 fissions of Pu-239 after 100 days of decay /22/.

S_K is the oxygen-to-metal-ratio (O/M) of the kth fission product oxide in the fuel.

The sum $\Sigma\ S_K Y_K$ includes only those fission products wich form oxides of greater stability than CO. Due to their stronger negative free enthalpy of reaction these oxides are shown in Fig. 6 above the curve for CO /23/. They are the oxides of lanthanides and of zirconium.

Starting from stoichiometric fuel, the number of oxygen atoms which are left for the formation of carbon oxide are given by:

$$Z_O^C = Z_O - Z_O^{fp} = b\ Z_f \cdot 10^{-2} \cdot (200 - \Sigma\ S_K\ Y_K) \tag{17}$$

This oxygen allows the formation of a carbon oxide gas and an oxidation state of the fuel which corresponds to the pressure of this gas. Since the equilibrium partial pressure of the slightly hyperstoichiometric fuel is very high already, the state of oxidation of the fuel is subjected to only negligible variations up to high pressures. Consequently, the oxygen which is hyperstoichiometrically bound in the fuel can be neglected in the calculation of the pressure. Assuming at first that only CO and no CO_2 is formed, the pressure is obtained from the formula:

$$P(CO) = \frac{2.24 \cdot 10^4}{V_p \; L} \cdot \frac{T}{T_o} \cdot Z_O^C \qquad (18)$$

where V_P = total pore volume
L = Avogadro number
T = absolute temperature
T_o = room temperature

Having calculated the number of fuel atoms, Z_f, we obtain

$$P(CO) = 8.28 \cdot 10^{-1} \cdot b(200-\Sigma \; S_K \; Y_K) \cdot \rho_F \cdot \frac{V_F}{V_P} \frac{T}{T_o} \qquad (19)$$

where ρ_F = fuel density (= 0.83ρ)
V_F = fuel volume.

For a higher burnup, a pore volume, which is dependent on "b", must be taken into account as a result of fuel swelling. Like in equation (6) we assume:

$$V_P = V_{Po} - bV_{Fo} = V_{Po}-at \qquad (20)$$

Now, only the sum $\Sigma \; S_K \; Y_K$ remains to be calculated. Taking into account that the rare earth elements contained in $(U, Pu)O_2$ are dissolved in the tetravalent state and that they bind the oxygen in the temperature range considered more strongly than carbon /24/, we obtain from Table 1:

$$S_K Y_K = 146.4$$

<u>Table 1:</u>

fission product	Ce	Pr	Nd	Ba	Sm	Pm	La	Sr	Y	Zr
oxide	CeO_2	PrO_2	Nd_2O_3	BaO	SmO_2	PmO_2	LaO_2	SrO	YO_2	ZrO_2
Y_K	15,7	5,3	15,8	6,3	5,04	1,94	5,78	3,9	1,58	21
$S_K \; Y_K$	30,3	10,6	23,65	6,31	10,08	3,88	12,56	3,9	3,16	42

The result of the calculation is shown in Fig. 7. The upper family of curves is obtained through calculation of the pressure from the oxygen balance according to Eq. (18) and by assumption that only CO is formed. Actually, a gas mixture of CO and CO_2 is formed at a lower pressure, the composition of which is given in Fig. 4 as a function of temperature for various stoichiometric parameters y. The actual pressure of the gas mixture corresponding to the pressure calculated with Eq. (18) in the upper family of curves of Fig. 7 is found by varying y until the oxygen balance is equalized for the respective gas composition of CO and CO_2 and it is shown by the lower family of curves given in Fig. 7

A means of pressure reduction is provided by the use of substoichiometric fuel. When a fuel composed of $(U,Pu)O_{2-y_o}$ is used, this fuel become stoichiometric at a given burnup b_s. This burnup is expressed by the equation:

$$b_s = \frac{y_o}{2-10^{-2}\cdot\Sigma S_K\ Y_K} \qquad (21)$$

Up to this burnup the fuel remains substoichiometric and, thus, the carbon oxide pressure is below 5 atm. The CO-CO_2-pressure which prevails after 11% of burn-up is shown in Fig. 8 as a function of y_o. A fuel composed of $(U,Pu)O_{1.94}$ remains substoichiometric up to 11% of burnup. This result is in accordance with the experiments and calculations of Davies et al. [25]. A reduction of $(U_{0.8}Pu_{0.2})O_2$ to $(U_{0.8}Pu_{0.2})O_{1.94}$ is possible in laboratory with negligille losses of plutonium by means of reduction with hydrogen [26]. Flowers and Horsley obtained $(U_{0.75}Pu_{0.25})O_{1.944}$ by reduction of stochiometric oxide at 1500°C with CO at 1 Atm in a container of graphite [27]. For temperatures below 1100°C one must take into account of the effect of the fission product molybdenum, which forms MoO_2, for which $S_KY_K = 47$. When the equilibrium partial pressure of CO/CO_2 over MoO_2 is attained, the pressure remains constant until all molybdenum is oxidized (horizontal lines in Fig.8).

5. OPERATION TEMPERATURE AND SiC LAYER THICKNESS FOR CREEP STRAIN $\leqslant 0.3\%$

Table 2 shows the fission gases and CO/CO_2 pressure for $(U_{0.8}Pu_{0.2}O)_{1.95}$ at 100 000 MWD/t in the temperature range 800 - 1000°C with the assumption that the voidage in the buffer layer of porous PyC is 100% available to take the gases. Horsley suggests that in reality only 50% of this space is available [15]. Table 3 shows the same pressures calculated in the case of 50% space availability in the buffer layer. The Cs and Te pressures remain invariated because they are the vapour pressures of these metals. The pressures of Kr, Xe, Rb ($T<1200^\circ C$) and CO/CO_2 have been calculated by multiplying the values of Table 2 with the voidage volume ratio at 11.1% Fima:

$$\frac{0.1126 - 0.111 \times 0.2669}{0.1126 - 0.111 \times 0.2669 - \frac{0.05791}{2}} = 1.536$$

and the pressures of Cd and Rb ($T\geqslant 1200^\circ C$) by multiplying with the total volume ratio (fuel + voidage):

$$\frac{0.1126 + 0.2669}{0.1126 + 0.2669 - \frac{0.05791}{2}} = 1.083$$

The total gas pressures in the two cases are shown by Fig. 9 as well. The strong decrease of gas pressure below 1000°C is given by the reduction of CO/CO_2 pressure due to the fission product molybdenum, while the other strong decrease between 1300 and 1100°C is given by the smaller surface of fuel per unit weight (see Fig. 1).

Price et al. have estimated the creep constant of pyrolitic SiC under irradiation [14]. The irradiations were performed at 650°C to a neutron dosis of 3.8×10^{21} nvt ($E\geqslant 0.18$Mev) and at 900°C to 4.2×10^{21} nvt ($E\geqslant 0.18$Mev). Assuming that the creep rate is a linear function of stress:

$$\xi = K_o \sigma \phi t \qquad (22)$$

and that the samples failed on reaching their fracture stress, they estimated at 650°C K_o to be between 1.5 and 2×10^{-9} $(\text{psi})^{-1}(10^{20}\text{nvt})^{-1}$ and to be less than $3 \times 10^{-9}(\text{psi})^{-1}(10^{20}\text{nvt})^{-1}$ at 900°C. In our calculation we assume, pessimistically, that Ko is equal to 3×10^{-9} $(\text{psi})^{-1}(10^{20}\text{nvt})^{-1} = 4.41 \times 10^{-8}$ $(\text{Atms})^{-1}(10^{20}\text{nvt})^{-1}$. Furthermore we assume that:

- K_o is constant up to 1400°C.
  This seems reasonable because we are considering essentially radiation induced creep. Temperature induced creep should be smaller at the temperatures considered, although above 1000°C it might not be negligible /‾29_7.
- K_o is constant up to $\phi t = 0.75 \times 10^{23}$nvt ($E \geq 0.18$MeV).
  This means an estrapolation of 20 times in respect of the measured values, but it is the only one possible because no data at higher fast neutrons exposures are available.

Price et al. found also that SiC could withstand a creep strain of 0.3%, while samples with 0.37% strain presented hairline cracks. We shall therefore calculate from equation (22) the stress σ which produce a strain of 0.3%. If we assume, again pessimistically, that the pressure build up inside the particle is linear with time and the outer helium pressure is 70Atms, then the average pressure differential ΔP_m between pressure inside the particle and outside pressure - during the period when this inside pressure is higher than the outside one - and the time (in terms of ϕt) during which this occurs, can be easily calculated (see Table 4). The value of ΔP_m is independent from the fact that helium can diffuse or not inside the particle during the initial period when the inner pressure is smaller than the outer pressure, because when the inner pressure becomes greater than the outer helium pressure, the helium diffuses again out of the particle.

"s" is the thickness of the SiC layer required by equation (22) for the condition $\xi \leqslant 0.3\%$ and "r" is the inner radius of the SiC layer.

Table 4 gives the relationship between P_{tot}, pressure inside the particle at 100 000 MWD/t, and "s", Tables 2 and 3 the relationship between P_{tot} and the particle temperature. Fig. 9 shows the thickness "s" as function of particle temperature, as obtained by the values of Tables 2, 3 and 4. With $(U_{0.8}Pu_{0.2}O)_{1.95}$ and a maximum burn-up of 100 000 MWD/t, an operation temperature of 1100°C would require a SiC layer of either 12 or 50µm, when the space in the buffer layer is 100% or 50% available, respectively.

6. CONCLUSIONS

No definitive conclusions are possible at this stage, essentially because no experimental data are available on the behaviour of pyrolitic carbon and SiC at fast neutron exposures typical of a GCFR, i.e. $\phi t = 0.75 \times 10^{23}$ nvt ($E \geqslant 0.18$ Mev). However, the idea of using SiC as the pressure vessel of the particle for GCFR application seems promising because of the very good dimensional stability of SiC under fast irradiation, particularly at high temperatures.

Some tentative conclusions can be drawn:

1. As far as strength of the SiC layer is concerned, the creep seems to be the limiting condition rather than the short time stress. At 1100°C and 100 000 MWD/t a SiC layer of 50μm might be sufficient, rather than the 100μm originally suggested [1] [2], provided that:

- the fuel is initially (i.e. at zero burn-up) substoichiometric to reduce the CO/CO_2 pressure build-up. $(U_{0.8}Pu_{0.2}O)_{1.95}$ gives sufficiently low CO/CO_2 pressures and can be obtained from stoichiometric oxide by simple reduction with CO.
- the swelling pressure under irradiation of the inner dense pyrolitic carbon sealing layer is small, possibly has been eliminated altogether. A problem which might arise, when the sealing layer is cracked by the fast irradiation, is that the fuel would react and damage the SiC layer, this is particularly effective in presence of a temperature gradient between two opposite zones of the inner surface of the SiC layer - Amoeba effect, unless a protective SiO_2 layer is formed.
- the outer and inner surface of the SiC layer is very smooth. SiC is a very fragile material, lacking of plasticity, therefore stress concentrations are possible in corrispondence of geometrical disuniformities.

- the outer surface of the SiC is not corroded by impurities contained in the helium coolant. Again, a protective layer of SiO_2 can be deposited on the outer surface and maintained there by a convenient oxidizing atmosphere - for instance a few % of CO_2 in helium.

2. The reduction of the SiC layer thickness from 100μm to 50μm has as a consequence an improvement of the breeding ratio from 1.2 to about 1.3, and of the doubling time from 30 to about 20 years. It is therefore very important from a strategical point view and in reducing fuel cycle costs.

3. A 1100°C temperature on the coated particle means an helium mixed mean temperature at reactor outlet of 850°C, which is already very interesting for a gas turbine cycle. In this case the inner tube of the fuel element cannot be of steel, but rather should be made of a ceramic material, for instance silicon carbide.

ACKNOWLEDGMENT

The authors wish to thank Mr. G.W. Horsley and M. Bober for the many useful suggestions and discussions.

NOMENCLATURE

A = $\frac{SD}{X}\left[\frac{1}{V_F}+\frac{1}{V_P}\right]$ [sec^{-1}]

a = fuel volume swelling per unit time [cm^3/sec]

B = $\frac{SDK}{XV_F}$ [number of atoms/sec^2]

b = burn up = ratio of atoms fissioned to initial heavy metals atoms

b_s = burn up at which the fuel becomes stoichiometric by the released oxygen

b_{max} = maximum burn up, corresponding to 100 000 MWD/t

$\frac{dC}{dx}$ = atoms concentration gradient [number of atoms/cm^4]

D = diffusion coefficient [cm^2/sec]

$\overline{\Delta G}_{O2}(F)$ = partial molar free enthalpy of the oxygen in the fuel [cal/mol]

ΔG (CO) = free enthalpy of formation of CO [cal/mol]

L = Avogadro number

K = number of atoms produced by fission in the fuel kernel per unit of time [number of atoms /sec]

K_o = creep constant [$\text{Atms}^{-1}(\text{nvt})^{-1}$]

k = Boltzmann constant = 8.61×10^{-5} ev/°K

$n_F(t)$ = number of atoms contained in the fuel kernel at the time t [number of atoms]

$n_p(t)$ = number of atoms in the pores inside the particle at the time t [number of atoms]

P_{Cd} = pressure due to atoms of cadmium inside the particle at 100 000 MWD/t [Atms]

P_{Cs} = pressure due to atoms of cesium inside the particle at 100 000 MWD/t [Atms]

P_{Kr} = pressure due to atoms of krypton inside the particle at 100 000 MWD/t [Atms]

P_{Rb} = pressure due to atoms of rubidium inside the particle at 100 000 MWD/t [Atms]

P_{Te} = pressure due to atoms of tellurium inside the particle at 100 000 MWD/t [Atms]

P_{Xe} = pressure due to atoms of xenon inside the particle at 100 000 MWD/t [Atms]

P_{CO/CO_2} = pressure due to atoms of CO/CO_2 inside the particle at 100 000 MWD/t [Atms]

$P_{\text{fission products}}$ = $P_{Cd} + P_{Cs} + P_{Kr} + P_{Rb} + P_{Te} + P_{Xe}$ [Atms]

P_{tot} = $P_{\text{fission products}} + P_{CO/CO_2}$ [Atms]

ΔP_m = average pressure differential between pressure inside the particle and outside helium pressure during the time when the internal pressure is higher than the outer pressure [Atms]

$[P(CO)]$ = equilibrium pressure of CO [Atms]

$[P(CO_2)]$ = equilibrium pressure of CO_2 [Atms]

$[P_{O2}(F)]$ = equilibrium partial pressure of oxygen over the fuel [Atms]

$[P_{O2}(CO)]$ = equilibrium partial pressure of oxygen in CO [Atms]

$p(t)$ = Xe and Kr pressure inside the particle at the time t [Atms]

r = inner radius of SiC coating layer [µm]

S = $S_o \rho V_{Fo}$ = total surface of the fuel in the particle kernel $[\text{cm}^2]$

S_o = surface of the fuel per unit weight $[\text{cm}^2/\text{gr}]$

S_K = O/M ratio of the Kth stable fission product oxide

s = thickness of SiC coating layer [µm]

T = particle temperature [°K]

T_o = room temperature [°K]

t = time [sec]

t_{max} = time corresponding to a burnup of 100 000 MWD/t [sec]

V_F = fuel volume in the particle kernel $[\text{cm}^3]$

V_{Fo} = fuel volume in the particle kernel for t = o $[\text{cm}^3]$

V_g = volume of fission gas at 20°C and 1 Atms produced by 1 gr of metal fuel after 1% burn-up [cm^3/gr%]

Z_f = number of fuel atoms in the particle kernel [number of atoms]

Z_O = number of oxygen atoms released by fission [number of atoms]

Z_O^C = number of oxygen atoms which form CO [number of atoms]

Z_O^{fp} = number of oxygen atoms which form stable fission product oxides [number of atoms]

ϕ = neutron flux [neutrons/cm^2sec]

Y_K = number of atoms of the fission product K related to 100 fissions of Pu239 after 100 days of decay

y = O/M-2, departure from the stoichiometric state of the fuel

y_o = y at time $t = o$

ξ = creep strain

ρ = theoretical density of fuel = 11gr/cm^3

ρ_F = density of the fuel = 0.83ρ [gr/cm^3]

σ = stress in SiC coating layer [Atms]

Table 2: Gas pressure inside the particle for $U_{0.8}Pu_{0.2}O_{1.95}$ (initial), 11.1% burn-up and 100% availability of space in buffer layer.

T(°C)	P_{Kr}	P_{Xe}	P_{Rb}	P_{Cs} (vapour pressure)	P_{Te} (vapour pressure)	P_{Cd}[**]	$P_{fission\ products}$	P_{CO/CO_2}	P_{tot} (Atms)
800	0.03	0.1	0.08[*]	2.03	0.15	1.49	3.88	3	6.9
900	0.09	0.33	0.24[*]	3.75	0.43	1.63	6.47	18	24.5
1000	0.27	1.16	0.69[*]	6.25	1.50	1.77	11.6	63	74.6
1100	0.84	4.61	2.19[*]	9.58	2.15	1.91	21.3	78.5	99.8
1200	2.55	18.5	5.86[**]	13.8	3.94	2.05	46.6	95.8	142
1300	5.43	61.8	6.25[**]	18.8	6.55	2.19	101	114	215
1400	6.51	89.3	6.65[**]	24.5	10.1	2.32	139	133	272

Table 3: Gas pressure inside the particle for $U_{0.8}Pu_{0.2}O_{1.95}$ (initial), 11.1% Burn-up and 50% availability of space in buffer layer.

T(°C)	P_{Kr}	P_{Xe}	P_{Rb}	P_{Cs} (vapour pressure)	P_{Te} (vapour pressure)	P_{Cd}[**]	$P_{fission\ products}$	P_{CO/CO_2}	P_{tot} (Atms)
800	0.05	0.15	0.12[*]	2.03	0.15	1.61	4.11	4.61	8.7
900	0.14	0.51	0.38[*]	3.75	0.43	1.76	6.97	27.7	34.6
1000	0.41	1.78	1.06[*]	6.25	1.50	1.92	12.9	98.3	111
1100	1.29	7.08	3.36[*]	9.58	2.15	2.07	25.5	121	146
1200	3.92	28.4	6.34[**]	13.8	3.94	2.22	58.6	147	206
1300	8.34	94.9	6.77[**]	18.8	6.55	2.37	138	175	313
1400	10.00	137	7.20[**]	24.5	10.1	2.51	191	204	395

[*] limited by the product DK

[**] limited by the number of atoms available (K)

Table 4: Calculation of the SiC layer thickness as a function of the total pressure inside the particle at 100 000 MWD/t.

P_{tot} [Atms]	ΔP_m [Atms]	ϕt $\times 10^{-23}$ [nvt]	$\sigma = \xi/K\phi t = 68/\phi t \times 10^{-23}$ [Atms]	$s = r\left(\sqrt{\frac{\Delta P_m}{\sigma} + 1} - 1\right)$ [µm]
70	0	0	0	0
80	5	0.0935	727	1.6
100	15	0.225	302	11.6
120	25	0.312	218	26.5
140	35	0.373	182	43.7
160	45	0.420	162	61.9
180	55	0.455	149	80.8
200	65	0.485	140	99.8
220	75	0.509	134	118

REFERENCES

[1] C.P. Gratton et al., "A Gas-Cooled Fast Reactor Using Coated Particle Fuel", J. of Brit. Nucl. En. Soc. 7, 233-242, July 1968.

[2] C.P. Gratton et al., "A Gas-Cooled Fast Reactor with Direct Cycle Potential" SM-111/67, IAEA Conf. Jülich, October 1968.

[3] L.W. Graham, "The Development and Performance of HTR Core Materials", ORNL Gas Cooled Reactor and Molten Salt Reactor Information Meetings, Conf. 700-401.

[4] J.C. Bokros, G.L. Gutheri, R.W. Dunlap and A.S. Schwartz, "Radiation Induced Dimensional changes and Creep in Carbonaceous Materials", GA 8700, August 30, 1968 (J.Nucl.Mat. 31,25, 1969).

[5] M.R. Everett, R. Blackstone, L.W. Graham and R.Manzel, "Dimensional Changes of High-Temperature Reactor Core Materials", Paper presented at the Euratom Meeting on the effect of fast neutron irradiation at temperatures above 600°C on the physical and mechanical properties of graphite and pyrocarbons, Brussels, Belgium, May 5 - 6, 1969.

[6] "The Dragon - KFA - Euratom Graphite Irradiation Experiment in H.F.R. Petten", Compiled by R.Blackstone and H.J.B. Lucas Myebse. RCN-Int-69-088.

[7] W. Delle, "Results of Graphite and Pyrocarbon Irradiations in the Dounreay Fast Reactor", Paper presented at Euratom Meeting on the effect of fast neutron irradiation at temperatures above 600°C on the physical and mechanical properties of graphite and pyrocarbons, Brussel, Belgium, May 5 - 6, 1969.

[8] J.C. Bokros and K. Koyama, "Interpretation of Dimensional Changes Caused in Pyrolytic Carbon by High-Fluence Neutron Irradiation", GA 9600, June 1, 1969.

[9] R.J. Price, "Effects of Fast-Neutron Irradiation on Pyrolytic Silicon Carbide", J.Nucl.Mat. 33, 17, 1969.

[10] K. Drittler, Communication Dragon Fuel Symposium, Bournemouth, November, 1969.

[11] T.D. Gulden, "Mechanical Properties of Pyrocrystalline SiC", GA - 9075, 1968.
T.D. Gulden, "Deposition and Microstructure of Vapor-Deposited Silicon Carbide", J. Am. Ceram. Soc. 51, 424, 1969.

[12] R.J. Price, "Structure and Properties of Pyrolytic Silicon Carbide", GA - 8883, 1968.

[13] P. Popper and J. Mohyuddin, "The Preparation and Properties of Pyrolytic Silicon Carbide", in "Special Ceramics 1964", P. Popper (ed) Academic Press, London and New York, 1965, p.45.

[14] R.J. Price, T.D. Gulden and J.L. Kaae, "Properties of Silicon Carbide Relevants to its Performance as a Coating for High Temperatures Nuclear Fuel Particles", GAMD 8415, March 1968.

[15] G.W. Horsley, Private Communication, 1970.

[16] D.S. Hughes, Internal Winfrith Report, 1970.

[17] J.R. Findlay, M.J. Waterman, R.H. Brooks and R.G. Taylor, "The Emission of Fission Products from Uranium-Plutonium Dioxide during Irradiation to High Burn-up", J. Nucl.Mat. 35, 1, 14-23, April 1970.

[18] K.Q. Bagley and D.M. Donaldson, "Fission Gas Release from Mixed Oxide Fuels", Plutonium 1965, Third International Conference on Plutonium, 1965.

/¯19_7 D. Geithoff, Karlsruhe, Private Communication, 1970

/¯20_7 Technical Reports Series No. 79. The Plutonium-Oxygen and Uranium-Plutonium-Oxygen Systems: A Thermochemical Assessment, IAEA Vienna, 1967

/¯21_7 M.H. Rand, T.L. Markin, "The Thermodynamics Aspects of $(U,Pu)O_2$ Solid Solutions and their Use as Nuclear Fuels",Thermodynamics of Nucl. Mat., Proc. IAEA Symp. Wien, 637 (1967)

/¯22_7 I.F. Croall, "Yields from Neutron Induced Fission" AERE-R 5086

/¯23_7 H. Beißwenger and G. Schumacher, Internal Karlsruhe Report, 1964

/¯24_7 H. Holleck, H. Kleykamp, "Zur Stöchiometrieänderung in einem oxidischen Brennelement bei hohem Abbrand", To be published, KFK-Report.

/¯25_7 J.H. Davies, F.T. Ewart and R.G. Taylor, "The Effect of Burnup on the O/M Ratio of Irradiated $(U,Pu)O_2$ and PuO_2" AERE-R 6264, December 1969

/¯26_7 C. Sari, U. Benedict, H. Blank, "A Study of Ternary System UO_2-PuO_2-Pu_2O_3", J.Nucl. Mat. 35, 3, 267-277, June 1970

/¯27_7 R.H. Flowers and G.W. Horsley, "The Influence of Oxide Kernels on the Manufacture and Performance of Coated Particle Fuel", AERE - R 5 949, 1968

/¯28_7 O. Kubaschewski and E.LL. Evans, Metallurgical Thermochemistry. Pergamon Press, New York, London, 1958

/¯29_7 P. Marshall and R.B. Jones, "Creep in Silicon Carbide", Powder Metallurgy, 12, 23, 193-208, 1969

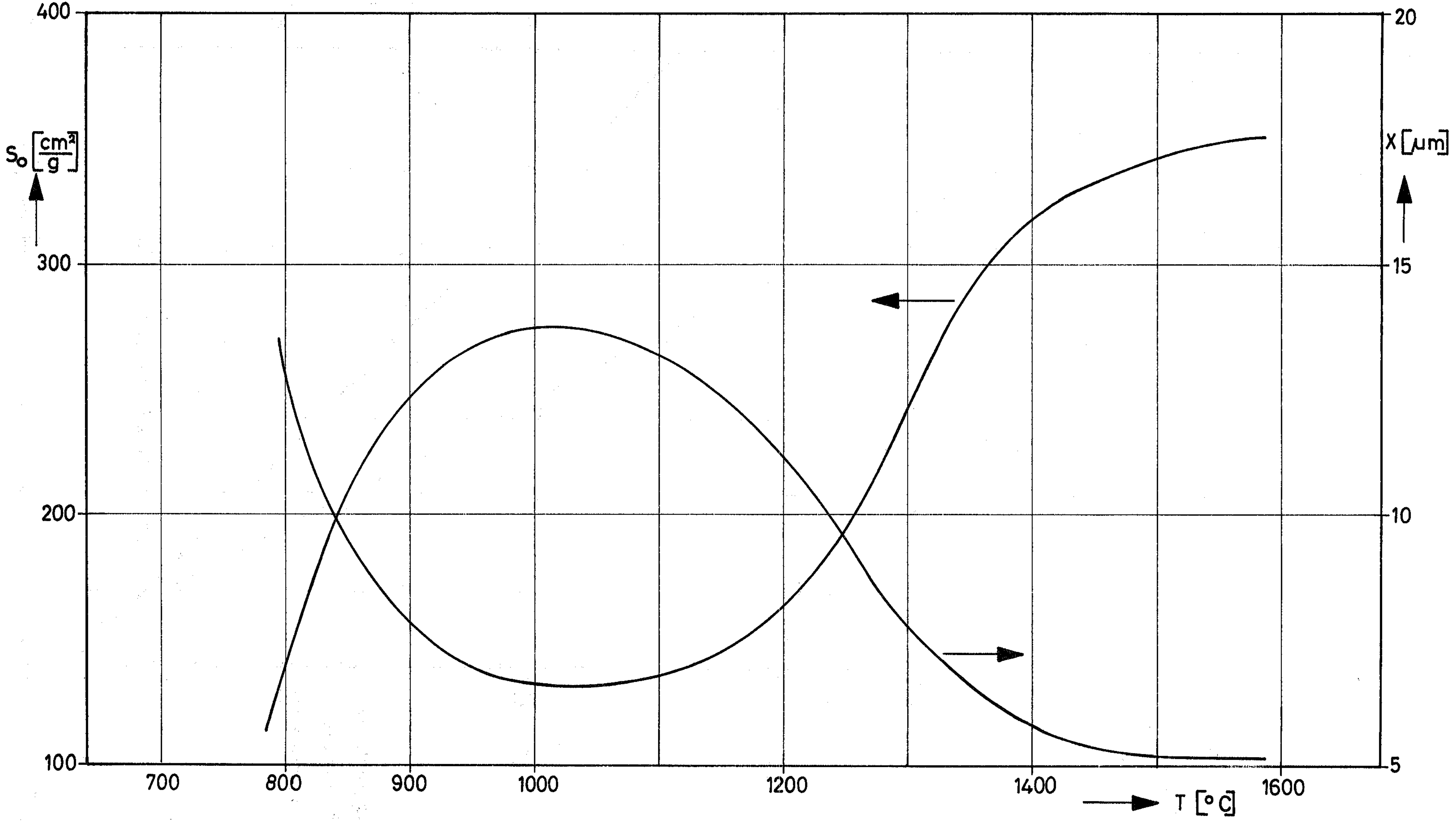

Fig.1: Surface area of irradiated (U,Pu) O_2 at high burn-ups[17]. X is the average distance that a diffusing atom has to run to reach the surface of the fuel grain.

$$X = \frac{2}{S_o \varrho}$$

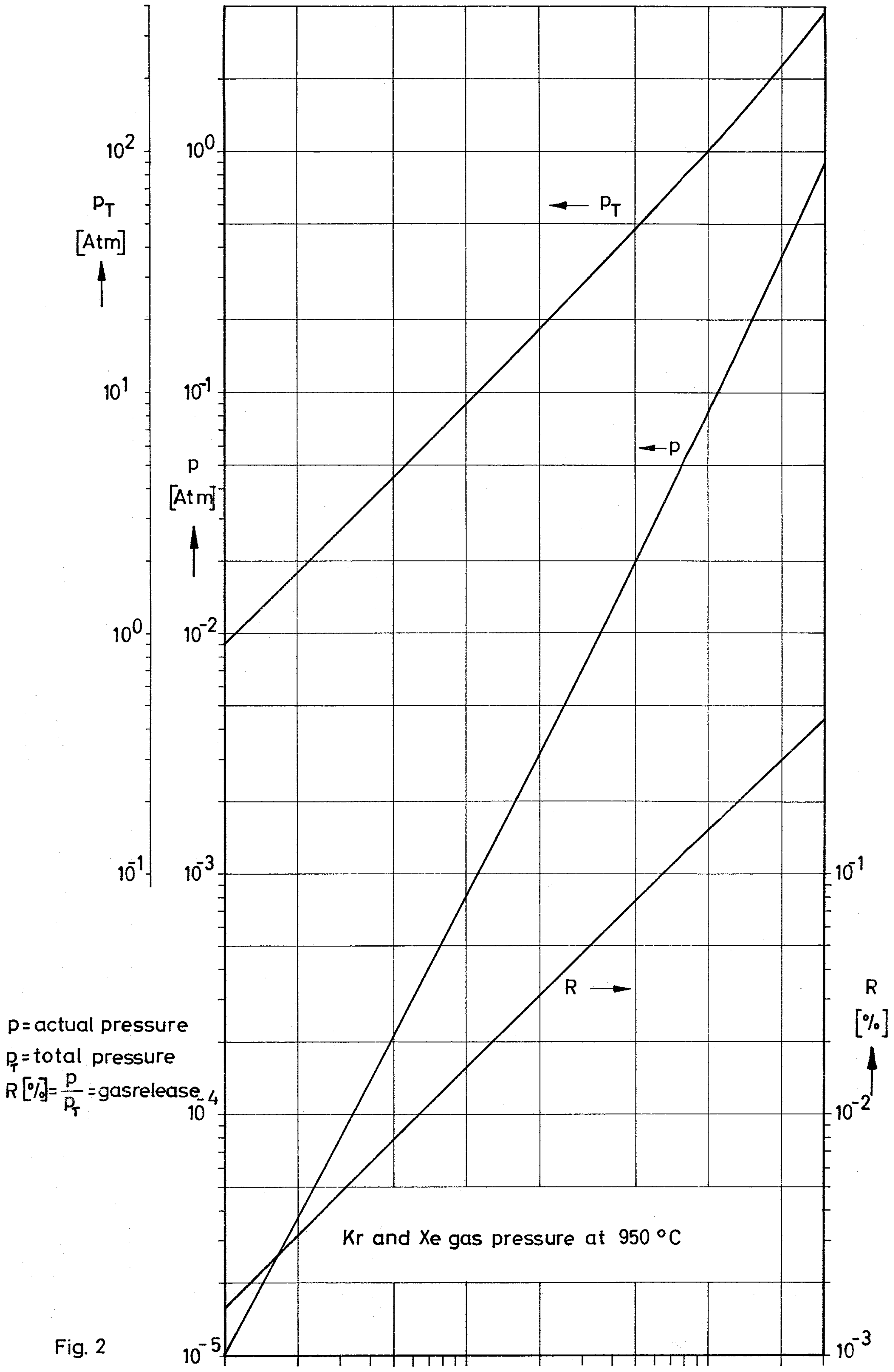
p_T [Atm]
10^2
10^1
10^0
10^{-1}
p [Atm]
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
← p_T
← p
R →
R [%]
10^{-1}
10^{-2}
10^{-3}
p = actual pressure
p_T = total pressure
R [%] = $\frac{p}{p_T}$ = gasrelease
Kr and Xe gas pressure at 950 °C

Fig. 2

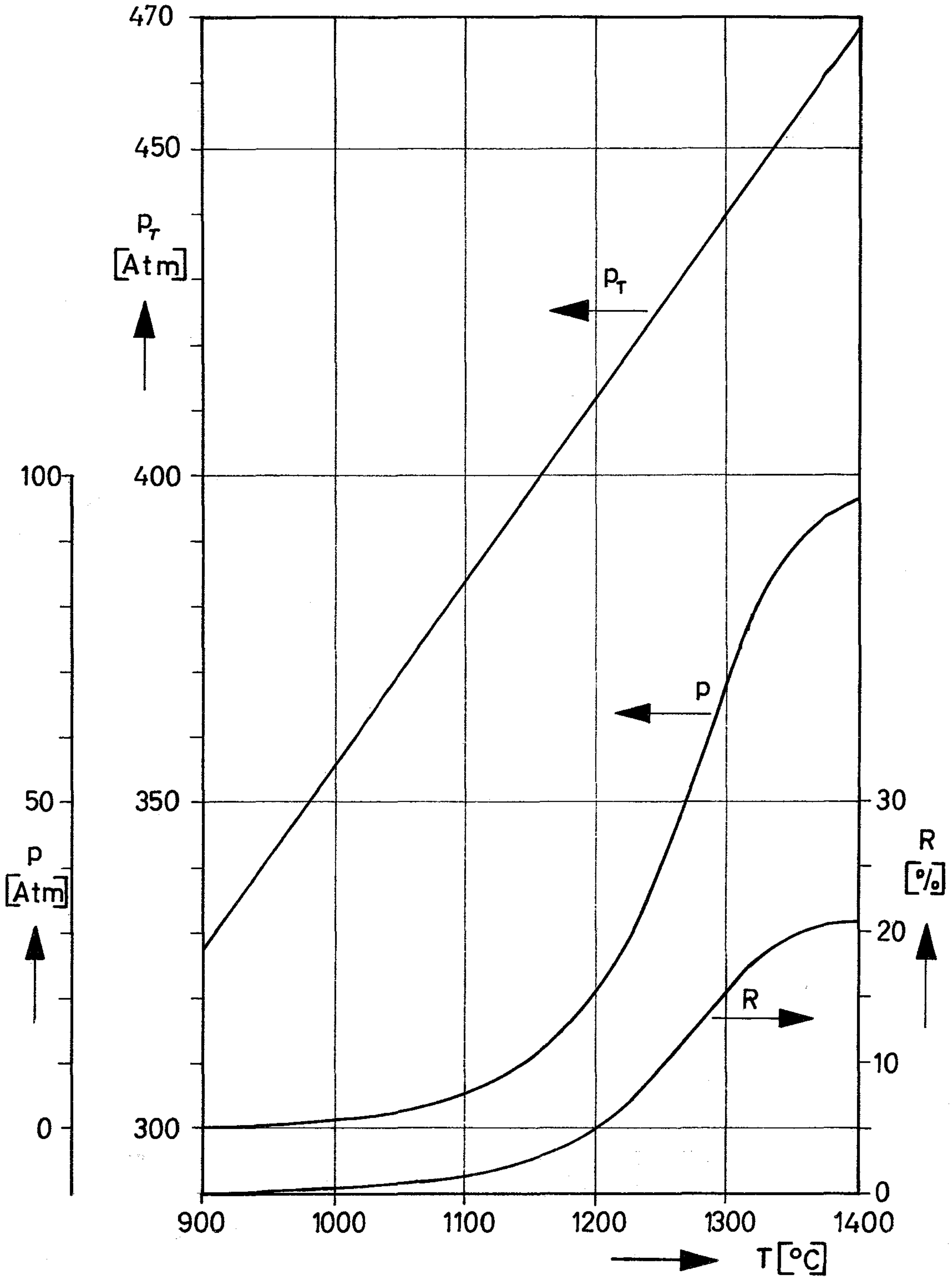

Fig.3: Kr and Xe gas pressure at 278.6 days (=100 000 MWD/t)

p = actual pressure

p_T = total pressure

$R[\%] = \frac{p}{p_T}$ = gasrelease

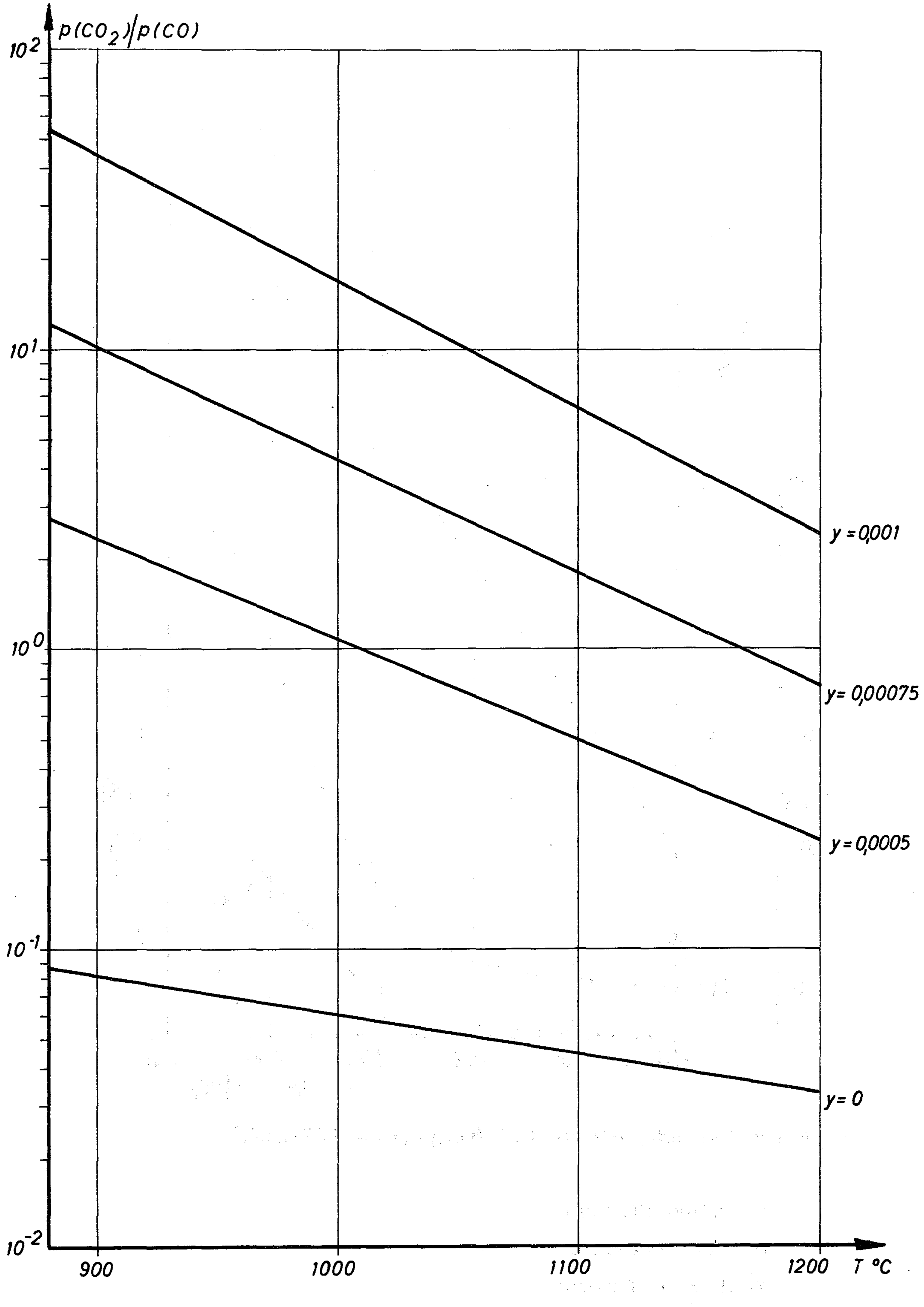

Fig. 4 Equilibrium pressure ratio of CO and CO_2 over $(U_{0.8}\ Pu_{0.2})O_{2+y}$ for small y

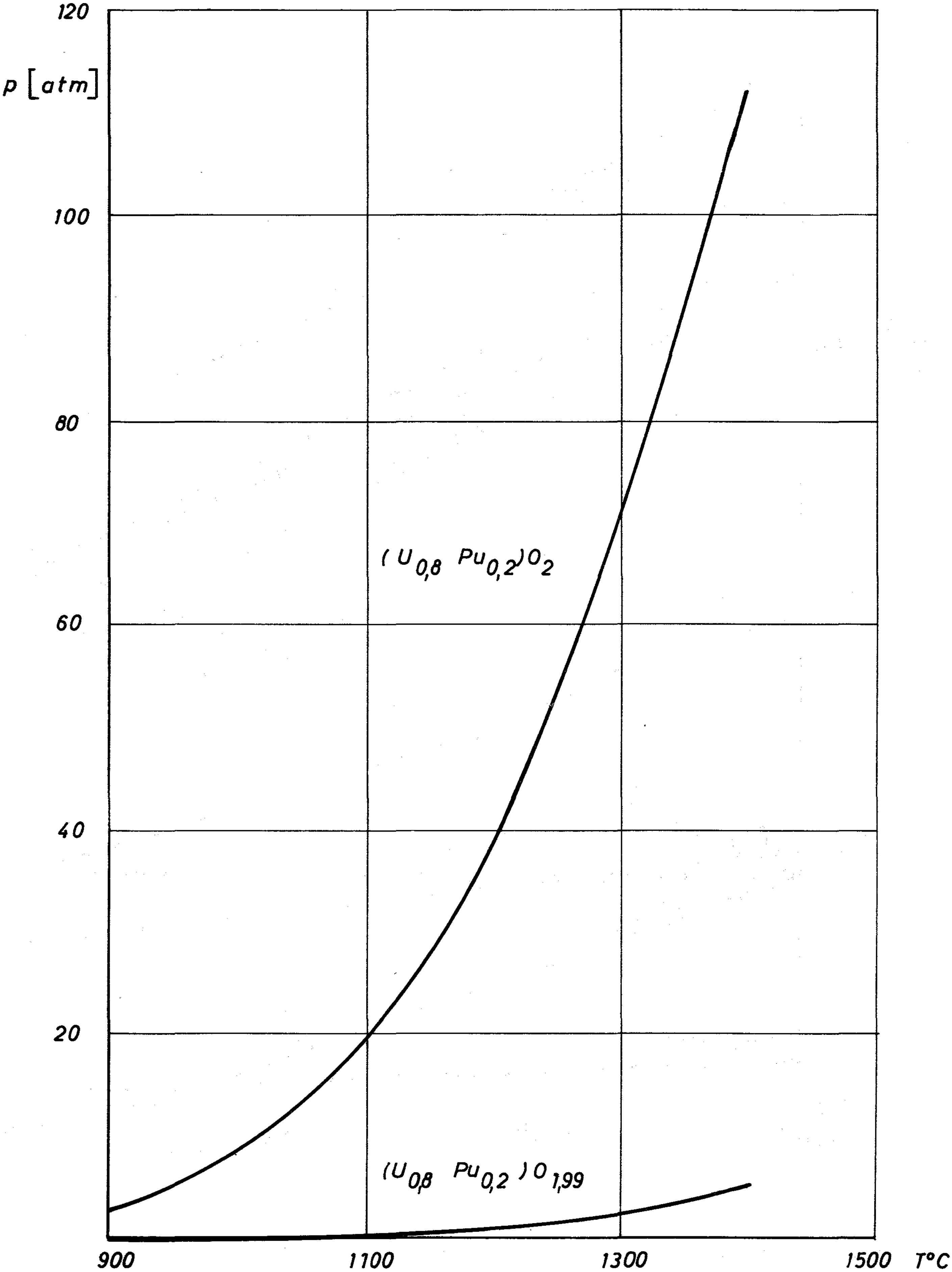

Fig. 5 Equilibrium pressure of carbon oxides over $(U_{0.8}\ Pu_{0.2})O_2$ and $(U_{0.8}\ Pu_{0.2})O_{1.99}$

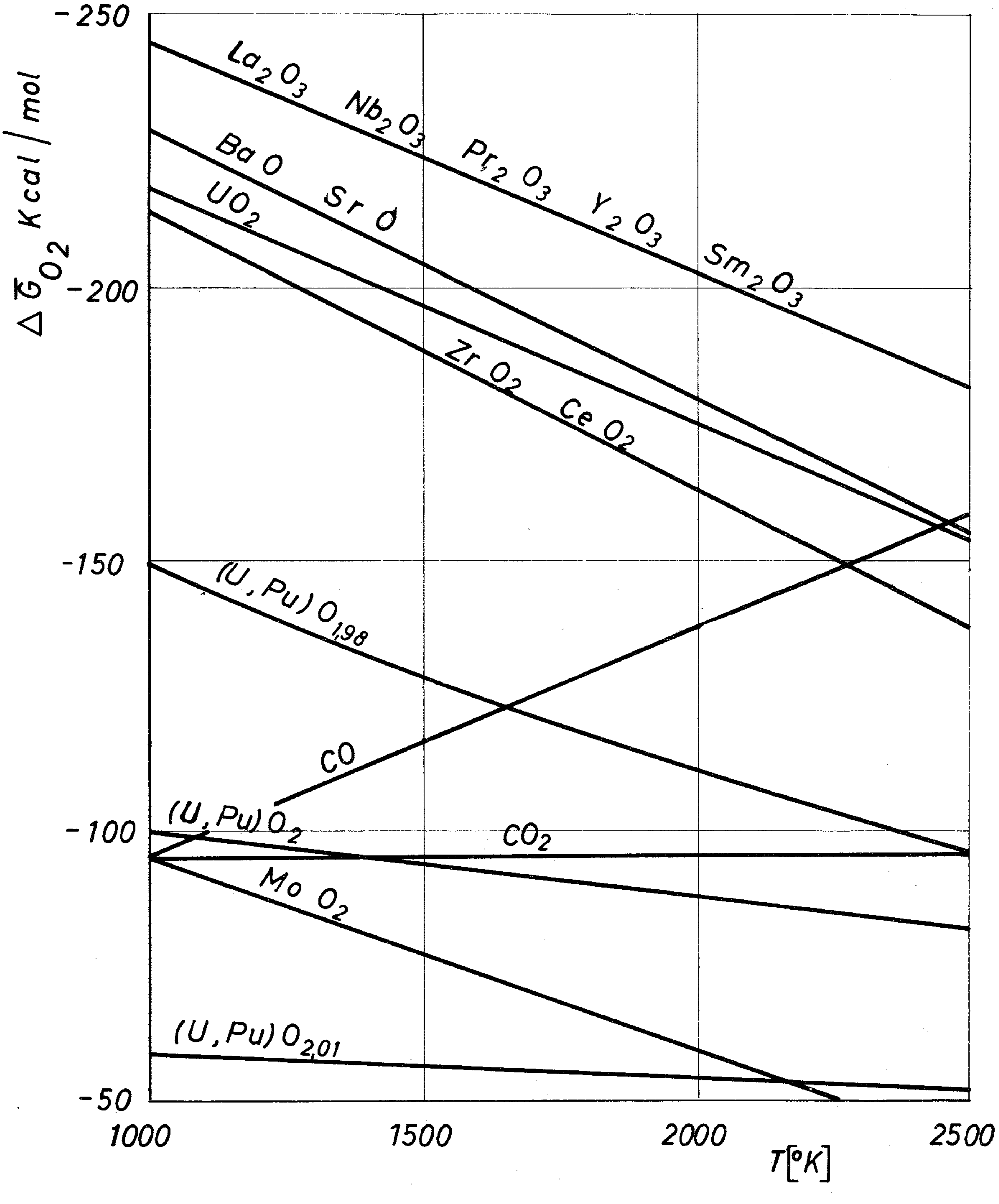

Fig. 6 Free enthalpies of formation of fission products and carbon oxides

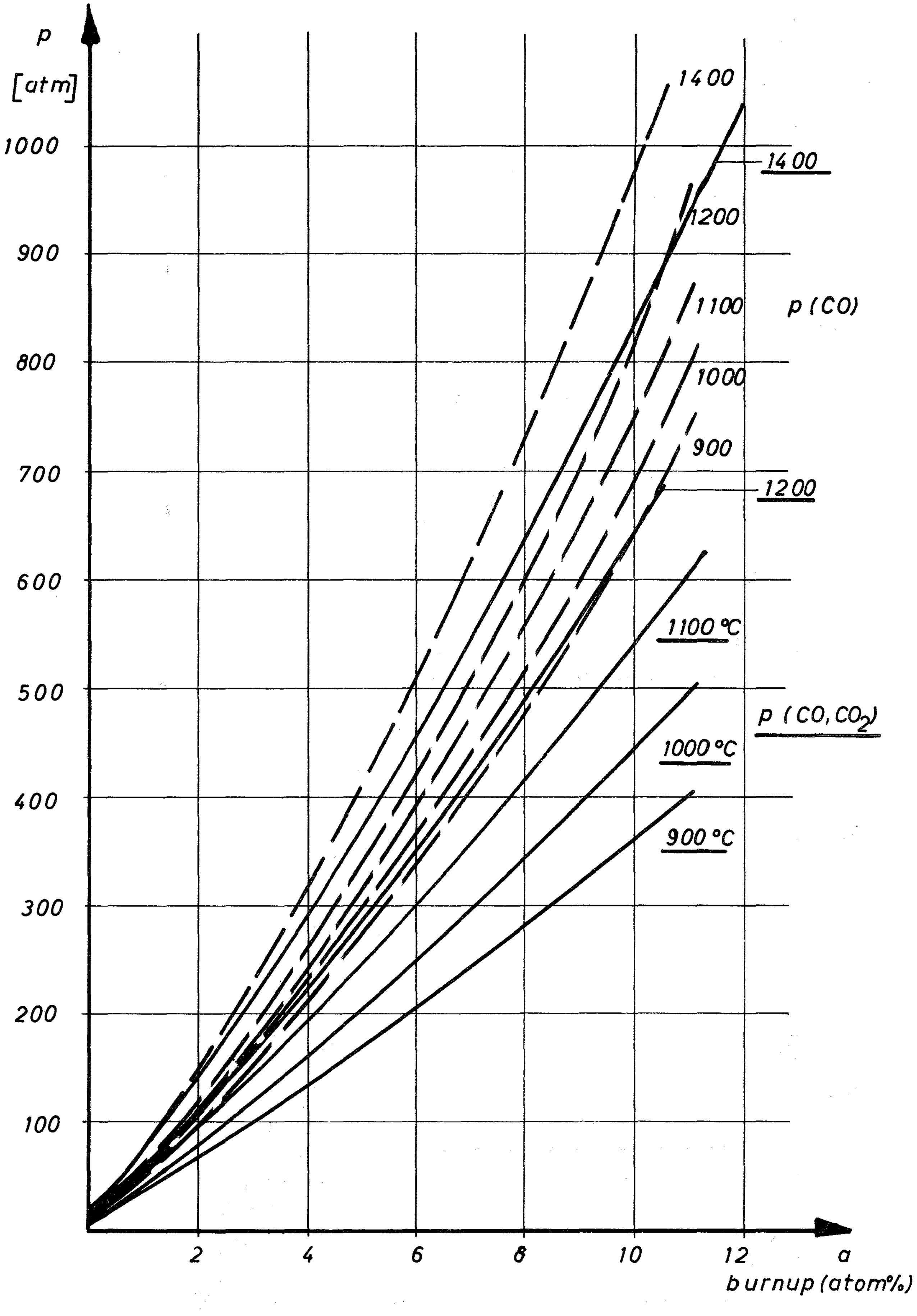

Fig. 7 Carbon oxide pressure in a coated particle without CO_2 (P(CO)) and with CO_2 (P(CO,CO_2)), starting from stoichiometric fuel

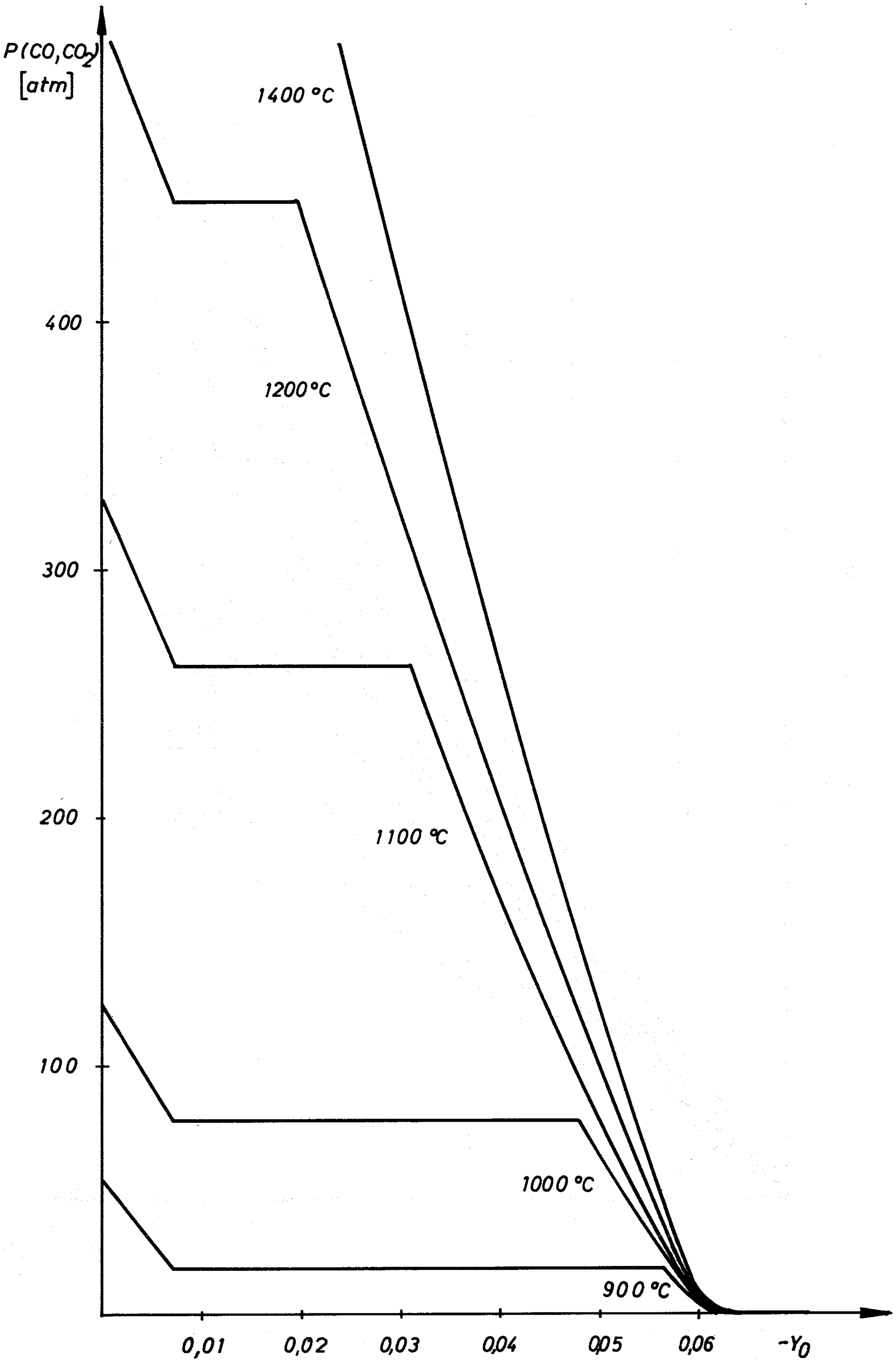

Fig. 8 Carbon oxide pressures in a coated particle versus the inital stoichiometry of $(U_{0.8}Pu_{0.2})O_{2-y_o}$ at 11% burnup

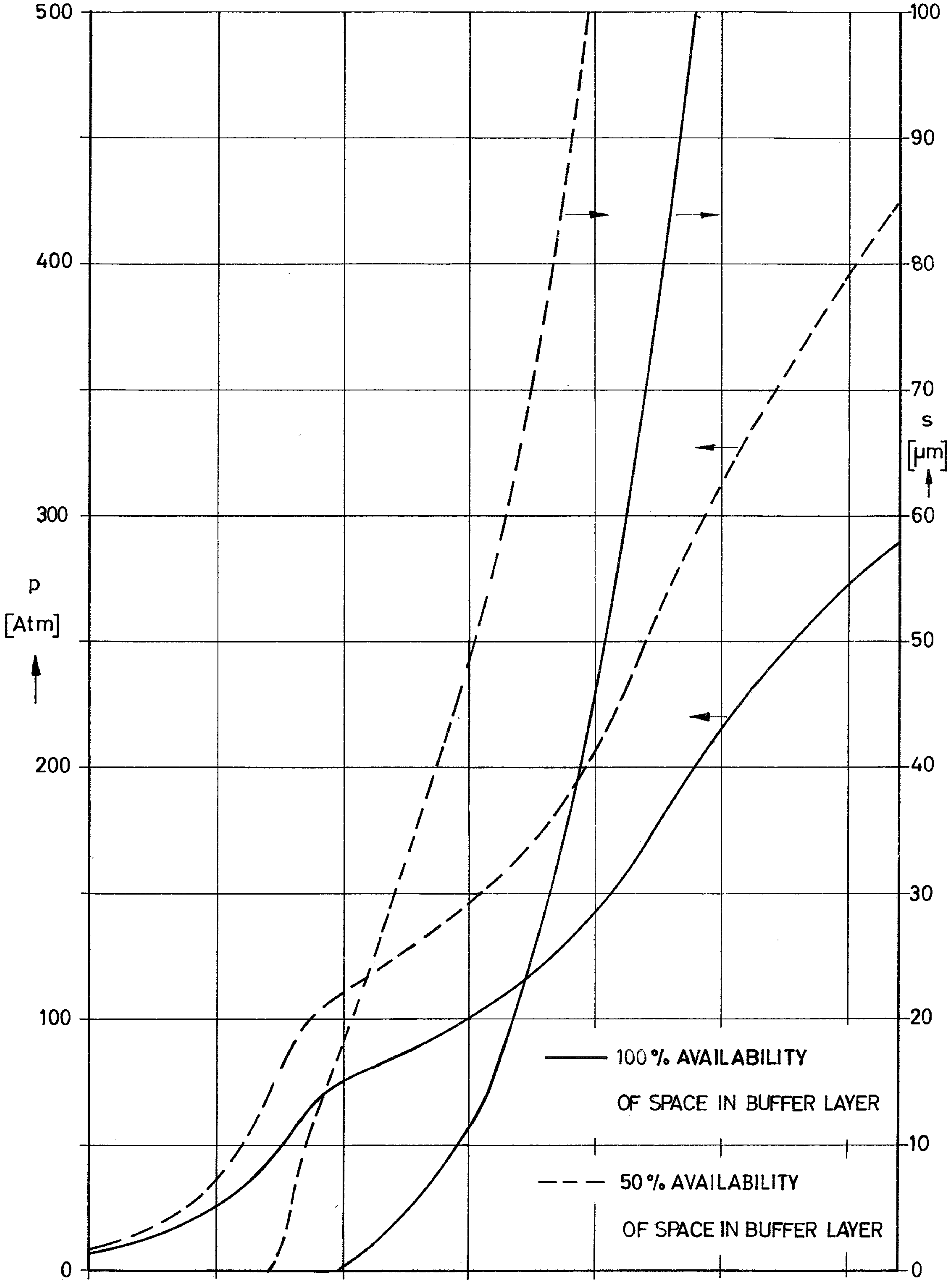

Fig. 9 Total gas pressure in the particle and SiC layer thickness required by condition creep strain ≤ 0.3 % for $U_{0.8}Pu_{0.2}O_{1.95}$ (initial) and 100 000 MWD/t.