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The chemical form of fission product tellurium during reactor accident conditions

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Abstract

The chemical form of the fission product tellurium during a reactor accident has been studied experimentally. Release experiments of tellurium were conducted under simulated LWR accident conditions. It is found that tellurium is retained by the Zircaloy cladding until oxidation of the cladding is almost complete. During this oxidation, tin in the cladding is segregated and reacts with tellurium. The release of tellurium is found to be dependent on the oxygen potential. High oxygen potentials lead to a release as elemental tellurium, low oxygen potentials lead to a release as tin telluride.

1. Introduction

Tellurium is an important fission product, which contributes largely to accident consequences once it is released from the primary cooling system [1]. Since tellurium is a precursor of the radiotoxic iodine, the release of tellurium partly determines the release of iodine and due to its volatility, elemental tellurium can be transported easily as a vapor through the primary cooling system of a reactor. Interaction of tellurium, however, with fuel, other fission products and surfaces of the structure materials of the primary system alters the chemical state of tellurium, and thus influences its release during a reactor accident. Accurate source term calculations require knowledge of the chemical state of the fission products during accident conditions. In normal operating conditions, tellurium can be present in LWR fuel as elemental tellurium in metallic precipitates, or as cesium telluride, Cs_2Te [2].

However, in the initial stage of an LWR accident, tellurium will be released from the fuel due to temperature increase. Tellurium then diffuses from the fuel towards the gap, where it reacts with the inner surface of the Zircaloy cladding to form a stable, non-volatile zirconium telluride compound, as was shown in our previous study [3]. During progression of the accident the cladding temperature will rise further and a rapid reaction of the cladding with steam to form zirconium oxide begins. This oxidation process may alter the chemical state of tellurium.

Collins et al. [4] conducted detailed experiments to investigate the role of Zircaloy on the release behavior of tellurium. They found that, only after almost complete oxidation of a Zircaloy test tube, a strong increase in the release of tellurium occurred. The authors concluded that in their experiments all tellurium was released as tin telluride. It was suggested that this compound should arise due to reaction of tellurium with the tin from the cladding. It is, however, still unknown how the formation of SnTe occurs and whether it will occur under most accident conditions.

Johnson and Johnson [5] reported on experiments to establish the chemical form of tellurium during reactor accident conditions. They heated synthetic fuel samples as well as irradiated fuel samples in an inert atmosphere. The vapors evolved from the Zircaloy clad fuel were analyzed by mass spectrometry. In their experiments tellurium was released as elemental tellurium, and only traces of tin telluride and cesium telluride were found.

Bowsher et al. [6] also heated small samples of Zircaloy which contained a zirconium telluride at the surface, in an inert atmosphere and analyzed the gaseous species evolved from the specimen by mass spectrometry. Elemental tel-

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lurium was found to be the major species released from the specimen and a small amount of tin telluride was found as well.

The experiments of Bowsher et al. [6] and of Johnson and Johnson [5], however, do not take into consideration the effect of cladding oxidation, which will certainly have influenced their results concerning the amount released, and the chemical form of tellurium. Furthermore there is no quantitative information given on the amount of tellurium released as a vapor in comparison to the total amount of tellurium present in the system. This paper describes several experiments, conducted to investigate the role of Zircaloy in the release of tellurium during reactor accident conditions and to establish the chemical state of tellurium released from the cladding.

2. Experimental

2.1. High temperature oxidation of Zircaloy tubes

A series of experiments was done to investigate the oxidation of Zircaloy at temperatures between 900 and 1600°C. The main interest in these experiments was focused on the behavior of tin in the cladding during the oxidation process. Cylindrical pieces of reactor-grade Zircaloy-4 tube (1.4 wt% Sn, 0.2 wt% Fe, 0.1 wt% Cr; dimensions: 14 mm height, 0.73 mm wall thickness, 9.3 mm inner diameter) were heated in a high-frequency induction furnace in an atmosphere of argon and oxygen ($p_{total} = 1$ bar) at different temperatures. The time of heating was varied in such a way that the oxide layer of the samples would be comparable in thickness. One separate experiment, in which an identical Zircaloy tube was heated in an atmosphere of argon and steam, was done to check the validity of the results of oxidation in oxygen compared to reactor accident conditions in a steam environment. All tubes were afterwards embedded in resin and sawn through. The cross-sections of the oxidized tubes were polished and were examined by SEM/EDX using a JEOL JXA 840 apparatus.

2.2. Oxidation of Zircaloy tubes containing zirconium telluride

Another series of experiments was conducted to investigate the behavior of tin in conjunction with tellurium during accident conditions. In these experiments a weighed amount of tellurium powder (Cerac 99.999%) contained in alumina crucibles was put inside a tube of Zircaloy-4 (70 mm length, 0.73 mm wall thickness, 9.3 mm inner diameter). The tube was closed at both ends with Zircaloy-4 screw caps, and was heated in a high-frequency induction furnace in a purified argon atmosphere ($p = 1$ bar). Tellurium then reacts at the inner surface of the Zircaloy tube, forming a zirconium telluride layer. After 2 h of heating at 1200°C oxygen was added to the argon atmosphere and oxidation of the outside of the cladding started. After considerable oxidation the heating was stopped and the Zircaloy tube was cooled rapidly. Small pieces of the inner and outer part of the tube were used to collect material for X-ray powder diffraction analysis on a Guinier type camera. The tubes were afterwards embedded in resin, radially sawn through at several positions and the cross-sections were polished and examined by SEM/EDX.

Additional experiments were done to analyze the chemical form of tellurium, released into the primary cooling system after complete oxidation of the cladding. Zircaloy-4 tubes (70 mm length, 0.73 mm wall thickness, 9.3 mm inner diameter) were again filled with a weighed amount of tellurium and were closed at both ends with a Zircaloy-4 screw cap. These tellurium containing tubes were heated inductively for 2 h at 1200°C in an argon atmosphere to prepare a layer of zirconium telluride at the inner surface. Next, the tubes were heated in a resistance furnace in an argon/oxygen atmosphere for several hours at 1200°C. The volatile compounds which then were released from the partly ruptured cladding tube, were condensed downstream on a cold trap inside the oven. The chemical form of the condensed species was analyzed by means of X-ray powder diffraction. The weight of the condensed vapor species was also determined.

One additional experiment was done to investigate the release of tellurium, when oxidation occurs directly on the zirconium telluride surface. This would resemble a situation in which steam is present in the gap after failure of the cladding, and the zirconium telluride at the inner cladding tube is directly exposed to an oxidizing atmosphere. Zircaloy-4 tubes (14 mm length, 0.73 mm wall thickness, 9.3 mm inner diameter) were used, which contained a zirconium telluride layer on the inner and outer surface. These tubes where heated to 1000°C in an argon/oxygen atmosphere and the volatile species were again condensed on a cold trap.

2.3. Oxidation of zirconium telluride in a steam / hydrogen atmosphere

A third series of experiments was done to investigate the influence of the oxygen potential on the chemical form of tellurium, released from the cladding. In these experiments a mixture of 85 wt% zirconium powder (Cerac, 99.7%), 10 wt% Zr_5Te_4 prepared by chemical reaction of the elements, and 5 wt% tin powder (Cerac, 99.995%) was pelletized and heated at 1000°C in an atmosphere containing steam and hydrogen ($p_{total} = 1$ bar). The mixture of steam and hydrogen was prepared by saturating argon carrier gas with water vapor and adding an amount of hydrogen gas to it. The amount of water vapor was controlled by the temperature of the condenser and the flux of argon carrier gas. The amount of hydrogen was controlled by a flow controller. Saturation of the argon with steam was verified prior to the experiments. The experimental set-up made it possible to use gas mixtures, containing relative molar amounts of steam over hydrogen, in the range between 100/1 to 1/100. The volatile species, which escaped from the pellet during oxidation, condensed in the colder region of the quartz furnace tube and were analyzed by means of X-ray powder diffraction.

These experiments were carried out to closely imitate reactor accident conditions. During a reactor accident, steam as well as hydrogen will be present in the primary system in varying amounts. Hydrogen is formed due to the reaction of steam with zirconium metal. The local oxygen potential is determined by the relative amounts of steam over hydrogen. It is estimated that the relative molar amounts of steam/hydrogen under accident conditions can vary between 100/1 and 1/100.

3. Results

3.1. Oxidation of Zircaloy tubes

SEM images of the cross-sections of the Zircaloy-4 tubes, oxidized in an 80% argon, 20% oxygen atmosphere at various temperatures (Section 2.1) are shown in Fig. 1. These images demonstrate that at temperatures of 1300°C and higher, light particles are segregated in a rim in the zirconium oxide layer. EDX analysis of the light inclusions in the oxide layer show that these particles consist mainly of tin, as is shown in Fig. 2. Before oxidation tin was dissolved in the Zircaloy matrix.

Oxidation of Zircaloy at 900°C did not reveal any segregation of tin in the oxide layer. At 1050°C, however, oxidation in a steam/argon atmosphere did reveal increasing concentrations of tin near the metal/oxide interface, although less distinct than at higher temperatures. Lorenz et al. [7], in their experiments also found a tin layer in the interface between the oxidized and non-oxidized layers. The morphology of the oxide layers, found in the present oxidation experiments is equal to the morphology of the oxide layers found in the oxidation experiments of Leistikow et al. [8]. These authors used at all temperatures a mixture of argon and steam to oxidize Zircaloy. Although Leistikow et al. presented SEM pictures of the cross-sections of the oxide layers, which are identical to the SEM pictures of the cross-sections found in the present experiments, they did not comment on the presence of a layer of tin in the oxide layers.

Based on the above observations, it is to be expected that during reactor accident conditions, when strong exothermic oxidation of the cladding occurs at temperatures between 900 and 1600°C, tin will be segregated in the zirconium oxide layer.

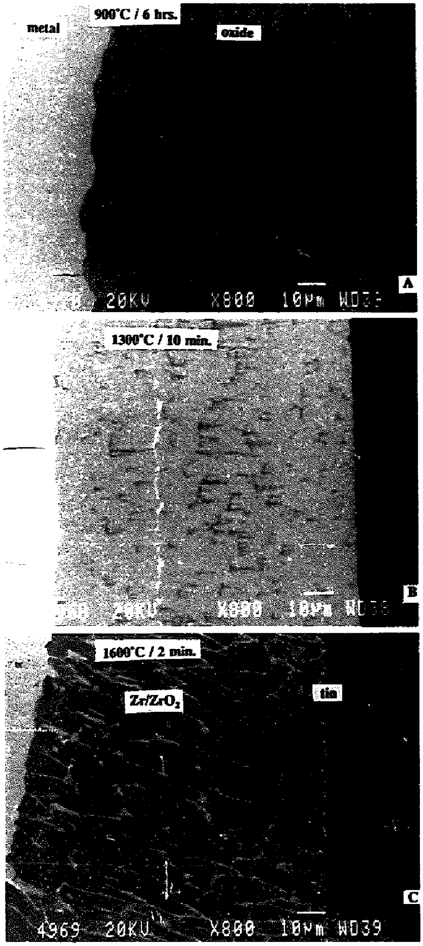

Fig. 1. SEM images of the cross sections of zirconium oxide layers formed at (A) 900°C, (B) 1300°C and (C) 1600°C.

3.2. Oxidation of Zircaloy tubes containing zirconium telluride

Before oxidation of the cladding tube, which was closed at both ends, the inner surface of the cladding tube reacted with tellurium vapor during 2 h at 1200°C. A layer of zirconium telluride was formed at the inner surface before oxidation of the outer surface started. This inner zirconium telluride layer consisted mainly of Zr_5Te_4, based on the X-ray powder diffraction analysis of a small amount of the inner surface of the Zircaloy tube. The tubes were oxidized

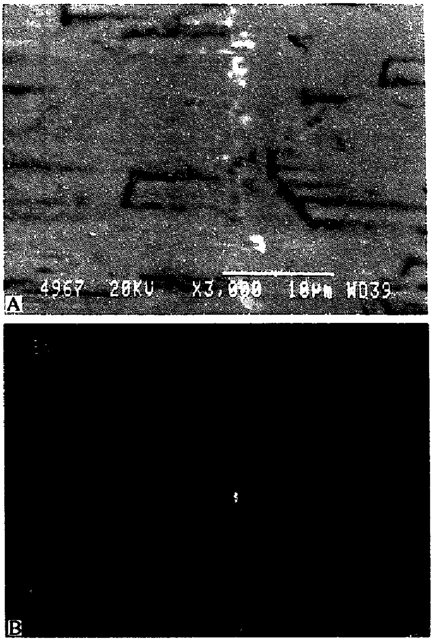

Fig. 2. SEM and tin distribution image of a detail of the cross-section of the oxide layer of Fig. 1(B), showing the segregation of tin in the oxide layer.

for different times, to investigate the chemical state of tellurium in different stages of an accident. The first three experiments (1, 2, 3) were intentionally stopped before failure of the cladding tube occurred. This provided information on the form in which tellurium was retained in the cladding, during the oxidation. In the latter three experiments (4, 5, 6) the cladding tubes were completely oxidized, to determine the chemical state in which tellurium was finally released from the cladding tubes. Samples of the cladding remainders and of the condensed vapor species were analyzed by means of X-ray powder diffraction. The results of these experiments are summarized in Table 1.

Based on the weight (170 mg, 1.06 mmol) of TeO_2, which condensed on the cold trap in experiment 5, it was concluded that all tellurium inside the tube (134 mg, 1.05 mmol) was released from the ruptured cladding at the end of the experiment.

Qualitative chemical analysis of the condensed vapor species of experiment 6 showed the presence of only tellurium and no tin in the vapor phase. Besides zirconium as the major component, traces of tellurium, tin, iron and chromium were found in the solid remainders of the cladding.

A SEM picture of the cross-section of the oxidized cladding of experiment 1 is shown in Fig. 3. This picture, again, clearly demonstrates that particles of tin are segregated in a rim in the oxide layer. It is also shown that this rim of tin is displaced towards the inside of the cladding along with the metal/oxide interface on increasing oxidation. In Fig. 4, SEM/EDX pictures are shown of a detail of the metal/oxide interface. In the oxide layer small particles with high concentrations of tin and tellurium are found. These pictures show that the formation of SnTe occurs in the oxide layer during cladding oxidation. However, in none of the experiments 4, 5 and 6, SnTe was found as a condensed vapor species. This was caused by the high partial oxygen pressures (0.2 to 0.5 bar) used in the above experiments, which were well above the equilibrium pressure for Eq. (1):

$$SnTe(s, l) + 2O_2(g) \rightleftharpoons SnO_2(s) + TeO_2(g). \qquad (1)$$

SnTe was thus oxidized as soon as it is was exposed to the gas atmosphere. SnO_2 is formed, which remains as a solid in the cladding remainders and TeO_2 is formed, which vaporizes and condenses on the cold trap.

Small amounts of the compound $ZrTe_3O_8$ were found in the solid remainders after oxidation of the cladding as well. This compound decomposes into gaseous TeO_2 and

Table 1
Results of the X-ray powder diffraction analysis after oxidation of zirconium telluride containing Zircaloy-4 tubes

Exp.	Oxidation (°C/min)	Atmosphere, Ar/O_2 (vol%)	Tube condition (after oxidation)	Cladding remainders	Condensed vapor species
1	1250/200	80/20	intact	ZrO_2, Zr, Zr_3Te, Zr_5Te_4	–
2	1200/120	50/50	intact	ZrO_2, Zr	–
3	1300/75	50/50	cracks	ZrO_2, Zr, SnO_2	–
4	1200/300	80/20	failed	ZrO_2, $ZrTe_3O_8$	TeO_2
5	1200/600	80/20	failed	ZrO_2, SnO_2	TeO_2
6 [a]	1000/180	50/50	–	ZrO_2, $ZrTe_3O_8$	TeO_2, Te

[a] Open Zircaloy tubes with zirconium telluride on both inner and outer surface.

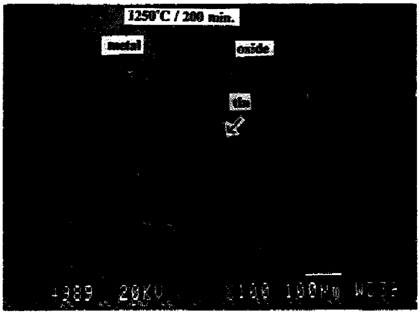

Fig. 3. SEM image of the cross-section of a Zircaloy-4 tube after oxidation for 200 min at 1250°C, showing the movement of tin towards the inner surface of the cladding.

solid ZrO_2 at higher temperatures, as was found by Samant et al. [9], who measured the TeO_2 vapor pressure above $ZrTe_3O_8$.

Table 2
Reaction conditions and results of tellurium release experiments in steam/hydrogen environment

Exp.	Oxidation (°C/h)	H_2O/H_2 (vol. ratio)	Solid remainders	Condensed vapor
7	1000/1	100/1	ZrO_2, SnO_2	Te
8	1000/18	100/1	ZrO_2, SnO_2	Te
9	1000/40	1/1	ZrO_2,	SnTe, Te [a]
10	1000/48	1/100	ZrO_2,	SnTe

[a] Very small amount.

3.3. Oxidation of zirconium telluride in steam/hydrogen atmosphere

Oxidation of a mixture of zirconium, zirconium telluride and tin was carried out in an atmosphere with varying ratios of steam/hydrogen. The vapor species released from the mixture, were condensed in the cold region of the quartz tube and analyzed with X-ray powder diffraction. The reaction conditions and the results of these experiments are summarized in Table 2.

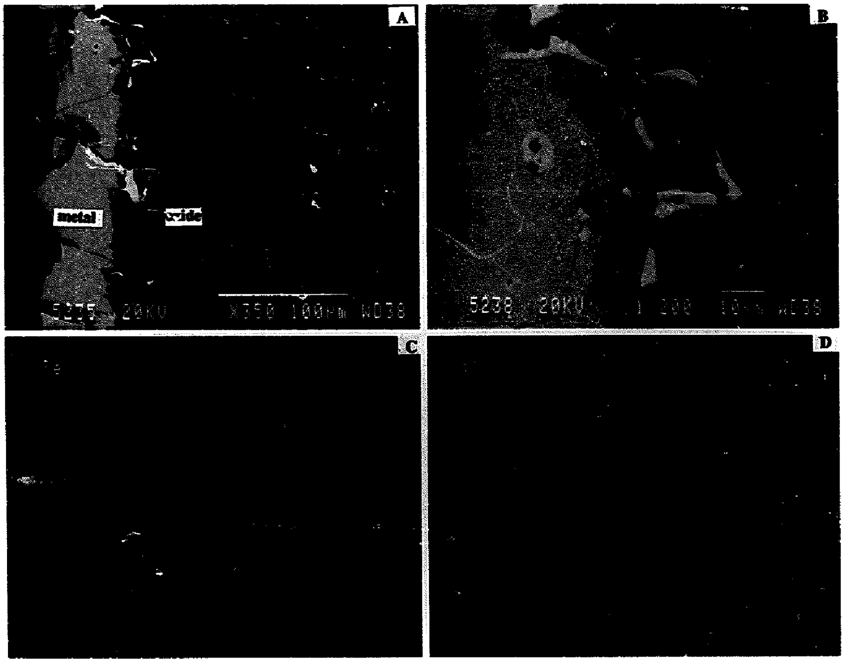

Fig. 4. SEM and tin and tellurium distribution images of the cross-section of a Zircaloy-4 tube at 1250°C after 200 min in argon/oxygen atmosphere (experiment 1). (A) Overview of metal/oxide interface; (B) detail of upper left part of (A); (C, D) tellurium and tin distribution images of (B), demonstrating that the light inclusions are enriched in tin and tellurium.

Due to the fact that only very small amounts of steam were present in the experiments 9 and 10, the oxidation of these samples progressed very slow as well as the release of the telluride compound. The results show that at high steam/hydrogen ratios (100/1) tin reacts with oxygen to form solid tin oxide and tellurium is vaporized. This selective oxidation of tin in the SnTe compound was also reported by Bettini and Richter [10]. However, at moderate and low steam/hydrogen ratios (1/1, 1/100) tellurium is released as tin telluride.

4. Discussion and conclusions

The experiments described above, were carried out to obtain more knowledge of the chemical state of tellurium during reactor accident conditions. The Zircaloy cladding plays an important role in the mechanism of the release of tellurium. In the initial stage of an accident, tellurium, released from the fuel matrix, is retained by the cladding as a zirconium telluride, provided that the inner surface of the cladding tube is not covered with a thick oxide layer due to steam ingression. When the cladding temperature rises further, the outer Zircaloy surface reacts rapidly with steam to form zirconium oxide. This strongly exothermic reaction causes the temperature inside the reactor pressure vessel to increase rapidly.

The experiments described in the preceding sections, reveal that under accident conditions a zirconium oxide layer is formed on the cladding, in which small particles of tin are segregated, in a rim parallel to the oxidized surface. When the thickness of the oxide layer increases the tin particles move along with the metal/oxide interface towards the inner surface of the cladding. Although oxidation experiments of Zircaloy tubes were primarily done using oxygen, it is found experimentally that also on oxidation with steam, areas enriched in tin are formed in the zirconium oxide layer. This is supported by the results of the experiments of Leistikow et al. [8], who investigated high-temperature steam oxidation of Zircaloy. The segregation of tin in the oxide layer is caused by the large difference in solid solubilities of tin in zirconium and in zirconium oxide. This was reported by Matsuda et al. [11], who found Sn dissolved in the oxide layer to 1 wt%, whereas Sn was dissolved in the Zircaloy metal up to 1.5 wt%. The lower solubility of tin in the zirconium oxide crystal lattice causes tin to be segregated as a second phase in the oxide layer. As the oxide layer becomes more stoichiometric from the outside of the cladding towards the inside, the tin particles are moved along with the 'oxidation front' towards the inside of the cladding.

The mechanism of segregation of tin in the oxide layer, and movement towards the inside of the cladding strongly enhances the formation of SnTe, when the Zircaloy tube is completely oxidized. At this stage tellurium is released due to reaction of zirconium telluride with oxygen, forming zirconium oxide and elemental tellurium, whereas tin is present in relatively high concentrations. Formation of tin telluride will then occur, provided that the oxygen potential is below the equilibrium value of Eq. (4). At higher oxygen potentials, SnTe will react with oxygen and form SnO_2 and tellurium. The oxygen pressure used in Section 3.2 was even higher as the equilibrium oxygen pressure of Eq. (5), which explains the fact that in none of these experiments SnTe was found as a condensed vapor species. The results of steam oxidation of a mixture of zirconium, zirconium telluride and tin (Section 3.3) showed that the relative amount of steam and hydrogen, which determines the oxygen pressure in the system, is of great importance for the chemical form in which tellurium will be released from the cladding. The results of these experiments are supported by calculations of the equilibrium oxygen pressures of the compounds and materials of interest for the chemical state of tellurium. Equilibrium oxygen pressures as a function of temperature of the following reactions are considered:

$$\mathrm{Zr(s)} + \mathrm{O_2(g)} \rightleftharpoons \mathrm{ZrO_2(s)}, \tag{2}$$

$$\mathrm{Sn(s,l)} + \mathrm{O_2(g)} \rightleftharpoons \mathrm{SnO_2(s)}, \tag{3}$$

$$\mathrm{SnTe(s,l)} + \mathrm{O_2(g)} \rightleftharpoons \mathrm{SnO_2(s)} + \mathrm{Te(l,g)}, \tag{4}$$

$$\mathrm{Te(l,g)} + \mathrm{O_2(g)} \rightleftharpoons \mathrm{TeO_2(s,l)}, \tag{5}$$

$$\mathrm{2H_2O(g)} \rightleftharpoons \mathrm{2H_2(g)} + \mathrm{O_2(g)}. \tag{6}$$

The equilibrium oxygen pressures as a function of temperature of reactions (Eqs. (2)–(5)) are shown in Fig. 5, together with the highest and lowest oxygen pressures of the hydrogen/steam mixtures, used in the release experiments of Section 3.3. All data used for the calculation of the equilibrium oxygen pressures are obtained from Cordfunke and Konings [12], except for the data of SnTe, which are obtained from Yamaguchi et al. [13]. When the oxygen pressure in a system is above the equilibrium value of a compound or element, formation of the oxide will occur. Fig. 5 shows that at high oxygen pressures ($H_2O/H_2 = 100/1$) tin will react with oxygen to form tin oxide. Tin telluride will react as well and form tin oxide and elemental tellurium. Thus at high oxygen pressures tellurium is released in its elemental form. At moderate and low oxygen pressures tin will react with tellurium to form tin telluride, which supports the experimental results. The shaded areas in Fig. 5 represent the ranges of oxygen potentials, which lead to release of tellurium either as tin telluride or as elemental tellurium. Fig. 5 also indicates that formation of tellurium oxide during the in vessel stage of a LWR reactor accident will not occur, because the equilibrium oxygen pressure of Eq. (5) is much higher than the range of oxygen pressures during a reactor accident.

It can be concluded that SnTe is the predominant compound of tellurium release from Zircaloy clad fuel during accident conditions. Only at oxygen pressures above

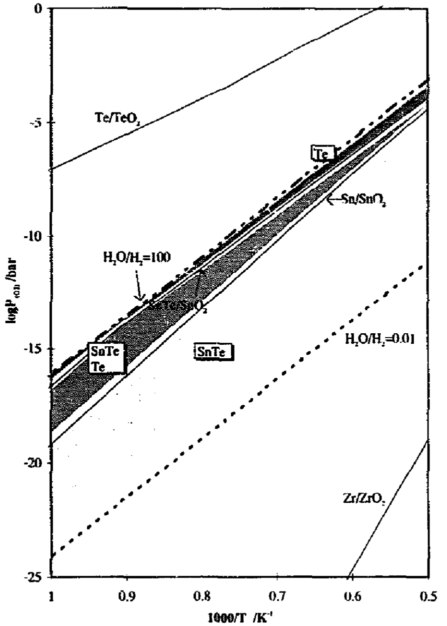

Fig. 5. Equilibrium oxygen pressures of elements and compounds of interest for the chemical form of tellurium during reactor accident conditions.

the equilibrium value of Sn/SnO$_2$ tellurium will be released in its elemental form. Collins et al. [4], in their experiments, found tellurium released as SnTe as well. Since they only added steam to their carrier gas, the presence of hydrogen gas, caused by the reaction of steam with Zircaloy, must have reduced the oxygen pressure below the equilibrium value of Sn/SnO$_2$.

Since the vapor pressure of elemental tellurium between 1000 and 1500 K is approximately 10 to 100 times higher than the vapor pressure of SnTe, elemental tellurium will have a significant higher release rate than tin telluride. Formation of SnTe thus leads to a lower release rate of tellurium, during a reactor accident.

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