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**THE ROLE OF CAESIUM IN CHEMICAL
INTERACTION OF AUSTENITIC STAINLESS STEELS
WITH URANIUM PLUTONIUM OXIDE FUELS**

by

R.W. OHSE and M. SCHLECHTER

1972



**Joint Nuclear Research Centre
Karlsruhe Establishment - Germany**

European Institute for Transuranium Elements

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ABSTRACT

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KEYWORDS

FUELS
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STAINLESS STEELS
AUSTENITE
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CESIUM
CHEMICAL REACTIONS
CHEMICAL POTENTIAL
OXYGEN
CHEMICAL REACTION KINETICS
PHASE DIAGRAMS
INTERFACES
BURNUP
DEFECTS

The Role of Caesium in Chemical Interaction of Austenitic Stainless Steels with Uranium Plutonium Oxide Fuels *)

1. INTRODUCTION

Swelling and clad corrosion are the main life limiting factors of a fuel element at high burn-up. As a consequence of the latest irradiation results [1,2], clad corrosion is given increasing priority. The high burn-up system under consideration is a multicomponent system formed under the irreversible conditions of radial temperature and composition gradients and fission product distribution. Considerable uncertainties exist with regard to chemical state and concentration of fission products. A practically uncontrollable crack formation during fuel cycling provides radial gas phase connections under high temperature gradients, thus enabling gas transport, which can lead to remarkable changes of fission product concentrations along the clad. Postirradiation examinations [3,4] of irradiated fuel pins reveal various kinds of chemical attacks, mainly depending on the oxygen potential, the temperature and burn-up, resulting in the formation of a layered structure, the dissolution of passivated oxide films, the ablation of the steel or matrix attack, and finally the intergranular attack.

For a successful approach it seems unavoidable to simplify the multicomponent system by restricting it to the main reaction products formed at the interface fuel cladding. The role of caesium, being regarded as the most aggressive fission product [5,6] in clad interaction, and the reaction mechanisms are discussed by comparing the initial state of oxidation of the austenitic stainless steel and its defect mechanism with the final reaction layers found at high burn-up.

*) Manuscript received on August 22, 1972

2. INITIAL OXIDATION STATE OF AUSTENITIC STAINLESS STEELS AT THE OXYGEN POTENTIAL OF THE URANIUM PLUTONIUM OXIDE FUEL

2.1 Phase Relationships and Oxygen Potentials of the Protective Oxide Scales and the Fuel

The chemical state and structure of oxide scales on the cladding of austenitic stainless steels [7] are given by the oxygen potential and temperature at the fuel surface and the phase relationships within the phase fields of significance of the Fe-Cr-O [8, 9, 10, 11], Ni-Cr-O [12] and Fe-Cr-Ni-O [12] diagrams.

The composition of the oxide scales depends strongly on the Cr concentration of the alloy, as shown in the phase diagram Fe-Cr-O and Ni-Cr-O given in Fig. 1 and 2. The principal oxides formed on pure iron oxidized on air [11, 13] above 570°C are FeO, Fe₃O₄ and α -Fe₂O₃. Above 700°C 95% of the oxide consists of wüstite FeO. Below 570°C only Fe₃O₄ and Fe₂O₃ are found. Small additions of Cr up to 2% increase the oxidation rate [14, 15]. From 2 - 13%, Fe-Cr alloys are in equilibrium with the spinel type (Fe,Cr)₃O₄. The oxidation rate decreases with increasing Cr content. Above 13% Cr, the Fe-Cr alloys are in equilibrium with Cr₂O₃. The range of Fe-Cr alloy solid solutions coexisting with the spinel type oxide (Fe,Cr)₃O₄ seems rather uncertain [10, 11]. The same applies to FeO coexisting with chromite intermediate compositions of the magnetite Fe₃O₄ - FeCr₂O₄. Both composition limits marked by A and B in Fig. 1 are subject to further investigation. In addition, the range of solid solutions Fe-Cr which coexist with wüstite FeO as a function of temperature is also open to further investigations. According to the phase diagram given by Seybolt [8], solid solutions of Fe-Cr below 13 wt.% are not compatible with the (Fe,Cr)₂O₃ type oxide. An ironchromite (Fe,Cr)₃O₄ spinel [16], i.e., a solid solution of Fe₃O₄ with FeCr₂O₄ as an intermediate layer, should be expected.

According to Fig. 2 [12], the oxide scale in equilibrium with Ni-Cr alloys at 1000°C is of the spinel type [16] below 10 at.% Cr and consists of Cr₂O₃ above 10 at.% Cr. Microprobe analysis at low Cr contents (< 10 at.% Cr) reveals an oxide layer of NiO above an oxide layer presumably consisting of a spinel in an NiO matrix. Above 10 at.% Cr the nickel content in the Cr₂O₃

layer was found to be as low as 0.7 at.%. The influence of nickel has been investigated by various authors [12, 17, 18, 19, 20]. Fig. 3 shows a plane section (in reality a three-dimensional surface) of the quaternary system Fe-Cr-Ni-O [12], based on the four ternary systems, at an oxygen concentration corresponding to the oxygen solubility limit of the ternary alloy Fe-Cr-Ni at 1000°C. The minimum chromium concentration at which the alloys is in equilibrium with Cr₂O₃, starting from 13 at.% Cr in the Fe-Cr system, passes through a minimum of 7 at.% Cr at 70 at.% Ni and 23 at.% Fe to 10 at.% Cr in the Ni-Cr system.

The chromium content of the alloy must, of course, be higher to compensate for the depletion caused by the formation of the Cr₂O₃ scale. A surface depletion as low as 10.8 at.% Cr at the interface metal-oxide was observed at a bulk concentration of 21.9 at.% Cr.

Fig. 4 gives the oxygen potential versus temperature of all compounds possibly involved in the initial pure system, which is assumed to be still free of fission products, compared to the potential of the oxide fuel at various valencies [21, 22, 23, 99]. As shown in Fig. 4, the oxygen potential of the oxide fuel is fixed by its temperature and valency. The valency is fixed by the fuel composition O/M and Pu/(U+Pu). To determine whether a Fe-Cr alloy with a given Cr/(Fe+Cr) mole fraction at the oxygen partial pressure [21, 24, 25] of the fuel surface is in equilibrium with the sesquioxide or the spinel type oxide, its constitution diagram, i.e., log p_{O₂} versus Cr/(Fe+Cr), must be known. The constitution diagram in Fig. 5 [8] is given for 1300°C. The oxygen partial pressure of a four-valent ternary oxide fuel at 1300°C is 10⁻¹⁵ atm, corresponding to an oxygen potential of -93 kcal/mole [21, 22, 23]. According to Fig. 5, only alloy compositions above 35% Cr would be in equilibrium with the sesquioxide. According to Fig. 4, the oxygen partial pressure at 1300°C above pure Cr₂O₃ in equilibrium with chromium metal is 10⁻¹⁶ atm, which is in agreement with the constitution diagram. The equilibrium oxygen pressure in Fig. 5, log p_{O₂}, at which the alloy is in equilibrium with the sesquioxide, however, increases too rapidly with decreasing chromium content. According to the diagram calculated by Schmalzried [27] from the values of Katsura and Muan [28], alloy compositions above only 10% Cr would already be in equilibrium with the

sesquioxide under the same conditions of an oxygen pressure of 10^{-15} atm and a temperature of 1300°C . The reason for these deviations seems to be the difficulty establishing equilibrium under the condition of relative small changes in oxygen pressure. According to Katsura and Muan [28], the oxygen pressure at which the alloys FeCr_2O_4 and Cr_2O_3 coexist, i.e., within the three-phase field of the phase diagram in Fig. 1, was determined to $p_{\text{O}_2} = 2.8 \cdot 10^{-14}$ atm. A valency increase of the fuel to 4.001 would increase the oxygen partial pressure to approximately 10^{-12} atm, i.e., into the two-phase field where the alloy is already in equilibrium with the spinel.

If we assume the singular point, at which the alloy is in equilibrium with the sesquioxide and the spinel, to be around 13 % Cr, as indicated by Seybolt [8, 9, 40], a depletion of Cr in the alloy to below 13% by the formation of Cr_2O_3 would lead to the formation of an intermediate spinel scale. The depletion or possibly variation of the Cr content in the alloy depends on the component diffusion coefficients [29, 11, 14, 16] in the alloy compared to those in the sesquioxide and spinel.

2.2 Defect Structure of the Protective Layers

To understand the role of fission product reactions on the protective, passivating properties of the $(\text{Fe,Cr})_2\text{O}_3$ oxide layer, it is necessary to investigate its defect structure [30, 31] at minimum oxidation rate. A minimum in oxidation rate assumes low rates of ionic transport, which can only be expected at low defect concentrations. The increase in oxidation rate by adding up to 2% Cr can be explained by an increase in cation defects. A Cr content of 2 - 13% results in the formation of iron chromites of the spinel type $(\text{Fe,Cr})_3\text{O}_4$, i.e., in a solid solution of Fe_3O_4 and FeCr_2O_4 . At higher Cr concentrations (13 - 30%), a minimum in oxidation rate is observed around 18 wt.% Cr. Cr_2O_3 and Fe_2O_3 form a continuous series of solid solutions [32]. Cr_2O_3 is considered as cation deficient [14]. Because of energetic reasons, oxygen interstitials are very unlikely [17]. Fe_2O_3 is oxygen deficient [14]. Transport rates via oxygen vacancies and iron interstitials are comparable and depend on temperature. This would mean an equilibrium between Schottky [32] and Frenkel [33] disorder. Some authors [14, 29, 35, 36, 37] consider iron interstitials as slightly more mobile than the larger oxygen vacancies.

Since the end members of the solid solution range are of opposite defect structure, it seems reasonable to assume a minimum in defect concentration, i.e., low oxidation rates at more stoichiometric compositions, which itself depends on temperature and oxygen pressure [14]. The oxidation rates are near to parabolic [38]. Cation diffusion through the M_2O_3 type oxide seems to be the predominant mechanism in the early stage. A minimum in ionic defect concentration was found at 4 mole % Fe_2O_3 [34, 17]. Cr_2O_3 containing less than 4% Fe_2O_3 behaved as a p-type semiconductor, whereas Cr_2O_3 containing more than 4% Fe_2O_3 was shown to be a n-type semiconductor.

Any disturbances of this "defect concentration equilibrium", be it by chemical interaction or under irradiation at a high neutron flux [39], will tend to increase the oxidation rate. The aim of further investigations should therefore be to explain a reduction of the protective properties of the oxide layers [43, 44], aside a possible irradiation influence, by reaction with fission product phases, possibly by Cr depletion, which may then lead to ruptures and cracks because of the formation of stresses and voids at the steel - oxide interface, since the cation diffusion through the M_2O_3 type oxide seems to be the predominant mechanism. The possibility of forming intermediate layers by chromium depletion [12, 18] and its consequences on stress development [9, 11, 15, 40, 41] by the various oxide to metal volume ratios [11, 42] has to be taken into account. Crack formation could, of course, also be due to differential contractions during temperature cycling under reactor operating conditions. Stress and crack formation [15, 17] could finally explain why these scales are lifted giving rise to a strongly increased corrosion rate.

3. FUEL CLAD INTERFACE AT HIGH BURN-UP

3.1 Determination of Reaction Products at the Interface Stainless Steel - Oxide Layers - Fission Product Phases

Since a purely thermodynamic approach to the irreversible interaction behaviour of the multicomponent system stainless steel - fission product - fuel necessarily contains many assumptions and uncertainties, a first selection among the possible reactions should be obtained by microprobe and

X-ray analysis of the reaction products formed under reactor conditions. As a main result of the various postirradiation examinations of irradiated fuels made in the various laboratories, caesium is in general accepted /6/ as one of the most aggressive elements in oxide fuel cladding interaction. The investigation of the role of caesium requires microprobe analysis of the reaction products of preoxidized stainless steel samples, brought into contact with liquid oxygen, containing caesium phases and (U,Pu)O₂ mixed oxides under a temperature gradient at 500 to 600°C clad temperature.

Both the composition of the various reaction zones formed between the clad and the fuel, and in the case of intergranular attack, the reaction products formed within the grain boundaries must be known as a function of oxygen potential and temperature in order to establish the brutto reaction and finally the reaction mechanism. Special attention is to be paid to adjacent fission product phases /45/ which possibly exist as liquid multicomponent electrolytes.

Postirradiation examinations /5, 46, 47, 48, 49/ of irradiated fuels with austenitic stainless steel cladding reveal three kinds of attack, the formation of a layered structure in the case of initially near to stoichiometric fuels, the dissolution of thin passivating layers, and the subsequent surface ablation of the steel in the presence of a liquid phase, and finally the intergranular attack of sensitized steels within the grain boundaries. All three types of attack are usually of a rather local and less uniform appearance, depending on the local concentration of fission products. In the case of a layered structure, it is assumed, that the passivating oxide layers, mainly consisting of Cr₂O₃, are formed before an appreciable amount of fission products has reached the fuel clad interface. Surface ablation is observed on the non-protected steel surface after a thin protective oxide film has been dissolved in the liquid phase. Intergranular attack is observed especially in sensitized steels, where Cr₂₃C₆ precipitations along the grain boundaries are oxidized. To give a complete treatment of the various kinds of chemical attacks, the reaction mechanism leading to a layered structure is discussed. Fig. 6 summarizes the general features of analytical results reported by the various laboratories /3, 50, 51, 52, 53, 54, 55/ giving the composition of the scale formation at the interface fuel clad after high burn-up. According to Fig. 6, the original M₂O₃ oxide layer is

separated from the steel by a liquid multicomponent phase of a similar fission product composition as the outer phase at the Cr_2O_3 fuel oxide interface. In addition to steel components in both intermediate layers, precipitations of Fe, Cr and Ni are found at the fuel surface. The assumption of ionic transport across the liquid phase, however, requires that a gradient in chemical potential exists, possibly realized by the precipitation of compounds at the oxygen rich interface towards the fuel. Further information can be obtained from the chemical state of the steel compounds found at the fuel surface. Any possible reaction mechanism must, therefore, be able to explain the initial increase in rate of oxidation, which by surface depletion of steel components, may lead to intermediate layers, causing cracks, and the final lifting of the layers, thus allowing the liquid phase to penetrate into the interface steel - M_2O_3 , leading to a rapid increase in corrosion.

3.2 Thermodynamics and Phase Relationships

Once the reaction products are known, it is necessary to determine under what conditions they are formed. The main parameters are temperature and oxygen potential at the interface fuel clad given by the temperature profile and the radial O/M composition gradient which itself is determined by the initial bulk composition, burn-up, the chemical state of fission products and their distribution. Therefore, the phase relationships of significance for these reaction compounds and their oxygen potential are to be investigated in the temperature range of the fuel clad interface. The following phase diagrams are of direct significance: U-Pu-O [57, 22], Cs-O [58, 59, 60], Cs-Cr(SS)-O, Cs-Mo-O [52, 61], Fe-Cr(Ni)-O [8, 9, 10, 11, 12] and Cs-(U, Pu)-O [56, 57]. Since the high Cs-oxides from Cs_2O onwards are not to be expected on behalf of the oxygen potential of the fuel surface, special attention has to be paid to the oxygen solubility in caesium and its partial molar free energy compared to that of the fuel. It should then be possible to predict under what conditions caesium - fuel compounds such as Cs_2UO_4 or caesium - fission product compounds such as Cs_2MoO_4 are formed and whether caesium could be stabilized [68, 69] in its radial position.

Fig. 7 and 8 and Table I [72-80] summarize the available thermodynamic data and phase relationships on caesium compounds for further discussion.

Fig. 7 contains the binary Cs-O phase diagram [59,60]. Fig. 8 gives the oxygen potentials of Cs_2O and oxygen dissolved in caesium, [58,81] and likewise the data for Na_2O [70,71] and oxygen dissolved in sodium, and for comparison the oxygen potential of the ternary (U, Pu)-oxides at the fuel surface for the valency range of technological interest at high burn up. According to Fig. 8 Cs_2O at the oxygen potential of a stoichiometric fuel with a valency of 4 can only be expected at temperatures below 450°C . At the temperature of the fuel clad interface of approximately 600°C , Cs_2O can only be formed at the oxygen potential of a hyperstoichiometric fuel with a valency of 4.001, corresponding to a O/M composition of 2.0004 at 20 mole % of PuO_2 . Besides this, the melting point of Cs_2O of 490°C (Table I) lies below the temperature range of 500 to 650°C , expected at the fuel clad interface. Therefore a liquid, most likely a multicomponent, thin layer of caesium, containing oxygen, and the more volatile fission products such as tellurium, selenium and rubidium is to be expected. The amount of caesium or other volatile fission products available at the fuel clad interface depends on the stability of compounds such as CsI , $\text{Cs}_2(\text{U, Pu})\text{O}_4$, Cs_2MoO_4 , Rb_2MoO_4 [61-67] as a function of the oxygen potential, and the density of the fuel with regard to interconnected porosity and radial crack formation. Simulation experiments on fission product transport by Evans and Aitken [69] and Crouthamel and Johnson [68] confirm transport towards the clad almost up to stoichiometric fuel compositions, whereas in hyperstoichiometric fuels caesium appeared to be fixed in its radial distribution by the formation of stable compounds. The postirradiation examinations clearly show that molten layers are not observed all along the fuel clad interface, but seem in general to be rather localized in areas of high radial crack formation. Local concentration changes of these volatile phases seem to be mainly due to gas transport facilities along interconnected radial gas phases, such as cracks, formed during temperature cycling. A dense fuel will show no appreciable migration of caesium towards the clad. According to the estimated values, [61-70] Na_2UO_4 and Cs_2UO_4 compounds are only expected at the oxygen potential of a slightly hyperstoichiometric fuel. Because of the stable CsI compound, the chemical state of caesium is of importance for chemical gas transport reactions of stainless steel components by the van Arkel - de Boer mass transfer mechanism. According to fission yield calculations [82-85] for a fast neutron flux, the ratio of Cs to I is of the order of 10 to 1. Free iodine will therefore only be available if caesium can form compounds with either fuel, fission product or cladding components

which are more stable than CsI.

3.3 Reaction Mechanism

A decision on the various possible reaction mechanisms requires a detailed investigation of the composition of the various reaction zones, i.e. the possible depletion of the steel components within the clad and oxide layer such as Cr, compared to the initial state of passivation. This should give evidence as to what extent the adjacent liquid phase [1,86,87,88,40] can alter the composition of the initial oxide layer by dissolving components, and, as a consequence of this, changing the defect concentration or even defect structure and thus the rate of oxidation. A further possibility to be noted here is the introduction of fission products into the protective oxide film, such as vanadium or molybdenum, which may increase the number of cation vacancies and hence also increase the rate of oxidation. In all considerations special attention has to be paid to questions of ionic transport, i.e. the gradient of the chemical potentials [89] of the various components, and their diffusion coefficients. In the following an attempt is made to point out possible reaction mechanisms.

3.3.1. Disturbance of the anion - cation defect concentration balance within the passivating oxide layer

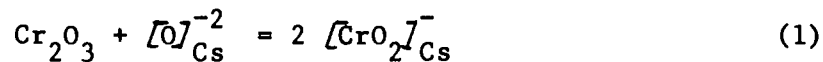
According to 2.2. the end members of the solid solution range Fe_2O_3 and Cr_2O_3 are of opposite defect structure [14]. A minimum in vacancy concentration and thus a minimum in oxidation rate is obtained by approaching a stoichiometric composition. The minimum of defect concentration was shown to be obtained at 4% Fe_2O_3 [7,34] in the solid solution. A reduction on either side would consequently again increase the defect concentration and thus the rate of oxidation.

The rate of oxidation in the case of spinel formation below 13 % Cr depends

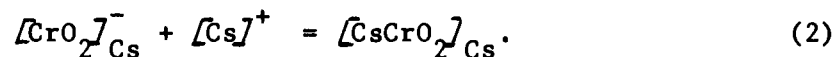
mainly on the phase width and stability of wüstite FeO which changes with temperature and alloy composition. Since the austenitic stainless steels 304, 316, 1.4988 and 1.4981, which are taken into consideration for cladding materials, are above 15 % Cr, the FeO influence will not be considered.

There is experimental evidence for a lowering of the Cr concentration in the (Fe,Cr)₂O₃-layer. It seems therefore reasonable to develop possible reaction mechanisms, which, in agreement with the thermodynamic data and phase relationships of the simplified system, can explain Cr dissolution into a liquid Cs phase, containing a sufficiently high concentration of oxygen, on behalf of an oxygen exchange mechanism, and subsequent compound formation, possibly as a chromite Cs-CrO₂ [5,91,92], to guarantee the necessary gradients of the chemical potentials.

Fig. 9 gives a schematic display of the possible reactions at the various phase boundaries. The chromium rich M₂O₃ type oxide (a_{Cr₂O₃} near to 1) is assumed to be dissolved in caesium containing oxygen according to



Of course the ionic chromium complex formed and its chromium valency depends on the oxygen potential at the fuel surface. Since the oxygen potential decreases with increasing temperature the solubility limit decreases and precipitation from the supersaturated solution will occur at the high temperature side of the liquid multicomponent caesium layer according to



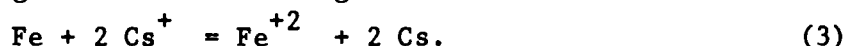
Because the activity of Fe₂O₃ in the M₂O₃ oxide is rather low, and the oxygen potential of CsFeO₂ calculated from the estimated values given by Fitts et al. [5,93] is above the oxygen potential of the ternary stoichiometric oxide fuel (U_{0.80}Pu_{0.20})_{2.00} at a valency of 4, the formation of CsFeO₂ can only be expected at the chromium depleted, iron rich surface of the oxide layers at an oxygen potential of a hyperstoichiometric oxide fuel.

Crack formation, within the fuel, as schematically indicated in Fig. 9, will allow the Cs vapour transport as either metal or iodide and the necessary oxygen transfer via the CO/CO₂ gas phase mechanism. The gas diffusion current [94] is mainly determined by the pressure, the temperature gradient and the diffusion coefficient. According to Hall measurements [60] caesium and oxygen exist to a high extent in their ionic state within the liquid caesium.

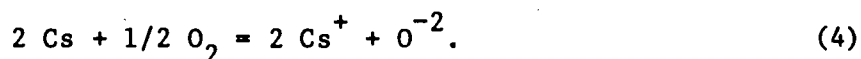
The selective dissolution of the M₂O₃ oxide layer will disturb the defect concentration balance and increase the rate of chromium diffusion to the liquid oxygen containing Cs phase. As a result of this, chromium depletion will occur at the metal surface, leading to the formation of an intermediate layer of the spinel type oxide. It is assumed that stress development within these layers during the temperature cycling under reactor operating conditions will lead to cracks and finally to the lifting of the oxide scale [18]. The penetration of the liquid multicomponent phase in between the oxide layer and the metal would then give rise to an increased corrosion by surface ablation and intergranular attack.

3.3.2. Surface Ablation and Intergranular Attack

Though there are cases, where a transition from a thin protective film to a thick non-protective scale occurs, in general thin oxide films of the M₂O₃ type are assumed to be dissolved before a spinel formation can take place. Surface ablation of the unprotected alloy may consist of a simple dissolution [96], up to the solubility limit of the steel component within the liquid phase. With increasing oxygen dissolved in caesium, and increasing temperature, the rate of corrosion greatly increases and finally leads to intergranular attack. The concentration of caesium ions in liquid caesium increases with increasing oxygen content. It is assumed that the metal components of the steel alloy go into solution by reducing Cs⁺ to Cs according to



Cs⁺ is formed again at the oxygen potential of the fuel by reducing oxygen according to



The dissolution mechanism by oxidizing iron and reducing the caesium ion according to reaction (3) can likewise be formulated by the iron reacting with the active oxygen ion O^{-2} in the diffusion layer at the phase boundary alloy - liquid phase to



where the caesium is again oxidized to the caesium ion according to reaction (4) by dissolving oxygen in the liquid fission product layer at the fuel surface.

The formation of FeO at the chromium depleted iron rich, unprotected alloy surface depends on the oxygen potential and the temperature, and should be possible above 570°C and an oxygen potential of -100 kcal/mole. Since the oxygen potential of FeO increases with temperature far more rapidly than that of the four valent $(\text{U}, \text{Pu})\text{O}_2$ FeO would become unstable at the high temperature side of the liquid layer towards the fuel.

Apart from the proposed Van Arkel - de Boer gas transport mechanism [5,99 - 104] this could give a possible explanation for the Fe, Cr and Ni transfer in a liquid fission product phase towards the fuel surface [97,98]. The possible reaction mechanism is schematically shown in Fig. 9.

As shown in Fig. 6, Cs, Mo, O and I were found in the grain boundaries of the austenitic stainless steel. Various assumptions [61, 106] were made on the formation of low melting eutectic compositions such as offered in the $\text{Cs}_2\text{MoO}_4 - \text{MoO}_3$ phase diagram at 450°C [105]. The formation of such compounds would however require a rather high oxygen potential. Besides this, they do not explain the Fe, Cr and Ni depletion reported along the attacked grain boundaries.

Though the presence of Mo could possibly be explained by a chemical gas transport reaction involving MoOI_2 similar to the WO_2I_2 oxyiodide [107] gas transport reported by Schäfer, Cs-Cr-O compounds, such as discussed above are necessary to explain the Cr depletion.

The formation of molybdenum compounds such as Cs_2MoO_4 could possibly liberate iodine for further gas transport reactions where Fe is transported as FeI_2 towards the fuel surface.

The intergranular oxidation attack, observed in sensitized steels [50, 108, 109], can be explained by the oxidation of chromium carbide phases, such as Cr_{23}C_6 , precipitated along the grain boundaries of

the stainless steel. Since the formation of Cr_{23}C_6 phases in the grain boundaries leads to a chromium depletion at the grain surface, intergranular attack by the oxygen-containing liquid caesium phase, penetrating into the grain boundaries [46,63,53,110,111,112], occurs more easily. The intercrystalline corrosion proceeds along the grain boundaries by dissolving the steel components as discribed above and leads to an appreciable reduction in strenght and elongation. Differential contractions during thermal cycling can now well explain the formation of circular cracks and fracture observed within the area of grain boundary attack.

REFERENCES

- [1] ANS-Conference on Fast Reactor Fuel Element Technology, New Orleans 1971, Trans. ANS (1971)
- [2] Annual ANS-Meeting, Boston 1971, Trans. ANS, 14 (1971)No.1
- [3] C.E. Johnson and C.E. Crouthamel, J.Nucl.Mat.34(1970) 101
- [4] K.J.Perry, C.N.Craig, Trans. ANS, 12(1969)564
- [5] R.B.Fitts, E.L. Long, and J.M.Leitnaker, ORNL-TM-3385(1971)
- [6] C.E.Johnson, C.E. Crouthamel, Trans. ANS, ANS-Conf. New Orleans 1971
- [7] S.J.Rosenberg, US NBS Monograph 106(1968) 116
- [8] A.U.Seybolt, J.Electrochem.Soc.,107 (1960)147
- [9] D. Lai, R.J.Borg, M.J.Brabers, J.D.Mackenzie and C.E. Birchenall, Corrosion 17(1961)109
- [10] D.Woodhouse and J.White, Trans.Brit.Ceram.Soc., 54(1955)333
- [11] C.E.Birchenall, Z. Elektrochemie 63(1959)790
- [12] J.E.Croll and G.R.Wallwork, Oxidation of Metals, 1(1969)55
- [13] M.H.Davies, M.T.Simnad and C.E.Birchenall, J. Metals 3(1951)889
- [14] K.A.Hay, F.G.Hicks and D.R.Holmes, Korrosion 23(1971)33
- [15] G.C. Wood, T.Hodgkiess and D.P.Whittle, Corrosion Science 6(1966)129
- [16] H.Schmalzried, Werkstoffe und Korrosion 22 (1971)371
- [17] W.B.A.Sharp, Corrosion Science 10(1970)283
- [18] M.G.Hobby and G.C.Wood, Oxidation of Metals 1(1969)23
- [19] G.C.Wood, I.G.Wright, T.Hodgkiess and D.P.Whittle Korrosion 23 (1971)16
- [20] H.Pfeiffer and K.Hauffe z.Metallkunde 43 (1952) 364
- [21] M.H.Rand and T.L.Markin, Thermodynamics of Nuclear Materials 1967, IAEA, Vienna 1968, p. 637
- [22] Panel on the plutonium-oxygen and uranium- plutonium-oxygen systems, Technical Report Series No. 79, IAEA, Vienna 1967
- [23] R.W.Ohse and C.Ciani, Thermodynamics of Nuclear Materials 1967, IAEA, Vienna 1968, p. 545
- [24] R.W.Ohse and W.M.Olson, Plutonium 1970, Proc.4th Int. Conf. on Plutonium and other actinides, Santa Fe, New Mexico, 1970
- [25] R.W.Ohse and W.M.Olson, EUR 4633 e (1971)
- [26] H. Rickert, Korrosion 21 (1968) 97
- [27] H.Schmalzried, private communication 1972
- [28] T.Katsura and A.Muan, Trans.AIME, 230 (1964)77
- [29] R.Lindner and Å.Åkerström, Z. Phys.Chem.,N.F.6(1956)162

- [30] C.Wagner and K.-E.Zimens, Acta Chemica Scandinavica 1(1947)547
- [31] C.Wagner, Trans.Far.Soc.,34(1938)851
- [32] W.Schottky, Thermodynamik, Springer-Verlag, Berlin 1929
- [33] J.Frenkel, Z.Physik 35(1926)652
- [34] P.K.Footner, D.R.Homes and D.Mortimer, Nature, Lond. 216(1967)54
- [35] R.Lindner, Archiv Kemi 4(1952)381
- [36] V.I.Izvekov, N.S.Gobunev and A.A.Badad-Zakhrapin, Fiz.Met.Metall.14
(1962)195
- [37] R.Lindner, Z.Naturforschung 10(1955)1027
- [38] C.Wagner, Korrosion 23(1971)2
- [39] J.O.Stiegler and E.E.Bloom, J.Nucl.Mat.,41(1971)341
- [40] G.Wood, Corrosion Science 2(1961)173
- [41] C.E.Birchenall, Corrosion 17(1961)109
- [42] N.B.Pilling and R.E.Bedworth, J.Inst.Metals 29(1923)529
- [43] W.Jaenicke, Passivierungs- und Anlaufvorgänge an
Metalloberflächen, H. Fischer, K. Hauffe und W. Wiederholt
Springer-Verlag 1956
- [44] R.W.Ohse, Dissertation Universität Erlangen-Nürnberg 1958
- [45] P.E.Potter, Report submitted to the IAEA Panel on the behaviour
and chemical state of fission products in irradiated fuels, Vienna 1962
- [46] J.W.Weber, E.D.Jensen, Trans.ANS meeting Boston 1971 ANS 14(1971)
175
- [47] R.B.Fitts, F.L.Long, J.M.Leitnaker, ANS Conf.New Orleans 1971,
Trans. ANS
- [48] M.Coquerelle, H.Andriessen, N.Hoppe, Reaktortagung Bonn 1971,
Deutsches Atomforum
- [49] F.Garzarolli, A.Trinkl, K.P.Francke, Reaktortagung Berlin
1970, Tagungsbericht, Deutsches Atomforum p. 525
- [50] C.E.Johnson and C.E.Crouthamel, Trans. ANS 14 (1971)No.1
Boston meeting 1971
- [51] C.E.Johnson, I.Johnson and C.E.Crouthamel, Nucl.Sci. and Eng.,(1971)
- [52] H.Huber, H.Kleykamp KFK 1324(1972)
- [53] K.J.Perry, G.E.Melde, R.N.Duncan, ANS Symp. on Fast Reactor Fuel
Technology, New Orleans 1971
- [54] N.R.Stalica, C.A.Seils, C.E.Crouthamel ANL-7550(1968)

- [55] M.Coquerelle et al. TUSR-10(1971), TUSR-13 (1972)
- [56] P.E.Blackburn, P.E.Johnson, C.E.Battles, J.E.Johnson,
A.E.Martin,M.Tetenbaum,C.E.Crouthamel, A.D.Tevebaugh,R.C.Vogel,
ANL-7822(1971)
- [57] C.Sari, U.Benedict and H.Blank, J.Nucl.Mat.,35(1970)267
- [58] G.Brauer, Z.anorg.Chemie, 255(1947)101
- [59] R.P.Elliott, Constitution of Binary Alloys, First Supplement,
McGraw-Hill Book Comp., 1965, p. 368
- [60] P.W.Kendall, J. Nucl.Mat., 35 (1970)41
- [61] V.I.Spitsyn and I.M.Kuleshov, USSR J.Gen.Chem.21(1951)445
- [62] V.I.Spitsyn and I.M.Kuleshov, USSR J.Gen.Chem.21(1951)1717
I.N.Belyaev and N.N.Chikova, Russ.J.Inorg.Chem.9(1964)1483
- [63] E.A.Aitken, S.K.Evans, H.S.Rosenbaum and B.E. Rubin,
ANS-meeting Boston 1971, Trans.ANS 14(1971)176
- [64] C.Keller, L.Koch and K.H.Walter, J. Inorg.Nucl.Chem., 27(1965)1225
- [65] E.A.Aitken, S.K.Evans, GEAP-12099(1970)
- [66] E.H.P.Cordfunke and B.O.Loopstra, J.Inorg.Nucl.Chem. 33(1971)2427
- [67] P.E.Blackburn, A.E. Martin, J.E.Battles, P.A.G.O'Hare,
W.N.Hubbard, ANS Conf. New Orleans 1971; Trans .ANS 14
(1971)20
- [68] C.E.Crouthamel and C.E.Johnson, ANL-7833(1971)
- [69] S.K.Evans and E.A.Aitken, 74th Ann.Meeting Amer.Cer.Soc.
Washington, D.C. 1972
- [70] E.A.Aitken, GEAP-5683(1968)
- [71] J.R.Weeks and C.J.Klamut, Corrosion of Reactor Materials, Vol.I,
IAEA, Vienna (1962)
- [72] O.Kubaschewski, E.L.Evans,C.B.Alcock, Metallurgical Thermodynamics,
Pergamon Press, Oxford 1967
- [73] D.R.Stull and G.C. Sinke,Thermodynamic Properties of the Elements
Amer.Chem.Soc., Washington, D.C. 1956
- [74] Handbook of Chemistry and Physics, Chemical Rubber Publishing Co.
1971-1972, 52.ed.
- [75] C.E.Wicks and F.E.Block, Bur. Mines Bull. 605(1963) 36,85
- [76] L.L.Quill, Chemistry and Metallurgy of Miscellaneous Materials,
Thermodynamics.McGraw-Hill Book Co., N.Y. 1950
- [77] V.I.Spitsyn, ed. ANL-Trans.33
Publishing House of Moscow University (1961)
- [78] H.Schäfer and W.J.Hönes, Z.anorg.u. allg.Chem., 288(1956)62

- [79] R.F.Rolsten, Iodide Metals and Metal iodides, John Wiley and Sons, Inc. New York, London 1961
- [80] C.E.Crouthamel, priv. communication
- [81] P.S.Maiya, ANL-7825 (1971)
- [82] D.R.O'Boyle, F.L. Brown and J.E.Sanecki, J.Nucl.Mat.,29(1969)27
- [83] R.G. Bedford, D.D.Jackson,UCRL -12314 (1965)
- [84] A.R.Olsen, R.B. Fitts, and C.M.Cox, ORNL-TM-2716 (1969)
- [85] J.H. Davies and F.T.Ewart, J.Nucl.Mat.,41(1971)143
- [86] C.Edeleanu and R. Littlewood, Electrochimica Acta,3(1960)195
- [87] R.F.Koenig and S.R.Vandenberg, Metal Progress 61(1952)71
- [88] I.A.Menzies, Werkstoffe und Korrosion 19(1968)1050
- [89] R.W.Ohse, Z.Elektrochemie, Ber.Bunsenges.physik.Chem.64(1960)1171
64(1960)1171
- [90] A.U.Seybolt, Oxidation of Metals, 2(1970)119
- [91] M.G.Chasanov, Nucl. Sci. and Eng., 30(1967)310
- [92] H.U.Borgstedt und G.Frees, Werkstoffe und Korrosion 21(1970)435
- [93] J.M.Leitnaker and K.E.Spear, ORNL-1440(1969)
- [94] R.W.Ohse and W.M.Olson, Reaktortagung Berlin 1970, Tagungsbericht Deutsches Atomforum p. 570
- [95] L.A.Neimark, C.E.Dickermann, J.D.B.Lambert, W.P.Murphy, ANS-Conf. New Orleans 1971, Trans. ANS 14:Supplement¹(1971)22
- [96] V.V.Zotov, B.A.Nevzorov and Ye.V.Umnyashkin, in Liquid Metals by P.L.Kirillov, NASA-TTF-522(May 1969)
- [97] R.H.Simon, J.R.Lindgren, J.N.Siltanen, and R.B.Fitts, GA-10262(1970)
- [98] J.M.Leitnaker, R.B.Fitts, D.R.Cuneo, E.L.Long, and K.E.Spear, ORNL-452+(1970)
- [99] K.E.Spear, A.R.Olsen and J.M.Leitnaker, ORNL-TM-2494(1969)
- [100] H.Schäfer, Chemische Transportreaktionen, Verlag Chemie, Weinheim/ Bergstrasse (1962)
- [101] R.W.Ohse, M.Schlechter and E.Zamorani, TUSR 10 (1970)26
- [102] R.W.Ohse, P.E.Potter and M.Schlechter, TUSR 12 (1972)30
- [103] W.E.Zaugg and N.W.Gregory, J.Phys.Chem.,70(1966)490
- [104] W.E.Zaugg and N.W.Gregory, J.Phys.Chem.,70(1966)486
- [105] E.M.Levin, H.F.McMurdie and F.P.Hall, Phase Diagrams for Ceramists, Amer. Cer.Soc. (1956)36
- [106] N.A.Javed and J.T.A.Roberts, ANL-7901(1972)

- 107 J.H.Dettingmeiyer, J.Tillack and H.Schäfer,
Z.anorg.u.allgem.Chem., 369(1969)161
- 108 C.S.Tedmon, D.A.Vermilyea and J.H.Rosolowski, J.Electrochem.
Soc.118(1971)192
- 109 O.Götzmann and R.W.Ohse, Report submitted to the IAEA panel
on the behaviour and chemical state of fission products in
irradiated fuels, Vienna 1972
- 110 F.Keroulas, R.Le Beuze, D.Calais, A.Van Craeynest et M.Conte,
J.Nucl.Mat., 43(1972)313
- 111 P.S.Maiya and D.E.Busch, ANL-7833(1971); ANL-7854(1971)
- 112 P.S.Maiya, D.E.Busch, J.E.Sanecki, ANL-RDP-3, p.5.13.

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Table I : Physical constants and thermodynamic data on caesium and iodine compounds

Table I : Physical constants and thermodynamic data on caesium and iodine compounds

	M.P. ($^{\circ}\text{C}$)	B.P. ($^{\circ}\text{C}$)	$G_{\text{f(c)}}^{\circ}$ (Kcal/mole)	$H_{298(\text{c})}^{\circ}$ (Kcal/mole)
Cs	28.40 \pm 0.01 [74]	678.4 [74]		
I	113.5 [74]	184.35 [74]		
Cs ₂ O	490 (in N ₂) [74]			
CsI	621 [74]	1280 [74]		- 80.5 [79]
CsFeO ₂				-137.8 [5]
Cs ₂ CrO ₄	(954) [62]			
Cs ₂ UO ₄				-478 [77]
Cs ₂ MoO ₄	(936) [62]			
FeI ₂	609 [79]	935 [78]	45.770 + 0.0069 T log T - 0.0512.T (298 - 867 $^{\circ}\text{K}$) [72]	- 30.0 \pm 2.0 [72]
CrI ₂	856 [74]	1248 [79]	- 26.000 (1000 $^{\circ}\text{K}$) [75]	- 37.8 \pm 1.4 [72]
NiI ₂	797 [74]		- 2.000 (1000 $^{\circ}\text{K}$) [75]	- 23.0 \pm 2.0 [72]

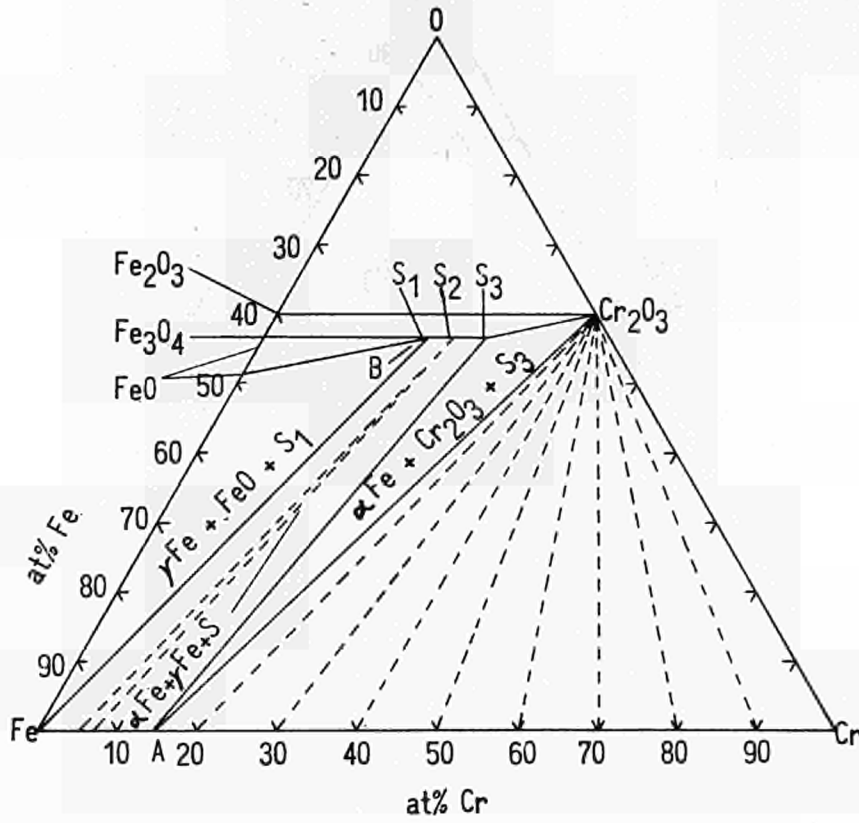


Fig.1: Fe-Cr-O phase diagram at 1300 °C (1000 °C)[8].

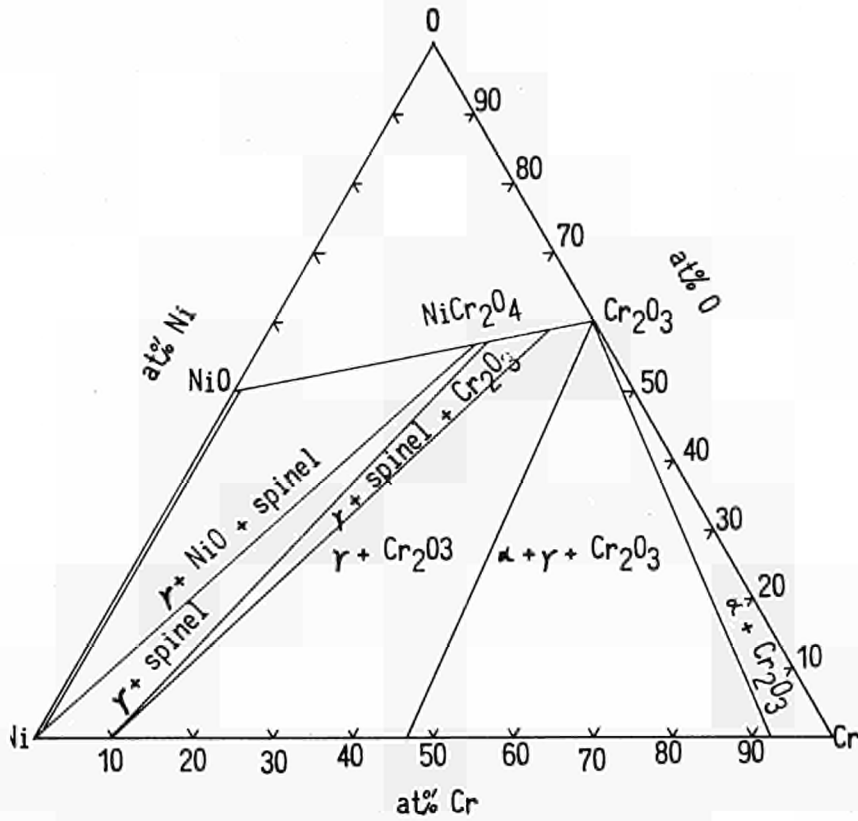


Fig.2: Ni-Cr-O phase diagram at 1000 °C [12].

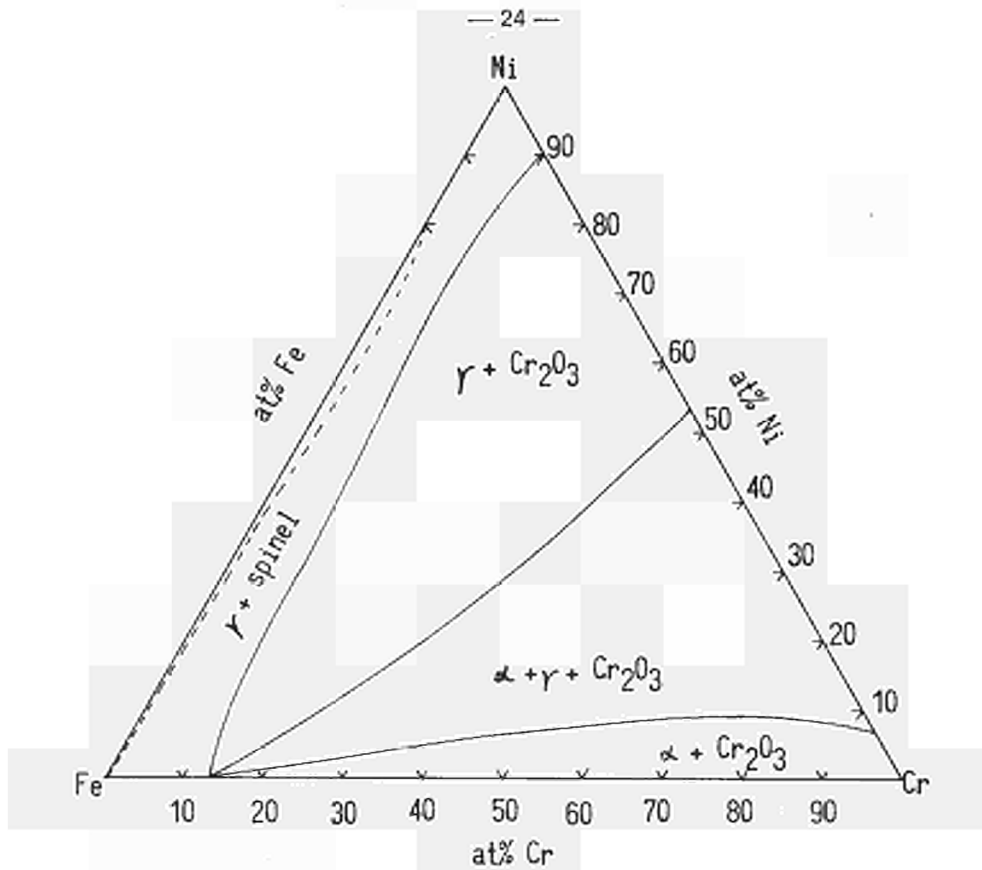


Fig.3: Plane section of the quaternary phase diagram Fe-Cr-Ni-O at 1000 °C [12].

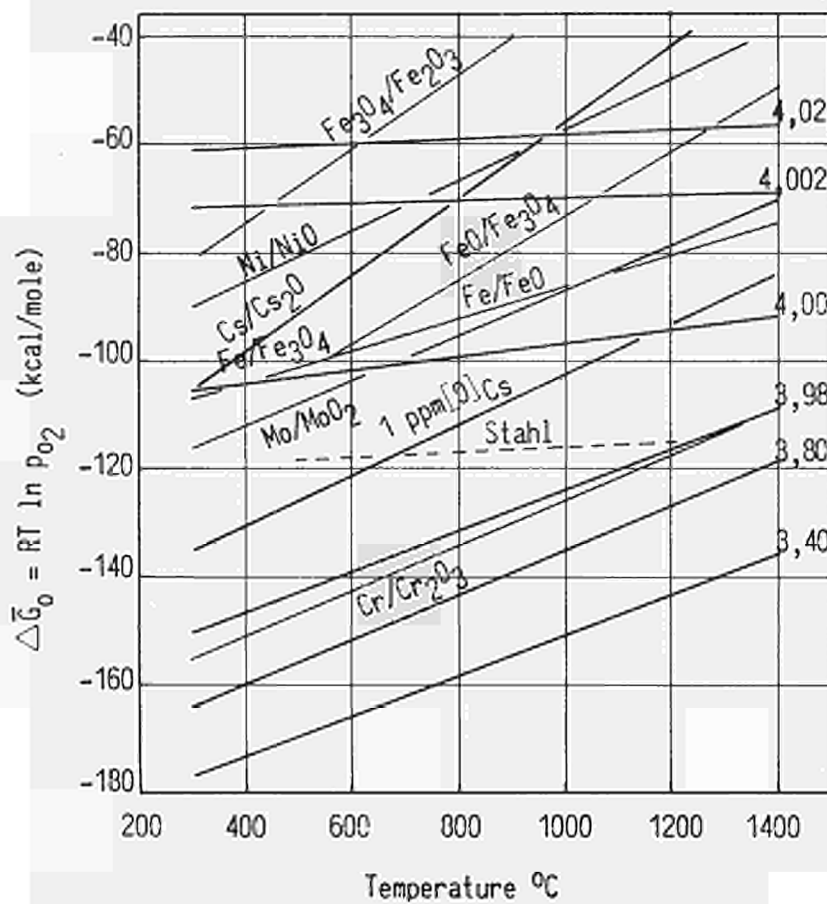


Fig.4: Oxygen potentials of compounds involved in fuel cladding interaction, and of uranium plutonium oxides as a function of valency.

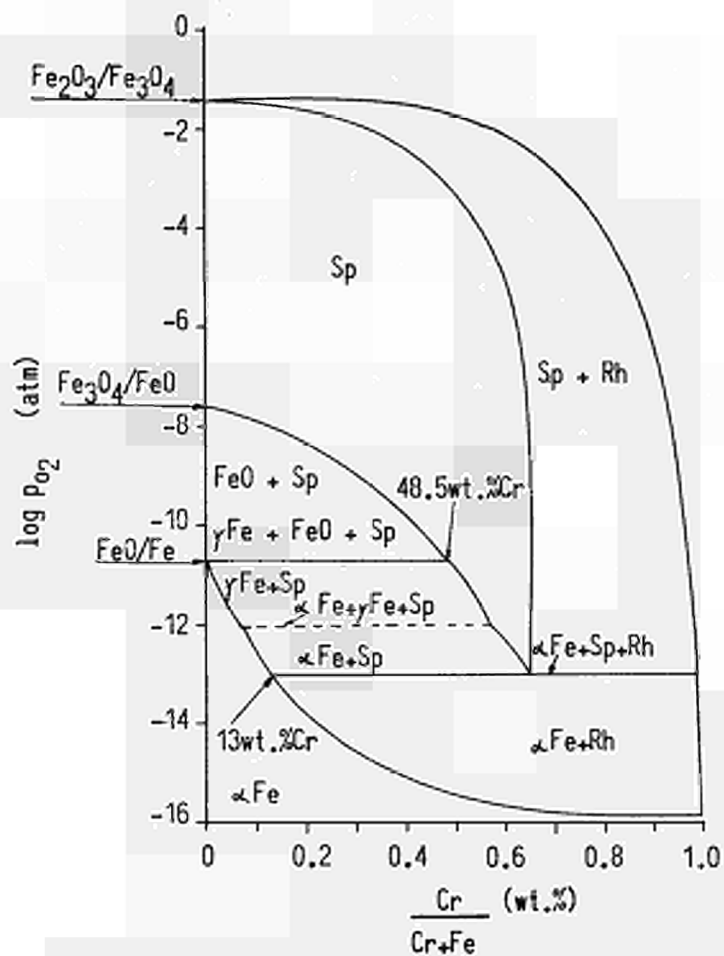


Fig.5: Fe-Cr-O constitution diagram, $\log p_{O_2}$ versus mole fraction $\frac{Cr}{Cr+Fe}$ [8].

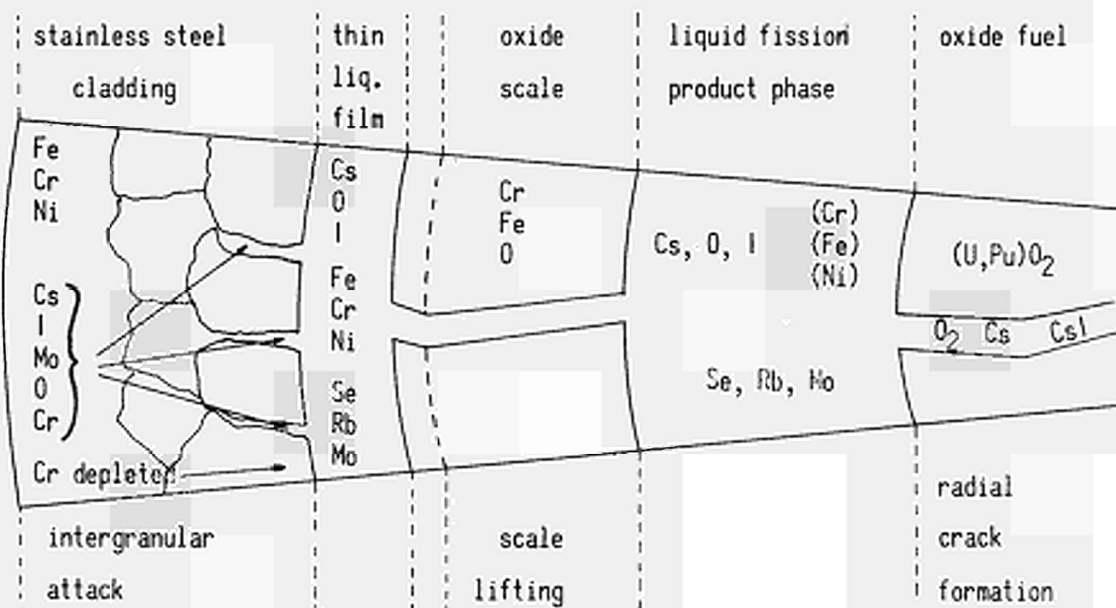


Fig.6: Schematic summary of fission products analysed within the layered structure at the interface fuel cladding after high burn-up.

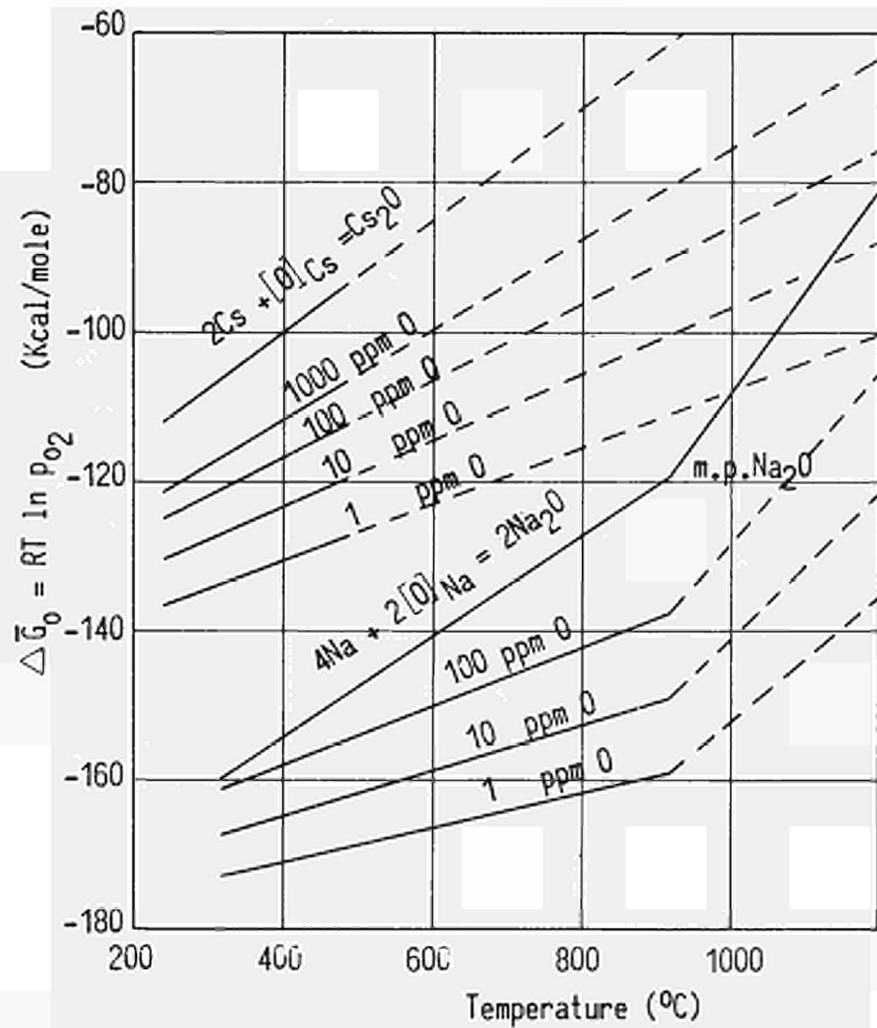


Fig.8: Oxygen potential of oxygen dissolved in caesium and sodium.

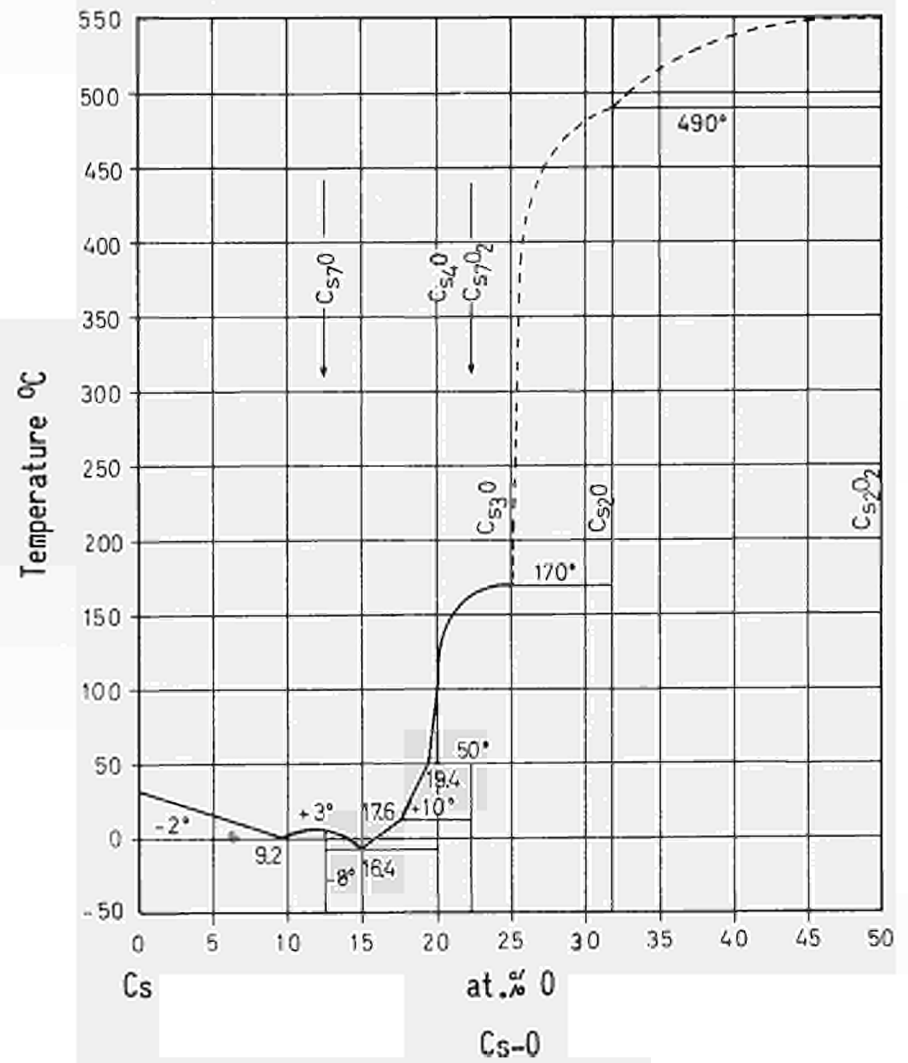


Fig.7: Cs-O phase diagram [59,60]

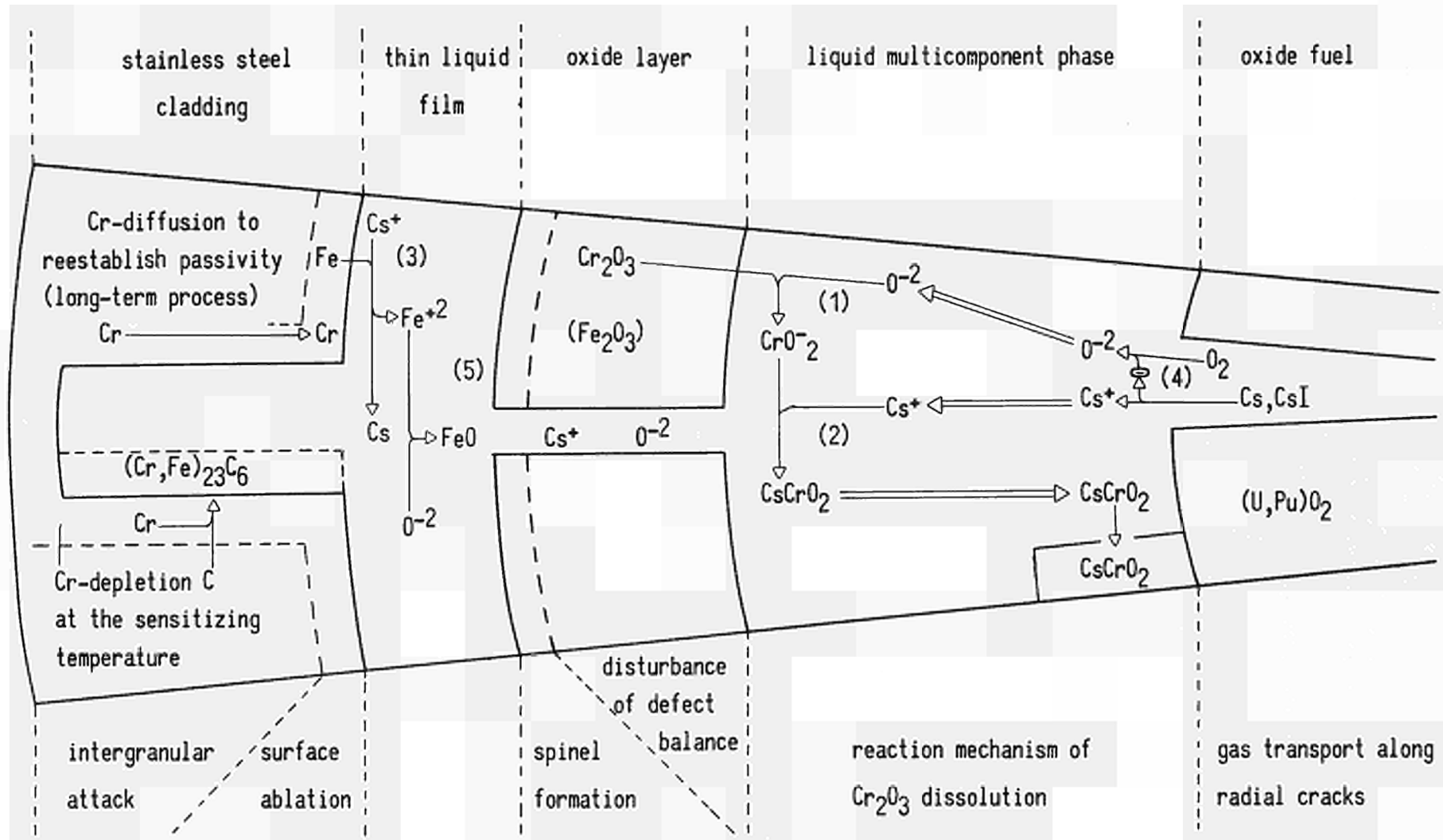


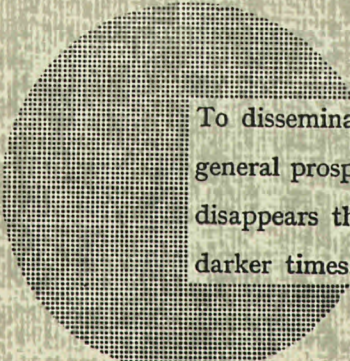
Fig.9: Schematic display of possible reaction mechanism of chemical interaction in oxide fuel at the interface fuel cladding.



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