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Compatibility Behaviour of Oxide and Carbide Fuels with Cladding Materials

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Abstract

The compatibility behaviour of oxide and carbide fuels with claddings of austenitic steels and vanadium base alloys is described.

Even though many out-of-pile investigations with oxide fuel and steel clads showed good compatibility, there occur strong cladding attacks in irradiation tests. This differing behaviour is caused by the changes the fuel undergoes during burnup. The changes themselves are dependent on the ratio of the fission isotopes in the fuel. This has consequences on the post irradiation evaluation.

According to thermochemical data, the compatibility between vanadium alloys and a U-Pu-mixed oxide fuel is bad. Out-of-pile investigations have shown heavy embrittlement at room temperature of vanadium claddings after reaction with mixed oxide fuel. However, there is a chance that the oxygen uptake does not cause embrittlement at higher temperatures.

Carbide fuel is not in a thermodynamic equilibrium with claddings of stainless steels or vanadium alloys. Compatibility tests up to 800°C showed still good compatibility between several types of steels and slightly hyperstoichiometric carbide. The reactions with some vanadium alloys are still slower, hence good compatibility can also be assumed between vanadium base alloys and carbide fuel up to temperatures of 800 or even 900°C. Embrittlement by carbide reaction is less severe than with oxide.

Zusammenfassung

Das Verträglichkeitsverhalten von oxidischen und karbidischen Kernbrennstoffen mit Hüllen aus austenitischen Stählen und Vanadinlegierungen wird besprochen.

Obwohl viele out-of-pile Untersuchungen mit oxidischem Brennstoff und Stahlumhüllungen gutes Verträglichkeitsverhalten zeigen, wird in bestrahlten Proben oft ein starker Hüllangriff beobachtet. Dies hat seine Ursache in der Veränderung des Brennstoffes durch den Abbrand. Diese Veränderung wird näher erläutert und auf die Unterschiede beim Einsatz verschiedener Spaltstoffisotope eingegangen.

Von den thermochemischen Daten her betrachtet ist die Verträglichkeit von U-Pu-Mischoxid mit den Vanadinlegierungen schlecht. In out-of-pile Untersuchungen wurden starke Versprödungen der Vanadinhüllen festgestellt. Eine Chance für den Einsatz der Vanadinlegierungen mit Oxidbrennstoff kann vielleicht noch darin gesehen werden, dass diese Versprödung sich nur bei Raumtemperatur und nicht bei den Einsatztemperaturen bemerkbar macht.

Karbidischer Brennstoff befindet sich mit Hüllen aus Stählen und Vanadinlegierungen nicht im thermodynamischen Gleichgewicht. Verträglichkeitsuntersuchungen bis 800°C ergaben jedoch auch mit überstöchiometrischem Karbid mit einigen Stahltypen noch gute Verträglichkeit. Die Reaktionen mit einigen Vanadinlegierungen sind noch langsamer, so dass auch hier gute Verträglichkeit angenommen werden kann. Die Versprödung durch die Reaktionen mit Karbid sind nicht so ausgeprägt wie mit dem Oxid.

The problem of compatibility of a nuclear fuel with its cladding is always the question of deterioration in cladding rupture behaviour as a result of chemical interactions with the fuel. If the suitability for practical operation of the cladding is not reduced beyond a reasonable amount, compatibility actually is no big problem.

If one includes in these considerations also the changes occurring in the fuel in the course of burnup, reactions are thermodynamically possible in any system of fuel and cladding material. However, this does not imply that they have to be incompatible. No reaction occurs below a certain temperature, and if it occurs there is still a possibility that the stress bearing capacity of the cladding will not be unduly diminished. Hence, with compatibility studies one should always take into account the changes in mechanical properties of the cladding material.

It was believed that for steel no major problems would arise with oxide fuels. Thermodynamical data for pure systems seemed to indicate good results as long as the fuel was not hyperstoichiometric. This assumption has been confirmed in many out-of-pile investigations of UO_2 and $(U,Pu)O_2$ with steel. However, this bright image has become rather dimmed in the meantime since more results have become available from post-irradiation investigations, especially those with higher burnups. Even if the results of such post-irradiation investigations are often contradictory and present no reliable picture of the compatibility situation, there are sufficient studies in which strong reactions have indeed been observed between the fuel and the cladding. Since the changes the fuel undergoes during burnup are known, this is not surprising. Elements thought to be particularly critical for the cladding are the fission products cesium, tellurium, and iodine. Since, on average, the fission products generated do not have the same high affinity for oxygen as the split atoms of uranium and plutonium, respectively, the result is an increase in the oxygen potential which is generally known as a shift in stoichiometry of the fuel during burnup. This is probably the most critical change as far as the compatibility behaviour is concerned. As can be seen from Fig.1, the oxygen potential may rise to quite considerable levels. This diagram shows the degree of burnup resulting in an O/M ratio in the fuel of 2.00 at a given initial stoichiometry. On the other hand, it is evident also from the diagram which initial stoichiometry must be selected so as not to get hyperstoichiometric fuel at a given target burnup. The margin of error takes into account the different data on the fission product yields[1]. Hence, at an initial stoichiometry of 1.97 an oxygen potential will have been reached in the fuel at a burnup of 4 at.% which allows the steel cladding to undergo oxidation. The oxidations of the cladding observed in burned-out samples have been much worse, however, than some out-of-pile investigations performed under the same conditions with the same amount of oxygen present. We assume that this is due to the presence of cesium. Cesium very much accelerates oxidation of the cladding [2]. Fig. 2 shows oxidations of steel by hyperstoichiometric UO_2 in the presence and absence of cesium. This is a very clear representation of the influence of cesium. The attack along the grain boundaries, which can frequently be seen in irradiated samples, is particularly significant. This type of attack is very dangerous as merely the formation of small amounts of reaction-products will destroy the grain structure of the cladding material to great depths. The reactions with tellurium do not depent on the oxygen potential. They are found in all samples irradiated over a prolonged period of time. We were able to detect very strong attacks on the cladding by tellurium in our simulation studies. The extent of this attack is a function of the steel type. In Fig.3, one can see a comparison between attacks of tellurium on the cladding of Sandvik steel and 4988 steel. The reactions are much more pronounced with Sandvik steel. Selenium may be even more aggressive with steel claddings than tellurium [3]. However, it is generated only in small quantities, so it does not cause problems of its own.

Iodine is frequently assumed to initiate a "van Arkel-type process" at the temperature gradient in the fuel by which components of the cladding material are transported into the interior of the fuel. This would allow a continuous attack upon the cladding material without ever consuming the reactive element, i.e., iodine. However, grave doubt is being shown about the occurrence of a van Arkel-type process as sofar nobody has succeeded in presenting a credible theory as to how sufficient free iodine can be made available in the fuel for this process. Since the quantity of cesium is roughly three times bigger than the amount of iodine generated, it may well be assumed that all the iodine is bonded. Since the affinity of cesium is greater for iodine than it is for all the other elements of components in the system, it is not very likely that iodine will be released by the cesium due to further bonding of the latter.

Hence, the causes of the attack on the cladding material will essentially be oxidation accelerated by cesium and a tellurium reaction. Consequently, post-irradiation results cannot be compared without further ado and cannot easily be projected onto new fuel pins. In many test pins used to study the operation behaviour of fast breeder fuel elements, the uranium-plutonium mixed oxide was and still is highly enriched in the fissile isotope U-235 in order to achieve high burnups with a relative short irradiation time. Since the fission of U-235 results in different chemical conditions than the fission of Pu-239, the results of these studies are no reliable indication of the behaviour of a uranium-plutonium mixed oxide fuel pin without U-235 enrichment. With respect to compatibility, conditions are more favorable in U-235 fission because the increase in the oxygen potential (cf. Fig.1) and the production of the reactive fission product tellurium [1] is lower at the same burnup than in the fission of Pu-239. This may be one of the reasons for the different results reported in the literature on in-pile compatibility behaviour. If, for instance, the behaviour of a breeder fuel without U-235 enrichment is to be compared with a test fuel having an enrichment of 85% U-235 at an initial stoichiometry of 1.97 and a burnup between 5 and 6% then theoretically the cladding of the breeder fuel would have to be attacked much more severely than that of the test fuel. This is because the latter has just reached the O/M ratio of 2.00, while the breeder fuel has already been supplied so much oxygen for oxidation of the cladding as would correspond to a fuel with an O/M ratio of 2.02 under out-of-pile conditions.

For the transition to higher reactor operating temperatures vanadium alloys could be used as the cladding materials. They have the advantage over steel of not undergoing any radiation induced high temperature embrittlement. However, they do have a very high affinity for oxygen. Hence, this advantage will probably not be able to become effective. Combined with UO_2, this high affinity for oxygen does not raise any problems because only small amounts of oxygen are exchanged in alloys having up to 10% of titanium [4,5]. However, this is different with a breeder fuel with plutonium enrichment because the oxygen potential is much higher in the hypostoichiometric mixed oxide than in UO_{2-x}. According to thermodynamic data, it is possible, that the vanadium cladding may reduce the plutonium to the trivalent state in some cases by the combined action of the temperature gradient in the fuel. Sufficient oxygen is available, even without an additional oxygen supply during burnup, which we have observed to be almost twice as high in the fission of Pu-239 as in the fission of U-235,to oxidize the cladding to significant oxygen concentrations (>1 wt.%), depending upon the affinity for oxygen of the other alloying constituent. It has already been proved that vanadium alloys take up oxygen from hypostoichiometric $(U,Pu)O_2$ without [6] and with a temperature gradient being present in the fuel [7]. There was always oxygen diffusion into the cladding which sometimes manifested itself in considerable increases in hardness. No formation of an oxide layer at the phase boundary was observed.

Now the question is to what extent will the uptake of oxygen impair the practical usefulness of vanadium claddings ? Information is available from similar studies [8]. Table 1 is a survey of the results obtaines with respect to the mechanical properties of various vanadium alloys after annealing in flowing sodium during which there was a considerable uptake of interstitial elements. It shows that there is still sufficient ductility at high interstititial concentrations at elevated temperatures, even if in some cases total embrittlement has already occured at room temperature. We found out by hot hardness measurement of V-1 Ti-15 Cr samples annealed in sodium that hardness decreases greatly with increasing temperature (Fig.4)

The following conclusions can be made from studies on the compatibility of vanadium alloys with media releasing oxygen [6,8,12,14].

1. Titanium-contained alloys (and pure vanadium) have a higher oxygen uptake than chromium-contained alloys.
2. The maximum hardness is higher with titanium-contained alloys than with chromium-contained alloys. The depth of penetration of oxygen into vanadium-chromium alloys is greater than it is with vanadium-titanium alloys. The hardness gradient is steeper with vanadium-titanium alloys than with vanadium-chromium alloys.
3. Ductility due to oxygen is reduced less with vanadium-titanium alloys than with vanadium-chromium alloys. The higher the titanium content, the better the ductility, even at higher oxygen uptake.
4. Oxygen is the interstitital element of the three taken up by vanadium from its environment, i.e., oxygen, nitrogen, carbon, which diffuses into the vanadium lattice the quickest and the furthest, carbon being the slowest of these elements. In most cases, carbon will be present to any major concentration only in the interfacial areas.
5. In vanadium alloys, the uptake of interstitial elements increases the temperature of the transition from brittle to ductile. There are vanadium alloys which still have sufficient ductility at elevated temperatures despite high concentrations of interstitial elements.

It is quite possible that the results shown above cannot be fully etrapolated to conditions in the fuel pins of breeder reactors. They were to indicate only that oxygen uptake of the cladding alone will not necessarily render vanadium alloys useless as cladding materials. They show better behaviour with fission product reactions (Te, Cs) (Fig.3), and there is no grain boundary attack.

Also carbide fuel is being envisaged for use in future reactor concepts. Although, according to thermodynamics data, even single-phase carbide fuel with steel or vanadium claddings is not stable, the main problem is believed to be the nonstoichiometric composition of the fuel. UC and also (U,Pu)C have a narrow area of homogeneity below 1000°C. Hence, industrial fabrication is concerned almost exclusively with two-phase fuel. In hypostoichiometric composition free metal is present as the second phase. In case of hyperstoichiometric composition it is M_2C_3 or MC_2. The second phase greatly increases the reaction potential relative to the single-phase product. Hypostoichiometric fuel is excluded at the beginning for fear of eutectic reactions in connection with steel. More rapid carbonization of the cladding is possible with hyperstoichiometric fuel. Hence, attempts have been made at an early date to stabilize the carbon potential in the fuel to a level tolerable for the cladding by means of suitable additives. Investigations carried out at our Institute [10], although at higher temperatures, have shown that stabilization does not always have to be an advantage.

Most probably, no stabilization of the fuel is required to solve the compatibility problem because carbon reactions would not yet greatly impair the suitability for practical use of steel claddings at contents of a few percent of higher carbide. This was shown by investigations at UNC [9] and by ourselves [11]. Steel can take up to 0.6% of carbon before becoming brittle [12]. Tests of the mechanical properties of 4988 steel after annealing with UC (carbon equivalent content ∿4.85%) at 600, 700 and 800°C did not show any decrease of ductility as opposed to the samples annealed in vacuum [13] (Fig.5). No carbonization was observed. Studies with clearly hyperstoichiometric UC (carbon equivalent content ∿4.95%, which corresponds to aproximately 3 vol.% of UC_2) showed carbide precipitates in the steel at 800°C already after relatively short periods of time (500 h). In some cases, the precipitation areas ranged up to 500µ. At longer periods af annealing (5000 h), the picture of the reaction did not deteriorate. Also at 900°C there were as yet no disastrous reactions with hyperstoichiometric UC. In this case, the carbon uptake was between 0.1 and 0.3% (Table 2). However, at 900°C, the different types of steel showed different reaction behaviours. Major grain boundary precipitation was found with 316 ss, much less so with 4988 steel. Sandvik steel (type 1.4970) behaved quite well at this temperature with hyperstoichiometric fuel, even after long annealing periods. However, in contact with practically single-phase UC (carbon equivalent content∼4.85) there were strong reactions to uraniferrous and carbide phases.

The results of our carbide investigations can be summarized as follows:

1. Nickel base alloys are no longer compatible with carbide fuel at 700°C.
2. Austenitic steels are compatible even with slightly hyperstoichiometrc fuel upto 800°C, except for alloys with higher nickel content, e.g. Incoloy 800.
3. A few types of steel behave well even at 900°C; however, there is already a danger of more pronounced reactions in steel stabilized with titanium.
4. At about 1000°C, there are strong reactions with all steels.
5. Reactions resulting in uraniferrous phases are more dangerous than carbide reactions because they accelerate the overall rate of reaction.

Hyperstoichiometric composition retards the generation of uraniferrous phases; hyperstoichiometry therefore should not be reduced by stabilization.

The in-pile behaviour does not differ too much from that found outside the reactor. Only a small amount of carbon is released during burnup. Fission product reactions are less dangerous than with oxide fuel as the oxygen potential is too low for any attacks of cesium. Tellurium may possibly be bonded by UC.

Vanadium alloys with carbide fuel have an even higher thermodynamical instability than steels. However, these reactions occur at a very low rate; there are no uraniferrous phases to accelerate the reactions, as in the case of steel. Carbon uptake in the vanadium lattice is lower than that of oxygen. At 900°C it took us a long time of annealing (5000 h), to detect any reaction effects with alloys of up to 5% Ti. The reaction zones differed depending on the composition of the alloy and varied between 5 and 20 µ. At 800°C, no effect was detected even after 5000 h. Measurements of the mechanical properties after annealing with UC at 800°C and for 800 h showed but minor effects (Fig.6 and 7). At these annealing conditions, the carbon uptake was aproximately 500 ppm (Table 3).

Literature

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Conditions of Sodium Exposure*	Sodium Vel. (fps)	Tensile Test Temp.** (°C)	Ultimate Tensile Strength (10^3 psi)	Yield Strength (10^3 psi)	Elongation (%)	Reduction of Area (%)
VANSTAR-9 (V-Fe-Nb-Zr-C)						
Uncorroded		RT	98.7	69.5	30	27
1500hr/770°C	14		100.0	95.5	2	0.5
Uncorroded		800	68.6	43.8	45	72
1500h/790°C	14		90.1	72.0	25	58
1500h/690°C	5		72.7	65.5	24	62
2650h/690°C	5		81.8	67	28	65
VANSTAR-8 (V-Cr-Ta-Zr-C)						
Uncorroded		RT	77.5	53.9	31	--
1500h/770°C	14		106.0	--	0	0
Uncorroded		800	58.1	31.8	28	--
1500h/790°C	14		98.0	68.4	22	49
V-20Ti						
Uncorroded		RT	104.0	88.4	18	20
1500h/770°C	14		79.0	71.3	12	18
2650h/700°C	5		87.7	69.2	15	29
Uncorroded		800	65.0	49.2	23	47
1500h/700°C	5		61.0	49.1	12	22
2650h/700°C	5		58.5	48.8	12	22

NOTE: Flat specimen 12.5 mm gauge length, 1.5 mm thick.

Element	Before Exposure (ppm)	After Exposure (ppm)	
		1500 hr	2650 hr
Nitrogen	79	22,000	35,000
Carbon	570	6,500	27,000
Oxygen	640	5,800	6,000

Tab. 1

Effect of Sodium Exposure on the Mechanical Properties of Some Vanadium Alloys (Strain Rate $\dot{\varepsilon} = 0.05\ \text{min}^{-1}$) and Interstitial Concentrations in 25 to 75 µm deep Surface Layer of Vanstar 9 Sample exposed to Flowing Sodium (< 10 ppm O_2 at $\sim 790^{o}C$) [8]

Type Steel	C (wt.%)
1.4981	0,39
1.4988	0,18
1.4970 (Sandvik 12R72HV)	0,18

Tab. 2 Carbon content of steels after annealing at 900°C for 500 h in contact with UC (4,95 % equiv C)

Concentration of	before annealing	after annealing at 600°	700°	800°C
C (ppm)	460	600	600	900
O "	850			
N "	530			

Tab. 3 Carbon uptake of V-10 Ti-15 Nb after annealing for 800 h at 600, 700 and 800°C in UC (equiv C ~ 4,83 %)

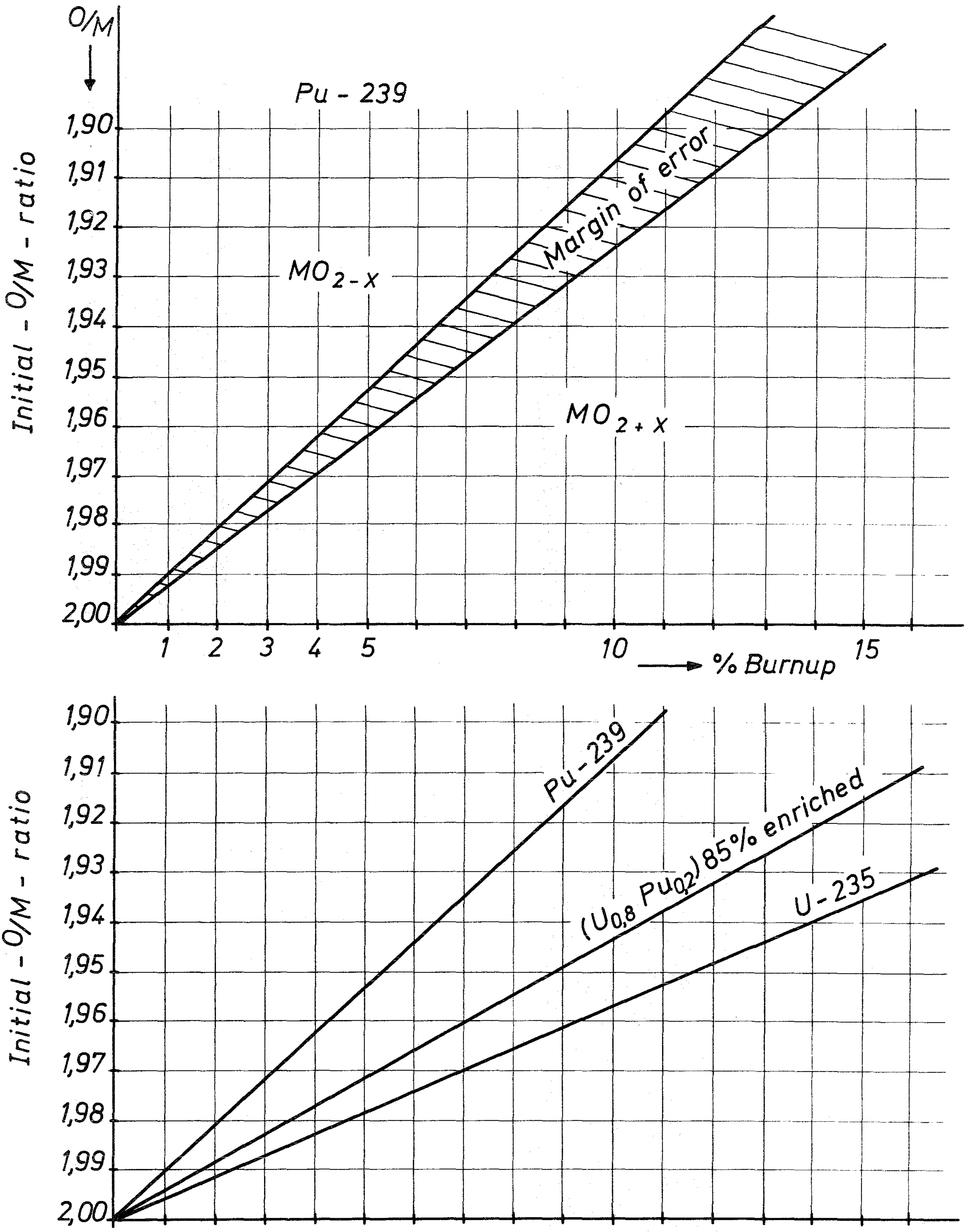
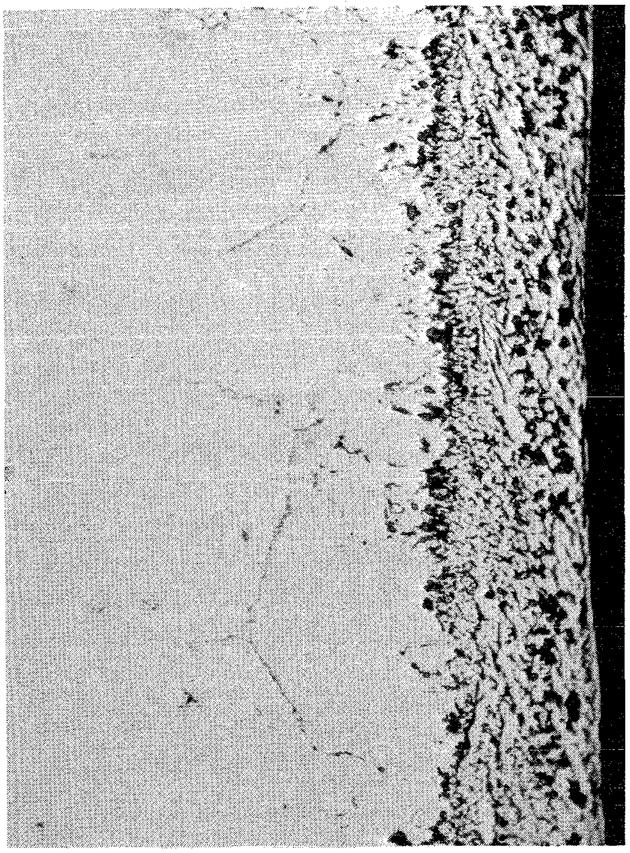
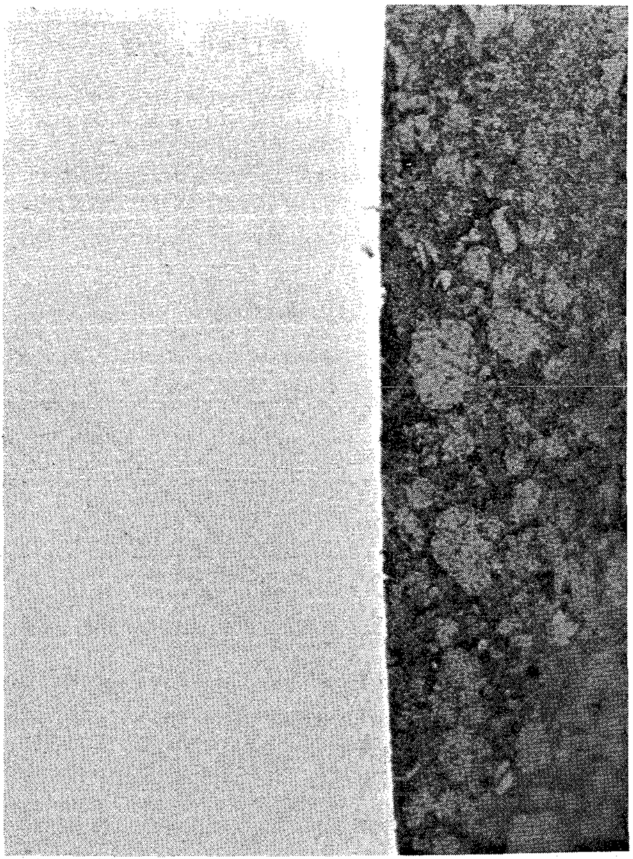


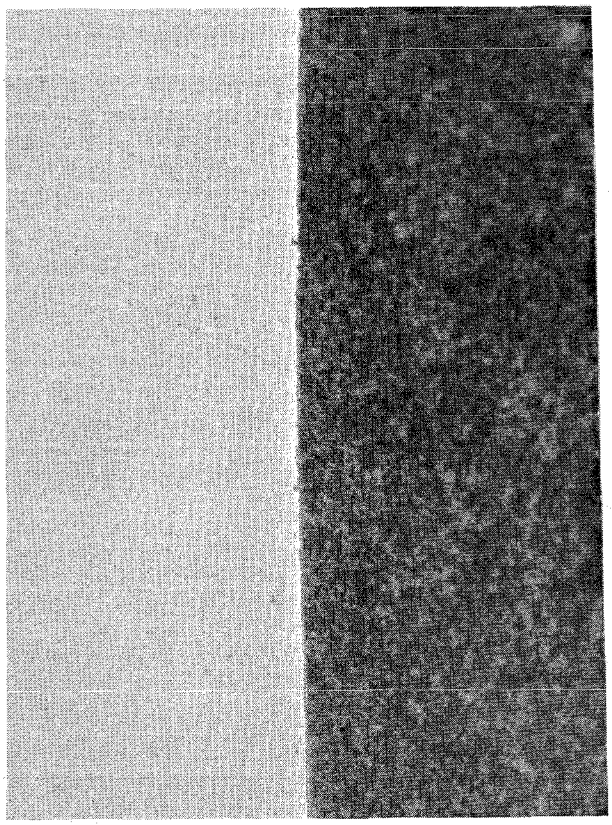
Fig. 1 Shift in stoichiometry by fission in oxide fuel
(Valency of rare earth elements assumed as 3)



$UO_{2,o8}$ + Cs



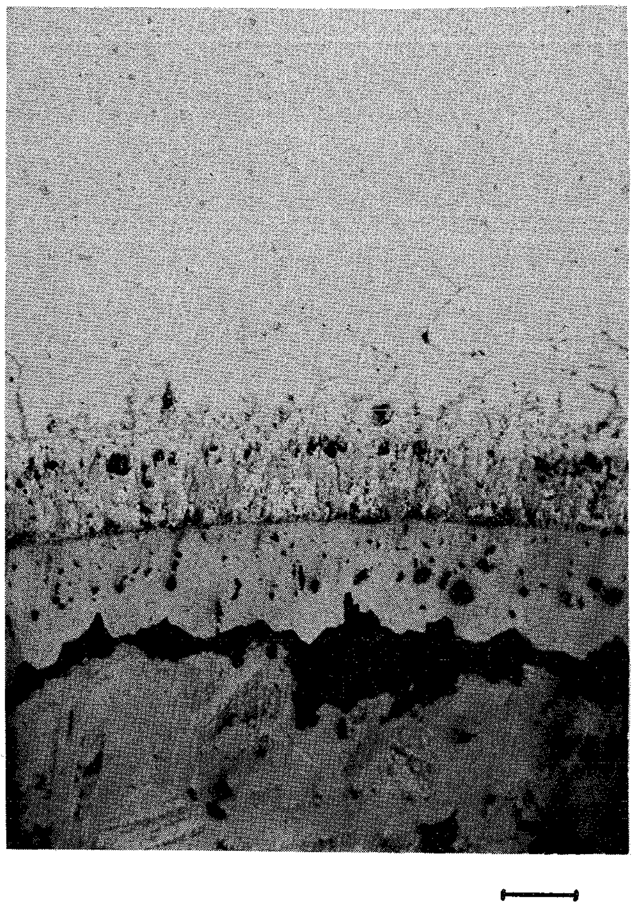
$UO_{2,oo}$ + Cs



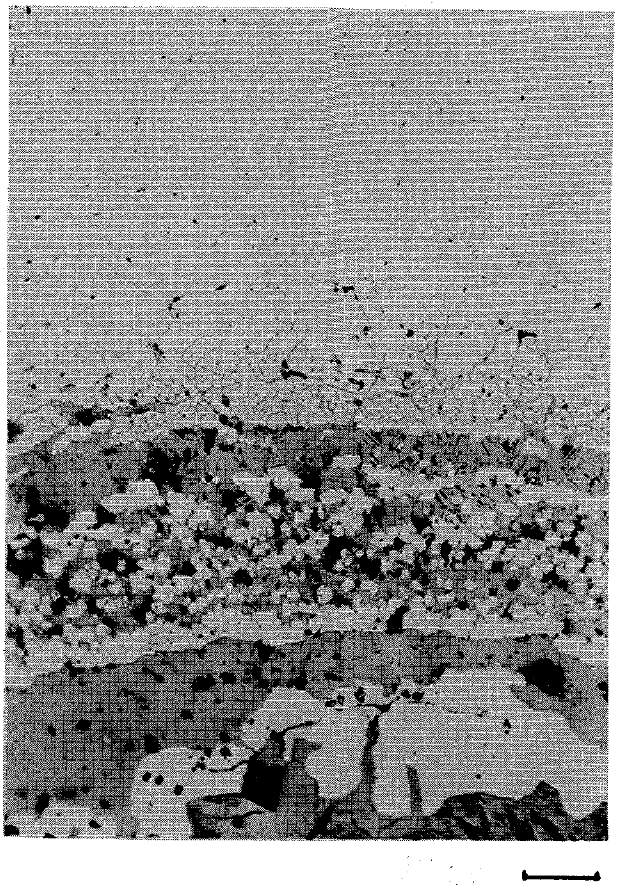
$UO_{2,o8}$

Fig. 2 Reactions of an Oxide Fuel of differing composition with Steel Type 1.4988 at 8oo°C/ 1ooo h

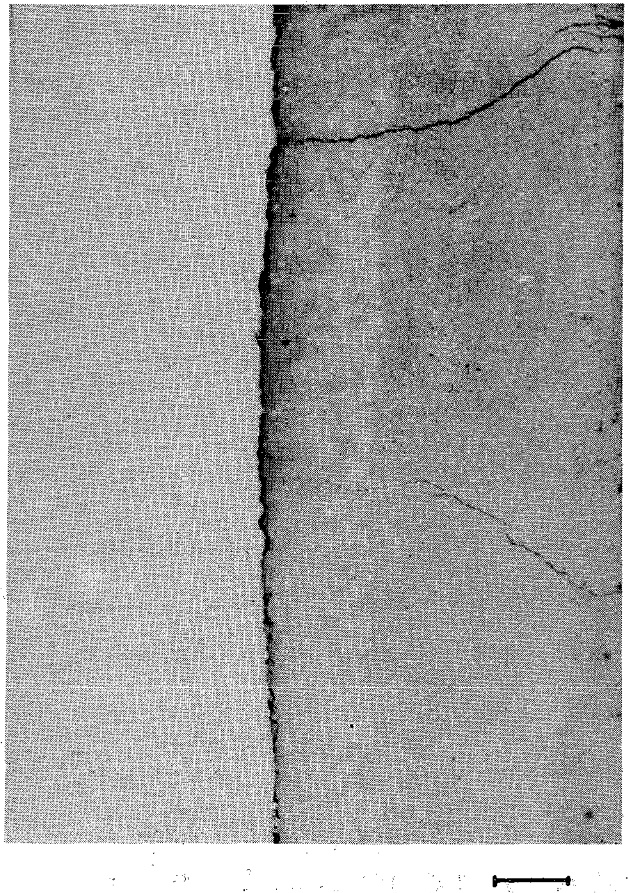
Note the effect of Cs



Steel Type 1.4988 100 µ



Steel Type 1.4970 100 µ



V-1 Ti-3 Si 20 µ

Fig. 3 Reactions of Tellurium with different cladding materials.
800°C / 1000 h

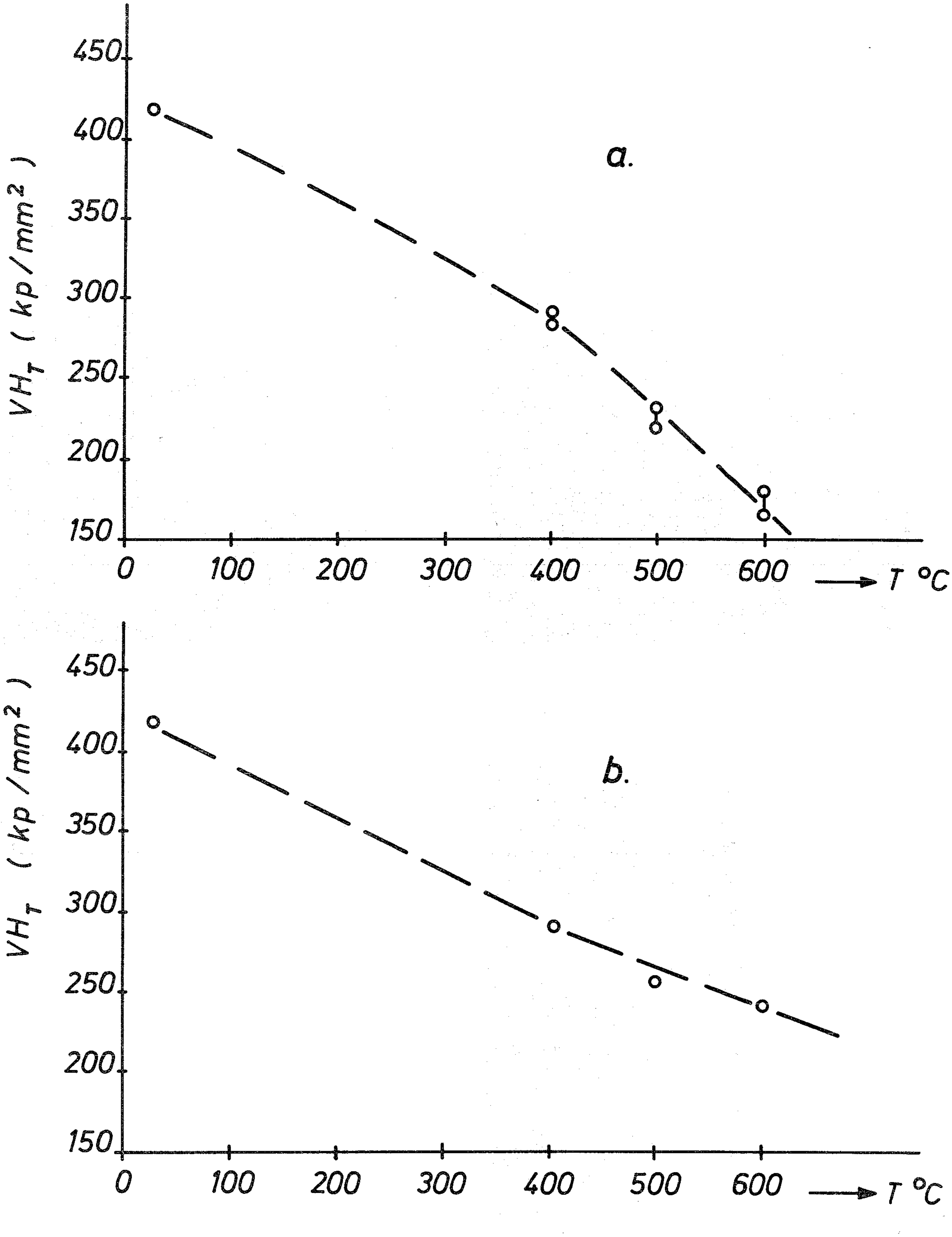


Fig. 4 Hothardness of corroded V-1Ti-15 Cr in Na
a., at 550° C / 2000 h (2800 ppm O_2)
b., at 600° C / 2000 h (3600 ppm O_2)
(HV_{RT} = 200 with 750 ppm O_2)

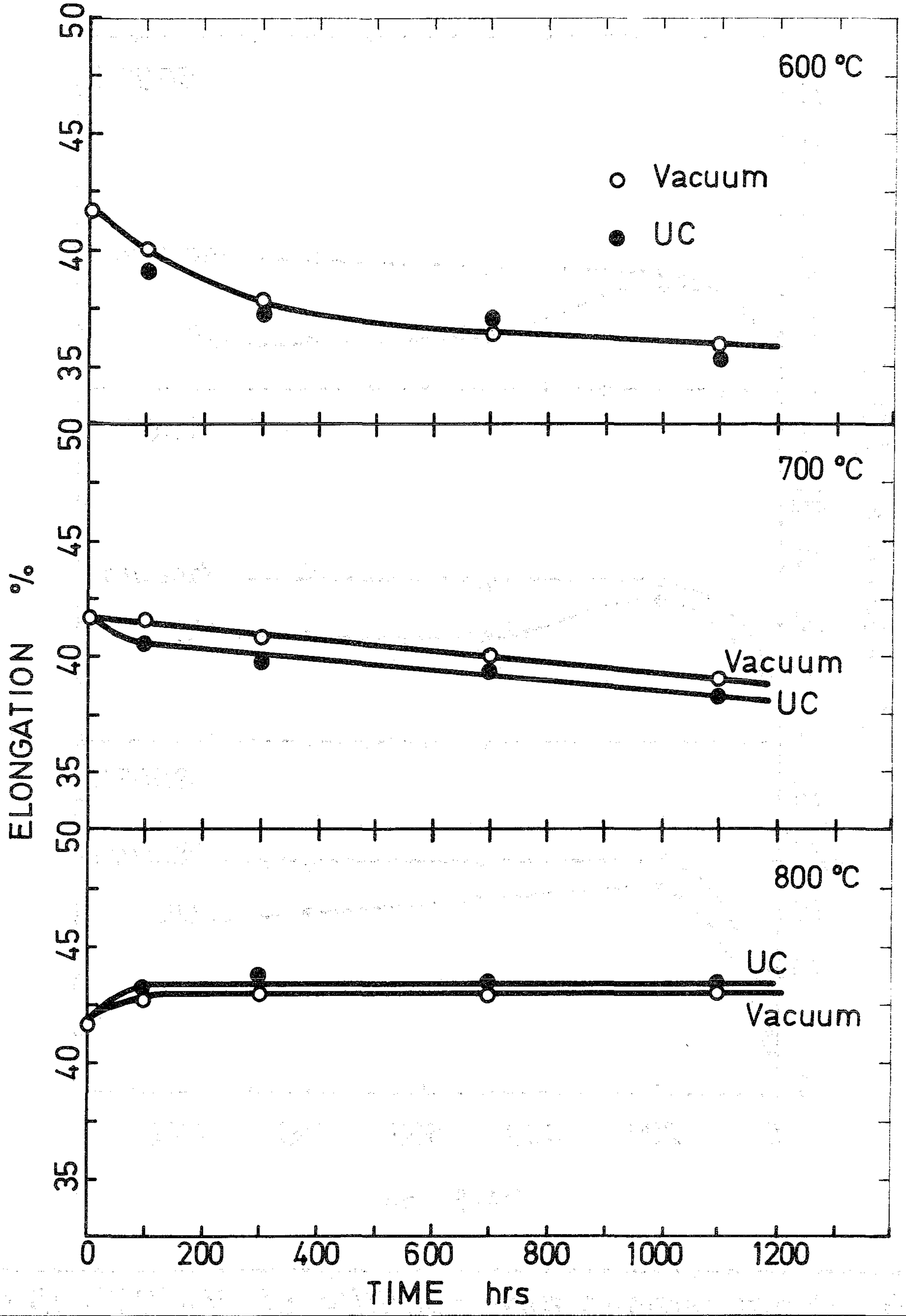


FIG. 5 Room temperature ductility of STEEL 4988, solution treated and aged 3 hrs at 750 °C and then annealed in vacuum (—○—) and in contact with UC (—●—)

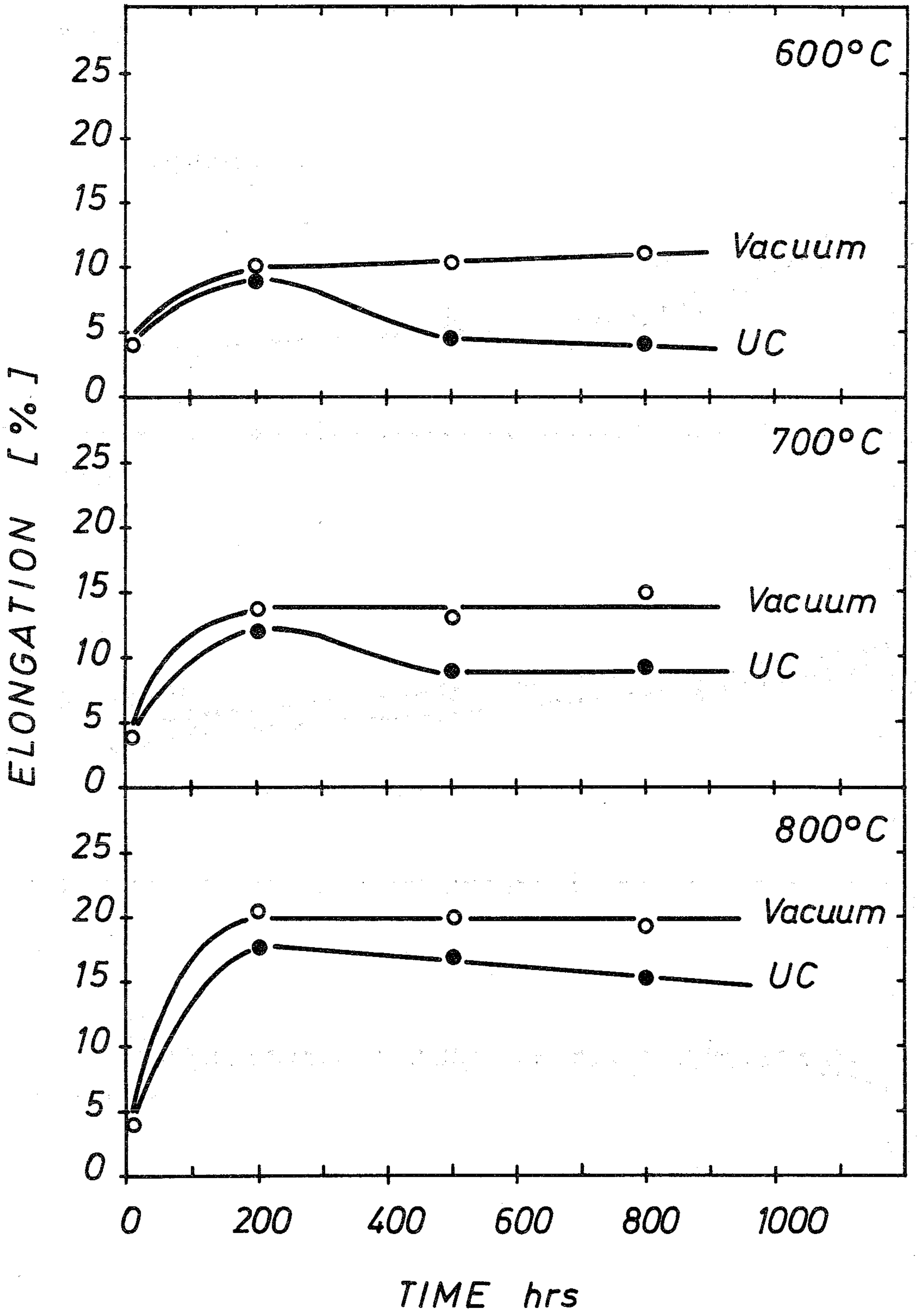


FIG. 6 Room temperature ductilily of V-10 Ti-15 Nb annealed in vacuum (-○-) and in contact with UC (-●-)

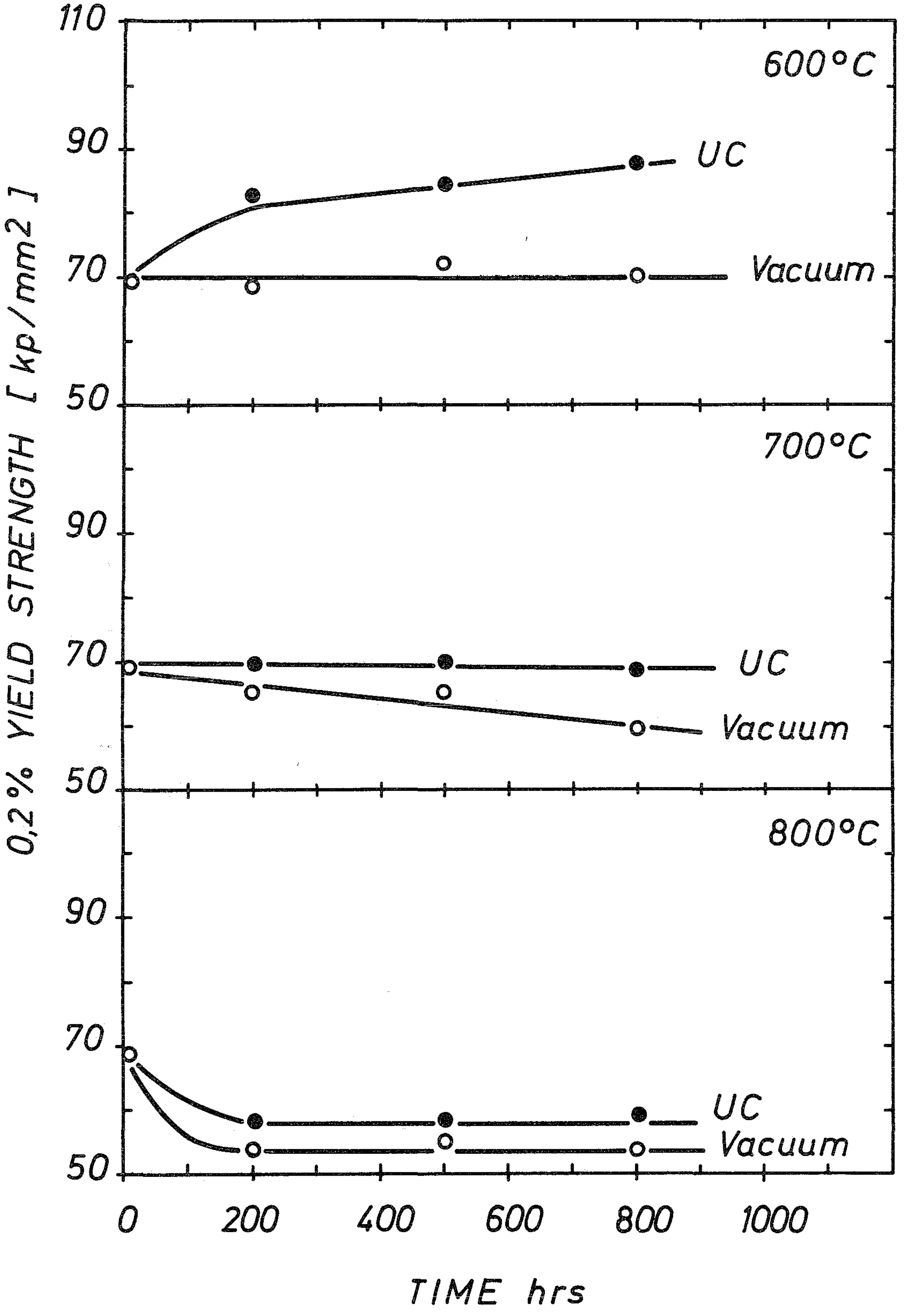


FIG. 7

Room temperature yield strength of V-10 Ti-15 Nb annealed in vacuum (–○–) and in contact with UC (–●–)