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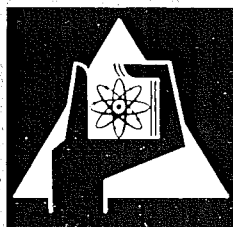
Mai 1971

KFK 1410

Institut für Neutronenphysik und Reaktortechnik
Projekt Schneller Brüter

Compatibility between Vanadium Alloys and
Oxides and Carbides under Irradiation

S. Dorner, G. Schumacher



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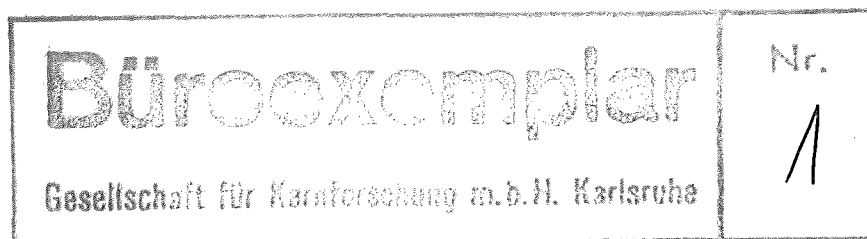
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Compatibility between Vanadium Alloys and
Oxides and Carbides under Irradiation^{*}

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^{*} Paper presented at Lugano Group-Third Specialists Meeting
on Fuel and Materials, Brussels, March 18-19, 1971

Abstract

Corrosion problems arising from the use of vanadium and its alloys in a gas-cooled fast reactor with mixed oxide and mixed carbide fuels respectively were studied. Calculations were made of the amounts of oxygen or carbon respectively which attacks the cladding. It is taken into account that oxygen and carbon is released by the fission processes and by conversion of uranium to plutonium. The calculations indicate that a major deterioration of mechanical properties of the vanadium cladding can be expected if mixed oxide fuel is used because oxygen transport by thermal diffusion and through the CO/CO₂-gas phase occurs due to the temperature gradient in the fuel element. A statement with respect to the carbides is more difficult since only incomplete thermodynamic data exist. With the data available it can be concluded, that no considerable transport processes are likely to occur and no additional carbon is delivered to the cladding by fission processes. Therefore, in reactor fuel elements with carbide fuel no increase of the reaction with the vanadium cladding is expected in comparison to the effect found in the isothermal out of pile experiment.

Zusammenfassung

Die Korrosionsprobleme, die durch den Einsatz von Vanadium und seinen Legierungen als Hüllmaterial für die Mischoxide und Mischkarbide des Urans und Plutoniums in gasgekühlten schnellen Reaktoren entstehen, werden untersucht. Es wird errechnet, welche Sauerstoff- und Kohlenstoffmengen mit der Hülle reagieren, wobei der durch den Spaltprozeß und durch Konversion des Urans gelieferte Sauerstoff- bzw. Kohlenstoff berücksichtigt wird. Die Berechnungen zeigen, daß durch den freigesetzten Sauerstoff eine starke Verschlechterung der mechanischen Eigenschaften der Vanadiumhülle zu erwarten ist, weil der Sauerstoff durch Thermodiffusion und über die CO/CO_2 -Gasphase im Temperaturgradienten des Brennelementes zur Hülle transportiert wird. Eine Aussage über die Verträglichkeit der Karbide mit der Hülle ist schwieriger, da die thermodynamischen Daten lückenhaft sind. Mit den vorhandenen Daten ergibt sich, daß kein wesentlicher Kohlenstofftransport zu erwarten ist und kein zusätzlicher Kohlenstoff durch die Spaltprozesse an die Hülle geliefert wird. Deshalb ist anzunehmen, daß auch im Reaktor die Reaktion des karbidischen Brennstoffs mit der Hülle ähnlich wie in den isothermen Laborexperimenten abläuft.

INTRODUCTION

It is known that vanadium and vanadium alloys, respectively, have a large affinity for oxygen and nitrogen and undergo drastic changes of their mechanical properties as a result of the uptake of these gases [1]. A vanadium alloy has been proposed as cladding material for fuel pins for a helium cooled fast breeder reactor [2]. Therefore, the compatibility between fuel and cladding is of interest.

No marked reaction is expected to occur between uranium oxide and vanadium [3]. Conditions will be different with uranium-plutonium mixed oxide due to its smaller affinity for oxygen. The corrosive attack of mixed oxide on the inside of the cladding is determined by the stoichiometric condition and by oxygen transport processes due to the temperature gradient in the fuel [4]. The compatibility of uranium carbide and uranium-plutonium mixed carbides depends strongly on temperature and on the stoichiometry of the carbides [5].

REACTION OF THE OXIDE FUEL WITH THE CLADDING

Stoichiometry of the fuel

The partial free enthalpy of the oxygen in the fuel $\overline{\Delta G}_{O_2}((U,Pu)O_2)$ depends on the stoichiometry of the fuel. There will be a major reaction with vanadium if the free enthalpy of formation for vanadium oxide $\Delta G_{O_2}(VO)$ is larger in terms of its amount than the partial free enthalpy of the oxygen in the fuel. If we look at a fuel with 15 mol% plutonium oxide, in an isothermic system the equilibrium is attained at a ratio of oxygen to metal, O/M, of 1.97 of the fuel. This corresponds to a deviation from stoichiometric state of $y = y_e = -0.03$. If y is higher, oxygen will be transferred to the vanadium until $y = -0.03$. Once this equilibrium has been established, there is further oxidation

due to the oxygen generated from plutonium and uranium oxides in the fission process. Some of this oxygen is bound by oxidation of fission products with an affinity for oxygen higher than vanadium. The other part is taken up by vanadium. Making an oxygen balance we obtain the number of oxygen atoms Z transferred to the cladding. The result is shown in equation (1)

$$Z = \left\{ \left[2 + \frac{y_e}{x_u} + \left(\frac{1}{x_{Pu}} - \frac{1}{x_u} \right) (f_{Pu} - a) y_e - \frac{\sum S_K Y_K}{100} \right] \cdot b + y_o - y_e \right\} \cdot Z_f \quad (1)$$

- where x_u, x_{Pu} = molar fractions of uranium and plutonium oxides
 f_{Pu} = fraction of plutonium fissions (here 0.88)
 a = breeding ratio (here 1.4)
 y_e, y_o = deviation from the stoichiometric state at equilibrium with vanadium and at initial state
 b = burn-up
 Z_f = number of fuel atoms per cm length of the fuel elements
 Y_K = number of atoms of the fission product k related to 100 fissions of Pu239 after 100 days of decay time
 S_K = oxygen-metal ration (O/M) of the k^{th} fission product oxide in the fuel

The sum $\sum S_K Y_K$ includes only those fission products which form oxides more stable than VO. In Fig. 1, these oxides have been entered below the curve for VO because of their more negative free reaction enthalpy. These are oxides of the lanthanides and of zirconium, strontium, and barium. With respect to the fact, that all these oxides are in the tetravalent state [6] it results $\sum S_K Y_K = 146.4$ [7].

Transport phenomena through the CO/CO₂ gas phase and by thermal diffusion cause an oxygen deficit in the interior of the fuel. These processes will be dealt with below.

Oxygen transport in the fuel

1. Thermal diffusion transport

In the fuel subjected to a temperature gradient there is a shift of the oxygen concentration. If one regards oxygen in the substoichiometric fuel as a transport of oxygen vacancies, the Soret coefficient S and the change in the deviation from stoichiometry y with temperature, is [8]

$$S = \frac{dy}{dT} = -y \frac{Q_s^x(y)}{RT^2} \quad (2)$$

where T = absolute temperature [°K]

Q_s^x = heat of transfer of thermal diffusion
of oxygen [$\frac{\text{cal}}{\text{mol}}$]

R = gas constant [$\frac{\text{cal}}{\text{°K mol}}$]

Experimentally determined values of the heat of transfer of oxygen are used in the calculation [9]. The steady state distribution of oxygen is plotted versus the temperature of the fuel in the radial direction in Fig. 2. The solid sections of the curves have been calculated, the dotted ones have been extrapolated because, for O/M ratios close to 2.0 and less than 1.94, no Q_s^x -values are known. The numbers indicated with the curves refer to the respective oxygen-metal ($\overline{O/M}$) ratio averaged over the radial fuel cross section. From the diagram it is evident that the stoichiometric condition remains intact at the periphery of the fuel zone at 1000 °K as a result of thermal diffusion transport of oxygen, even if the average ratio $\overline{O/M}$ decreases to some 1.97. Only in the case of major deviations from the average stoichiometric condition,

e.g., $\overline{O/M} = 1.944$, also the O/M ratio at the periphery will decrease below 2. If there is vanadium at the periphery which removes oxygen from the stoichiometric fuel until an O/M of 1.972 has been reached (see Fig. 1), the concentration distribution in the interior of the fuel will be equal to the dashed curve which begins at O/M = 1.972 and $T = 1000$ °K. For this curve, $\overline{O/M} = 1.931$ and $\bar{y}_e = -0.069$. If the temperature at the periphery of the fuel is 1100 °K or 1200 °K, respectively, the corresponding concentration distributions are indicated by the dashed curves which begin at O/M = 1.971 and $T = 1100$ °K and at O/M = 1.970 and $T = 1200$ °K, respectively. The average O/M-ratios for these concentration distributions are 1.933 and 1.935; the average deviations from the stoichiometric state are $\bar{y}_e = -0.067$ and $\bar{y}_e = -0.065$ respectively.

2. Transport through the CO₂/CO gas phase

As showed by Markin and Rand [10] the carbon impurities cause a transport of oxygen through the CO₂/CO gas phase in the oxide fuel element. The resulting oxygen distribution was calculated for a central temperature of 2500 °K and cladding temperature of 1000, 1100 and 1200 °K.

The distribution of oxygen concentration in the steady state is shown in Fig. 3. The solid curves show the changes of the O/M ratios with the temperature in the radial direction in the way they result for various ratios of P(CO₂)/P(CO). Especially with strongly substoichiometric fuel the curves have a similar shape as those generated by thermal diffusion transport (Fig. 2). The three dashed curves again indicate the concentration distributions in the case of vanadium cladding and temperatures of 1000, 1100 and 1200 °K on the periphery of the fuel.

3. Oxidation of the cladding

It is assumed that during operation in the reactor the steady state distributions of oxygen concentration shown in Fig. 2 and 3 will be reached in the fuel elements. Therefore, the average stoichiometric deviation \bar{y}_e substitutes y_e in equation (1).

For a fuel pin with 0.74 cm outer diameter and a thickness of the cladding wall of 0.04 cm the degree of oxidation of the cladding was calculated of fuel of density of 9.35 g/cm³. The result is shown in Fig. 4. As expected, the degree of oxidation increases with increasing burn-up; the temperature dependence is but small.

The isothermic experiments carried out by T.W. Latimer [11] on $(U_{0.8}Pu_{0.2})_{0.97}$ have confirmed that also in substoichiometric fuel there are reactions with vanadium and its alloys. This fuel with 20 mol% of plutonium oxide would reach thermodynamical equilibrium with pure vanadium at an O/M ratio of 1.963 in the mixed oxide. Therefore, the experiments showed an oxidation of the vanadium alloys through a reduction of $(U_{0.8}Pu_{0.2})_{0.97}$ together with a marked increase in hardness of the material. In reactor fuel elements this effect will be increased by the oxygen transport processes due to the temperature gradient. The hardness profile as a function of the distance from the reaction surface indicated that the V-20%Ti alloy has undergone internal oxidation in a thick peripheral layer of the material. This is due to the much greater affinity of titanium for oxygen than vanadium. In the alloys with chromium the hardness profile is not that high but much broader, which indicates a solution process. This is to be expected, because the affinity for oxygen of chromium is lower than that of vanadium.

REACTION OF THE CARBIDE FUEL WITH THE CLADDING

1. Thermodynamic considerations

For carbides similar considerations can be made as for oxides. However, due to the lack of data available for the enthalpies of formation it is not possible to make the same definite statements in this case. In Fig. 5 are listed the partial free enthalpies of the carbon [12] in some carbides. It appears that vanadium and titanium contained in the alloy produce more stable carbides than uranium and plutonium. This means that a reaction must be anticipated.

In the fission of plutonium, carbon is released. Figure 5 shows the partial free enthalpies of carbon in the known stable fission product carbides. For the calculation it is supposed that Nd, Sm and Y also form more stable carbides than U_2C_3 . The most likely carbides formed by Nd, Sm and Y are listed in Table 1 [13 - 17].

Table 1

	Ce	Pr	Nd	Sm	La	Y	Zr	Mo
Carbide	Ce_2C_3	PrC	Nd_2C_3	Sm_3C	La_2C_3	YC	ZrC	Mo_2C
ref	13	14	15	15	16	15	17;13	12
Y	15.7	5.3	15.8	5	5.78	1.58	21	20.0
$S_{K^Y_K}$	23.5	5.3	23.7	1.7	8.7	1.6	21	10

From Table 1 we get

$$\sum S_{K^Y_K} = 95.5$$

If we assume that Pr_2C , Y_2C , Pm_2C_3 and other rare-earth-carbides and earth alkaline-carbides (BaC_2 , SrC_2) are more stable than U_2C_3 we obtain

$$\sum S_{K^Y_K} > 100$$

This means that by hundred fissions either 95.5 or all carbon atoms respectively will be bound by fission products. Therefore, it seems likely that no U_2C_3 will be formed.

2. Consideration of possible transport processes

A considerable reaction with the cladding can only take place when the carbon has been transported to the cladding. Transport through the solid phase can be neglected, since diffusion of carbon in the carbide occurs at a very slow rate. For example, the diffusion coefficient of C in UC is $2 \cdot 10^{-12}$ cm²/sec at 1000 °C [18]. It seems that transport processes

through the gas phase are not likely to occur because CH_4 decomposes at temperatures above 600°C and the oxygen is gettered by the fuel or by the cladding. If a liquid metal bonding exists between the fuel and the cladding, however, important effects can be produced by transport processes. Carbon is dissolved in sodium and released to vanadium.

3. Attack of the cladding by carbides

Thermodynamic considerations show that at most 5% of the carbon generated by fission of plutonium and uranium is used by the formation of U_2C_3 . With respect to the fuel pin described before this means a carbon content of at most 0.6 at% carbon gets into the vanadium cladding at 10% burnup if all the hypostoichiometric carbon is transported to the cladding. Additional carbon is taken up by the cladding due to reaction of the stoichiometric $(\text{U,Pu})\text{C}$ with vanadium and its alloys.

A few compatibility tests of UC and $(\text{U,Pu})\text{C}$ with vanadium and its alloys were carried out. L.A. Neimark et al. [19] have studied the compatibility of $(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}$ fuel with vanadium and vanadium-20 w/o titanium-alloys. They observed a quite extensive reaction of $(\text{U,Pu})\text{C}$ with V-20 w/o Ti at 800°C and no reaction of $(\text{U,Pu})\text{C}$ with pure V at 950°C up to 17 days. After 42 days a few small grain boundary penetrations were observed. Compatibility experiments of UC and vanadium titanium alloys carried out by O. Götzmann et al. [20] yielded especially for alloys with a high content of titanium (>5 w/o) strong reaction at 800°C and 900°C after 20 days. No reaction was observed at 800°C with alloys having a low titanium content (<5 w/o) whilst at 900°C a reaction occurred with Ti precipitation in the cladding after 20 days. All experiments were carried out with isothermal arrangements. Although in reactor fuel elements a temperature gradient exists, results of isothermal experiments can be applied because no considerable transport processes are likely to occur and no additional carbon is delivered by fission.

CONCLUSIONS

The influence of dissolved oxygen on the properties of vanadium has been investigated repeatedly [1, 21]. According to Loria, the ductile-brittle transition temperature increases with increasing oxygen content at the rate of 140 °C per 0.3 at% oxygen in the low range of oxygen concentration [21]. The small-load Vickers hardness of vanadium also greatly increases with increasing oxygen content: from 50 to 550 kg/mm² for 5 at% oxygen content (Fig. 6).

Because of the high concentration of oxygen in vanadium calculated in this paper one can expect a major deterioration of the material properties. If no special measures are taken, a strong attack by oxygen must be anticipated in the use of vanadium and its alloys as a cladding material for an uranium-plutonium mixed oxide fuel. This is connected with a marked deterioration of the mechanical properties. Possibilities of preventing the reaction with the fuel include these measures:

- (a) Formation of a protective layer on the surface of the alloy.
- (b) Adding a protective coating of metal to the inside of the cladding.
- (c) Use of oxide fuel mixed with a component with an affinity for oxygen higher than that of vanadium.

The former two possibilities are very difficult to implement. Proof of the feasibility of the third measure still needs to be produced experimentally. A report will be published as soon as the results are available.

A statement with respect to the carbides is more difficult since not enough data, especially about the transport phenomena and the carbon activity in mixed (U,Pu)-carbides, are available. The carbon released by fission of the metals is likely to have only a minor effect. Furthermore, the reaction in a fuel element rod will be not increased compared to the effect found in the isothermal experiments by the temperature gradient in the fuel rod itself. Although detailed

investigations will still be required in this field until vanadium will be eligible as a cladding material for carbide fuel. Vanadium alloys with higher contents of titanium ($> 5\%$ of Ti) can be excluded already now as a result of the isothermal experiments [20].

The authors would like to thank Dr. M. Dalle Donne for many useful suggestions and discussions.

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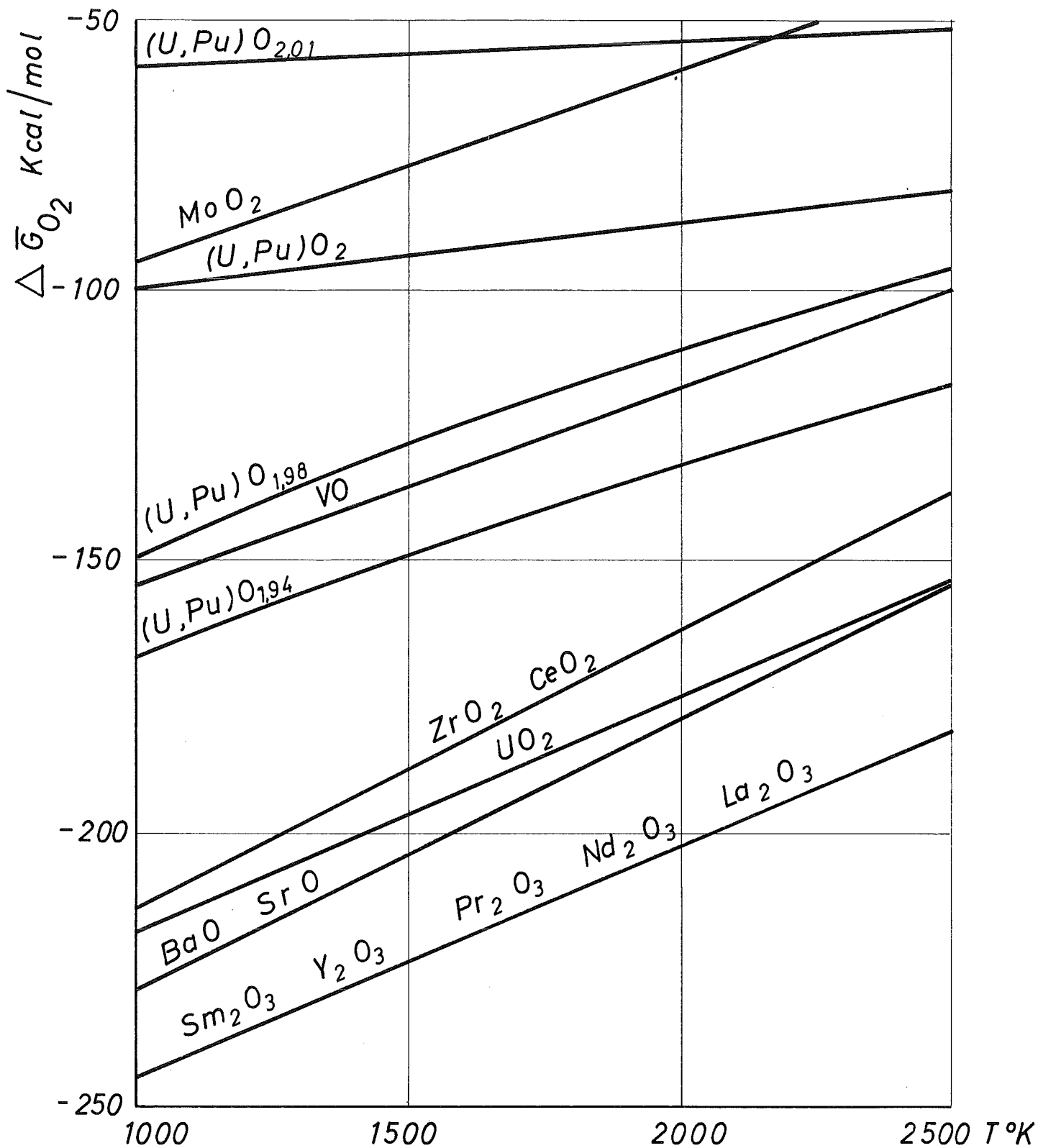


Fig. 1: Partial free molar enthalpies of oxygen in $(U_{0.85}Pu_{0.15})O_{2+y}$ in fission product oxides and in VO.

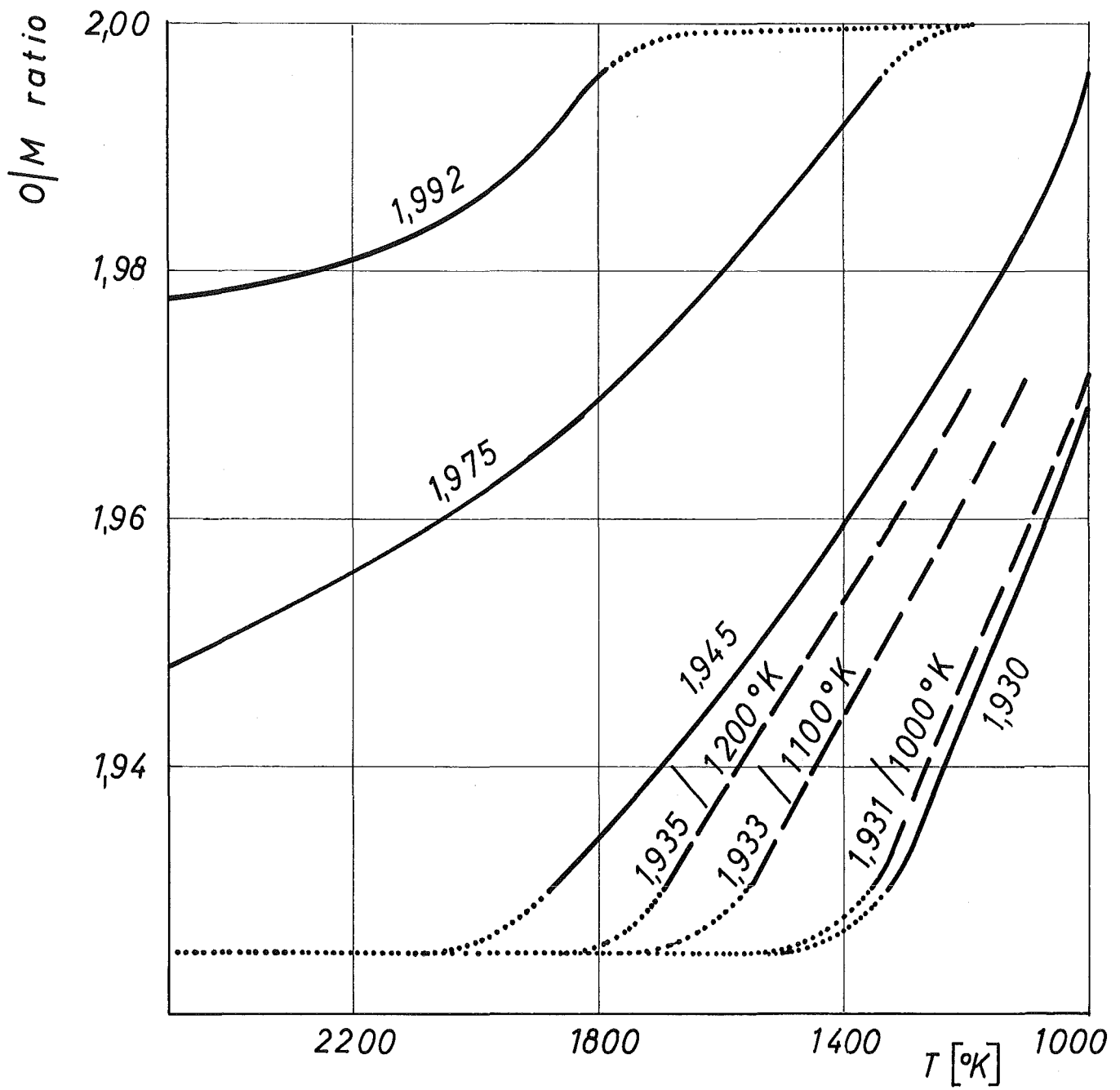


Fig. 2: O/M ratio in radial direction caused by thermal diffusion.

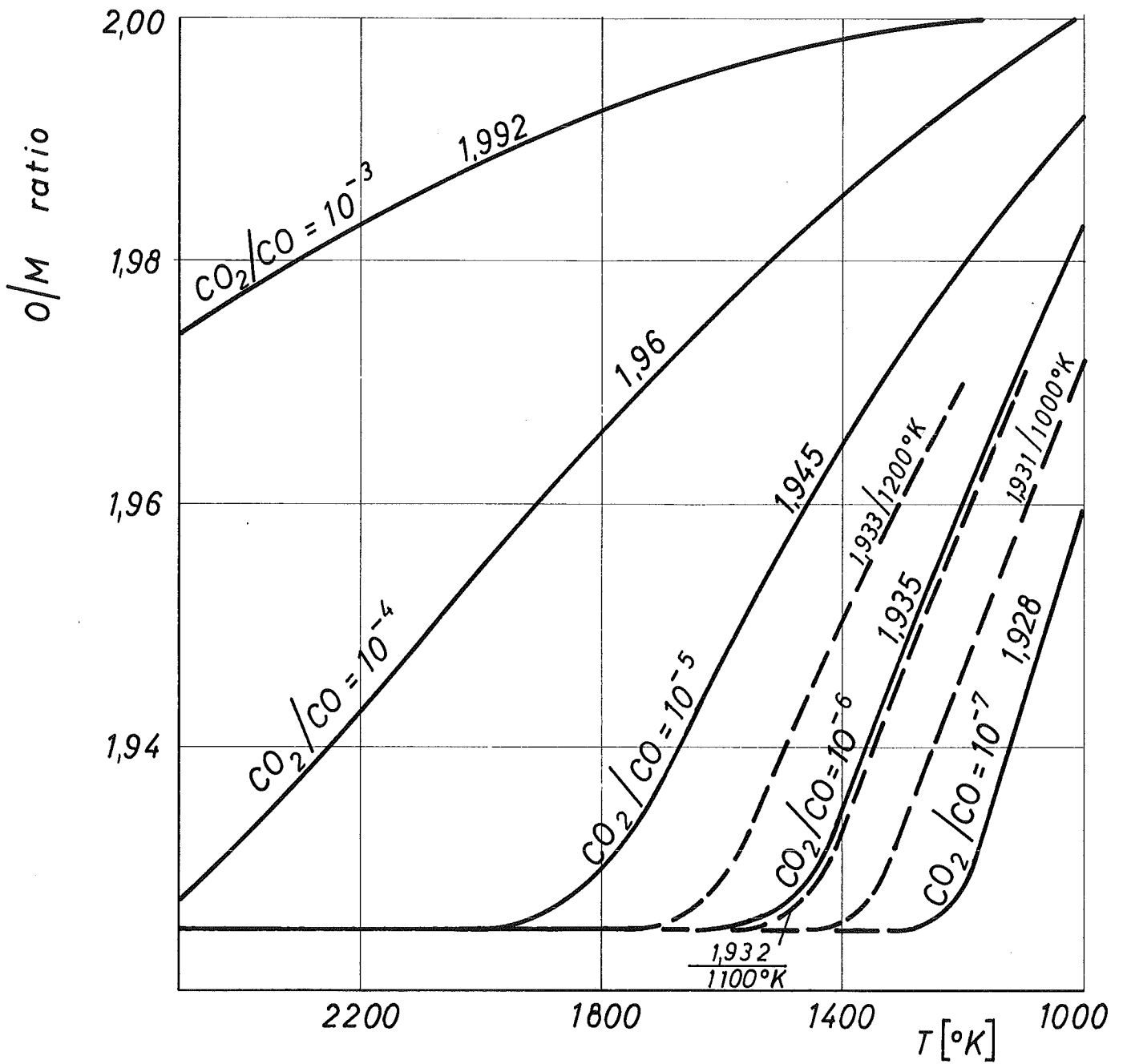


Fig. 3: O/M-ratio in radial direction caused by the CO/CO_2 transport mechanism.

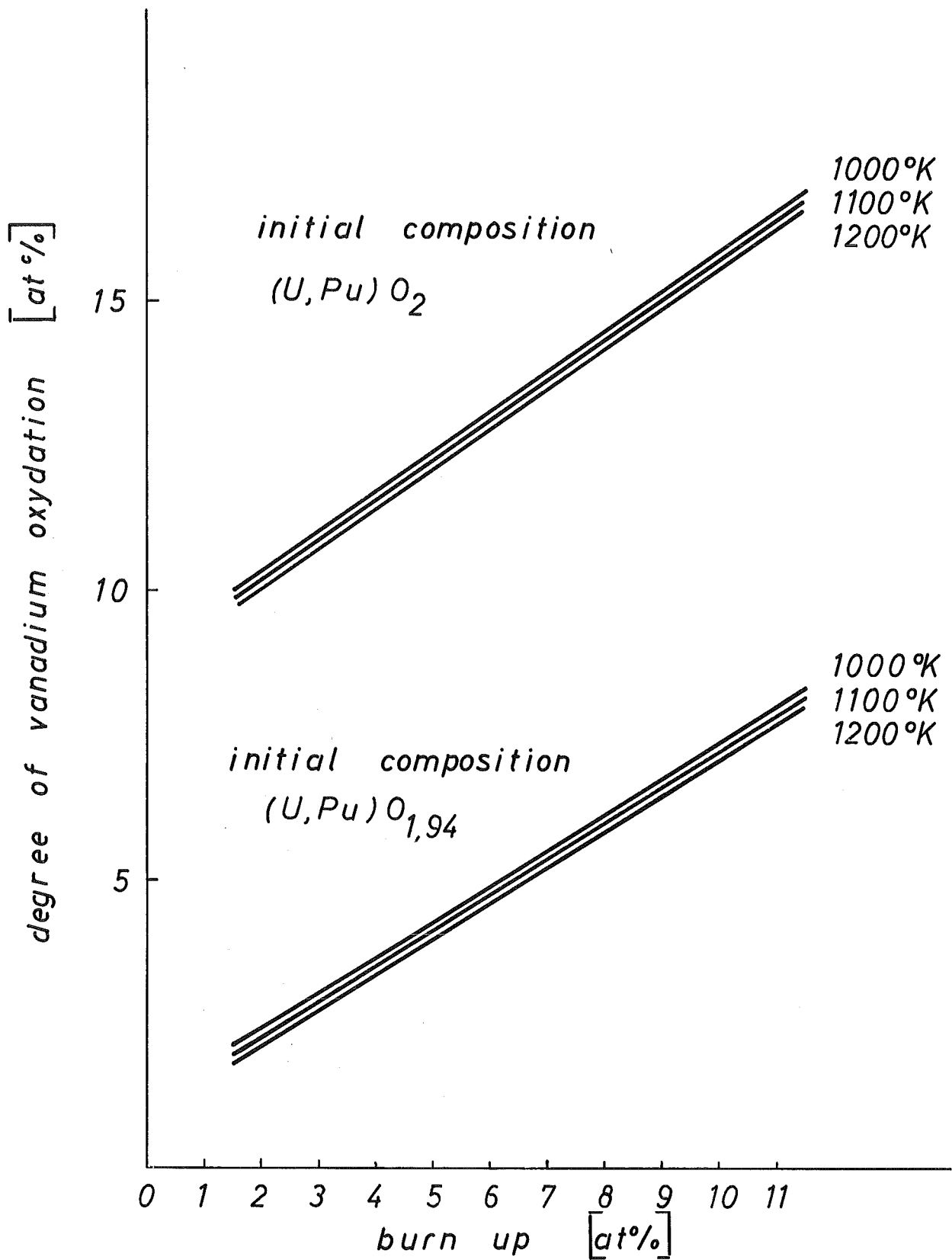


Fig. 4: Oxidation of a vanadium cladding after contact with $(U_{0.85}Pu_{0.15})O_{2+y}$ for $y=0$ and -0.06 .

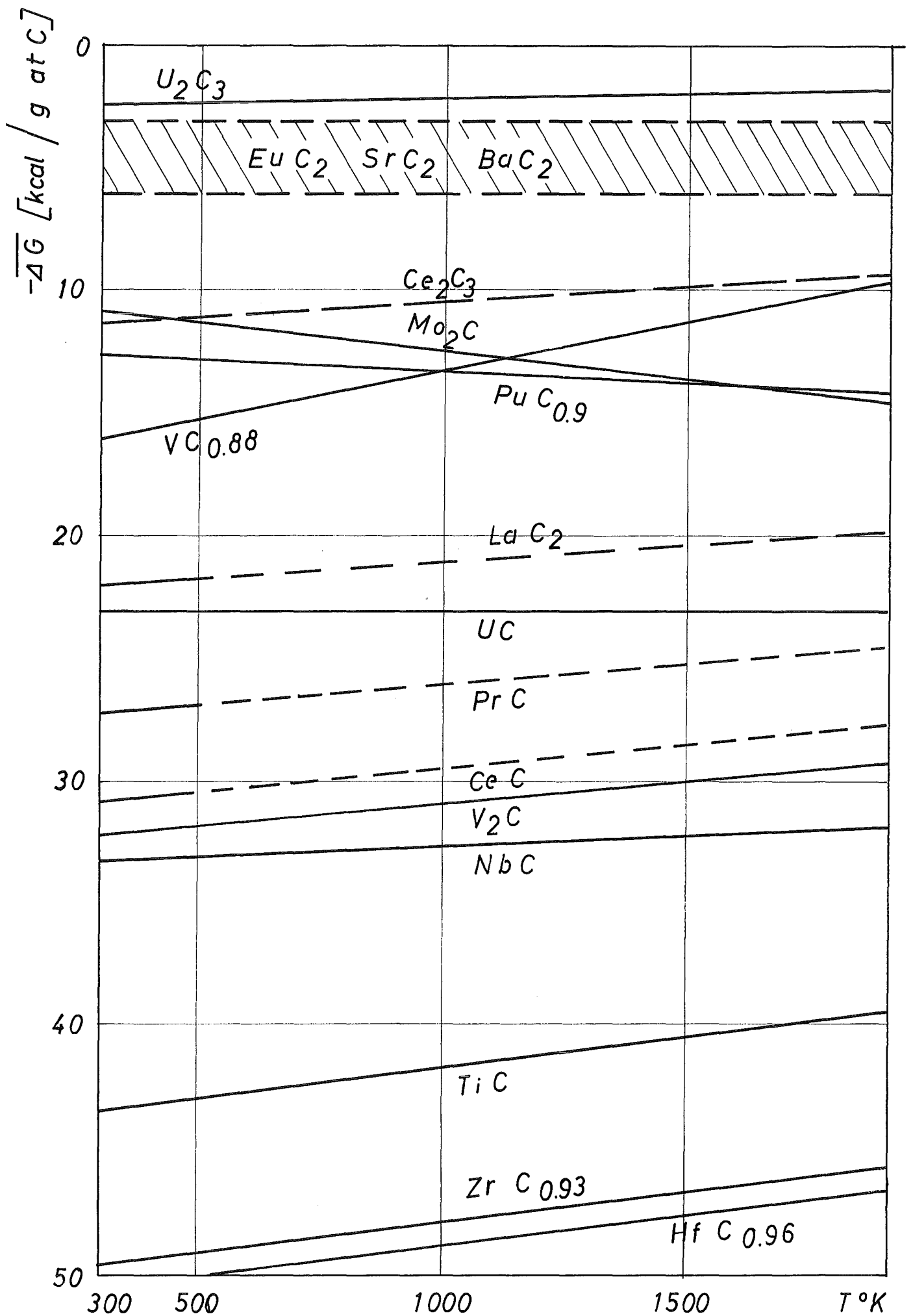


Fig. 5: Partial free enthalpies of carbon in the carbides of uranium, plutonium and of fission products.

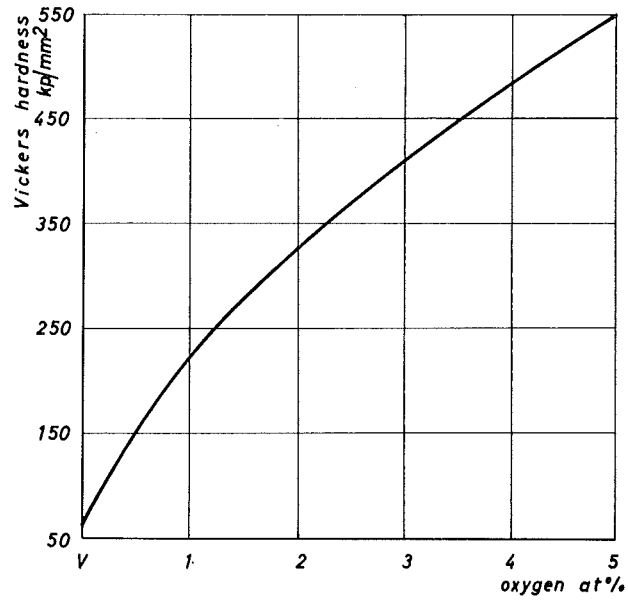


Fig 6: Vickers hardness of vanadium depending on oxygen content.