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REACTION OF TELLURIUM WITH ZIRCALOY-4

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Reaction of Tellurium with Zircaloy-4

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Abstract:
Interaction of tellurium vapour with Zircaloy during the initial stage of an accident will lead to retention of tellurium in the core. For reliable estimation of the release behaviour of tellurium, it is necessary to know which zirconium tellurides are formed during this interaction. In this work the reaction of tellurium with Zircaloy-4 has been studied, using various reaction temperatures and tellurium vapour pressures. The compound $ZrTe_{2-x}$ is formed on the surface of the Zircaloy in a broad range of reaction temperatures and vapour pressures. It is found that the formation of the more zirconium-rich compound Zr_5Te_4 is favoured at high reaction temperatures in combination with low tellurium vapour pressures.

1 Introduction

Tellurium is, as a precursor of radiotoxic iodine and due to its high volatility an important fission product. Alpert et al.[1] reported that release of tellurium during a nuclear reactor accident contributes largely to health- and environmental effects.
Imoto and Tanabe[2], and Cordfunke and Konings[3] calculated that under normal operating conditions tellurium is present in the fuel as Cs_2Te, PdTe or as elemental tellurium. During the initial stage of a reactor accident, the fuel temperature rises, and volatile fission products and compounds thereof are vaporized into the fuel-cladding gap. At this stage tellurium can interact with the Zircaloy cladding and form a solid solution of tellurium in Zircaloy or an intermetallic zirconium telluride compound.
Anand and Pruthi[4] investigated the reaction of tellurium with Zircaloy-4 and reported that tellurium was readily absorbed on the surface of Zircaloy forming a skin of zirconium telluride. However, they did not analyze which compounds were actually formed on this surface. Sallach et al.[5] determined vapour deposition velocities of tellurium on several cladding materials. Based on the X-ray powder diffraction pattern of their reaction products, they stated to have found ZrTe on the surface of Zircaloy-2 after reaction with tellurium vapour. Closer examination of their diffraction pattern, however, reveals that it corresponds with a mixture of $ZrTe_{2-x}$ and ZrO_2. Bowsher and Jenkins[6] studied the kinetics of telluride formation on the surface of Zircaloy.

They did not report which compounds were formed on the surface. They found, however, that an increasing degree of oxidation of the Zircaloy, significantly decreases the deposition velocity of tellurium on it. Furthermore, it was found by Bowsher et al.[7] that the deposition of tellurium on the surface of Zircaloy was constant with time, indicating a fast surface reaction and gas phase diffusion limited kinetics. The temperature dependence of the deposition velocity implied that the rate was limited either by a chemical reaction or by diffusion processes in the metal.

Although these studies led to useful kinetic information, it is still not unambiguously clarified which compounds are actually formed during interaction of tellurium vapour with the Zircaloy surface. For reliable source term calculations, knowledge of the compounds which are formed during interaction is necessary. Thermochemical data of these telluride compounds are required for calculation of their chemical stability. With these data more reliable estimates of the release behaviour of fission product tellurium are possible. The effect of the formation of zirconium tellurides on the volatility of tellurium in the primary system was calculated by Garisto[8], based on estimated thermodynamical data of the zirconium tellurides. These calculations demonstrated that the formation of Zr_5Te_4 in the fuel gap leads to very low vapour pressures of tellurium and telluride compounds, even at 2000 K.

In the present work the surface reaction of tellurium with Zircaloy-4 is investigated using several reaction temperatures and tellurium vapour pressures, to clarify which zirconium telluride compound is formed under accident conditions.

2 The Zr-Te phase diagram

In the zirconium-tellurium system the existence of several compounds has been reported in literature. The existence of $ZrTe_5$, $ZrTe_3$, $ZrTe_{2-x}$, ZrTe, Zr_5Te_4, and Zr_3Te has been reported by Cordfunke and Konings[9], mainly based on the work of Matkovic et al.[10] and Sodeck et al.[11]. Solution of tellurium in zirconium to an extent of 1 at.% at 1800 K was reported by Brattås and Kjekshus[12]. A tentative phase diagram of the zirconium-tellurium system is shown in figure 1, from which it is evident that uncertainties still exist as to the zirconium-rich part of the phase diagram. $ZrTe_{2-x}$ is the only compound in this system which has a homogeneity range.

The reaction of Zircaloy-4 with tellurium vapour can lead to several reaction products. Since the amount of Zircaloy is far in excess over the amount of tellurium in a nuclear reactor, formation of the most zirconium-rich compound or a solid solution of tellurium in Zircaloy will occur when chemical equilibrium is assumed. However, as was shown by Anand and Pruthi[4], reaction at 923-1273 K occurs at the surface of the Zircaloy leaving the bulk Zircaloy unattacked and, consequently, chemical equilibrium is not attained under these conditions.

3 Experimental

Reactor-grade Zircaloy-4 tube and Zircaloy-4 bar (1.4wt.% Sn, 0.2wt.% Fe, 0.1wt.% Cr) were used for reaction with tellurium. Before reaction tellurium (Merck) was purified by melting in a hydrogen atmosphere. Zircaloy was used for reaction in the form of cylindrical pellets (4*4mm diam.*height) and turnings fabricated from Zircaloy-4 bar. Cylindrical pieces (14mm in height 0.73mm wall-thickness and 9.3mm inner diameter) were cut from Zircaloy-4 tube. The pellets and turnings were degreased in hexane and annealed in purified argon atmosphere before reaction. Zircaloy-4 cylinders were only degreased in hexane before reaction.

Weighed amounts of tellurium and Zircaloy turnings or pellets were put in evacuated and sealed quartz ampoules. The ampoules, with tellurium and Zircaloy-4 positioned at each end, were placed in a resistance furnace which was preheated at the desired reaction temperature. At several intervals the surface of some Zircaloy pellets was photographed to analyze the growth behaviour of the surface layer of zirconium telluride. After reaction the ampoules were opened and the reaction products were removed from the Zircaloy surface with a stainless steel knife or using a mortar and pestle. The reaction products were analyzed with X-ray powder diffraction technique. Some pellets were after reaction embedded in resin, sawn through and metallurgically polished. The cross-sections were examined using SEM-EDX.

In another series of experiments, a Zircaloy-4 cylinder was placed in a vertical quartz ampoule and tellurium powder was put at the bottom of the ampoule. In an experimental setup using two vertical resistance furnaces, a temperature gradient was created and the evacuated and sealed ampoule was placed in such a way that Zircaloy-4 was kept at a high temperature and tellurium at a lower temperature. In this way surface reaction temperatures and tellurium vapour pressure were varied. Prior to use, the temperature gradient in the furnaces was measured for different combinations of set temperatures. The length of the ampoule was matched with the desired temperatures. A thermocouple was placed against the bottom of the ampoule to measure the tellurium temperature. The furnaces were preheated prior to reaction to avoid as much as possible the influence of temperature transients.

All material handlings were conducted in a glove box under purified argon to avoid any contact of Zircaloy and tellurium with air and moisture. X-ray powder diagrams were taken with a Guinier type camera. SEM/EDX analysis was done using a JEOL-JXA 840 apparatus. Identification of reaction products was based on the known diffraction patterns[13] of the zirconium tellurides.

4 Results

The reaction conditions and results of the reaction of tellurium with Zircaloy-4 turnings are presented in table 1, and with Zircaloy-4 pellets in table 2. [1]
Photographs of the formation of the zirconium telluride on the surface of the Zircaloy pellets are shown in figure 2 and 3. They demonstrate the growth of zirconium telluride in time at the two different reaction temperatures of experiments 7 (723 K) and 8 (873 K). The pictures show that volume expansion of the telluride layer occurs in time, finally leading to the loosening of the skin from the Zircaloy bulk. This latter phenomenon is clearly shown by the SEM-picture in figure 4 of the cross section of the reacted pellet of experiment 7.
SEM/EDX-micrographs from the cross section of the reacted Zircaloy-4 pellet of experiment 13 are given in figure 5. In this case a large part of the telluride layer was removed before examination. The pictures demonstrate that the bulk Zircaloy-4 is unattacked by the tellurium after 100 hrs at 1273 K.
The results of the reactions with Zircaloy-4 cylinders are given in table 3. An additional experiment was done in which two reacted Zircaloy-4 cylinders were used, which contained a zirconium telluride layer on the surface consisting of $ZrTe_{2-x}$ and $ZrTe_{2-x}$ and $ZrTe_3$ respectively. These cylinders were heated in argon atmosphere in an induction oven for 90 minutes at a temperature close to the melting point of the Zircaloy. After this treatment the reaction products were removed from the surface of the Zircaloy and analyzed. It appeared that both $ZrTe_{2-x}$ and $ZrTe_3$ had transformed into Zr_5Te_4.

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[1] Results in tables are ordered at increasing reaction temperatures

Table 1: Reaction of Zircaloy-4 turnings with tellurium

number	Temp. [K]	at.% Te	reaction time [hr]	reaction products
1	623	61	16	no reaction
2	673	61	120	$ZrTe_3$+ $ZrTe_5$
3	723	60	16	$ZrTe_3$+ $ZrTe_5$
4	723	27	40	$ZrTe_{2-x}$+ $ZrTe_3$
5	1073	22	40	Zr_5Te_4+ ZrTe+$ZrTe_{2-x}$

Table 2: Reaction of Zircaloy-4 pellets with tellurium

number	Temp. [K]	at.% Te	reaction time [hr]	reaction products
6	723	25	43	$ZrTe_3$+ $ZrTe_5$
7	723	25	100	$ZrTe_3$+ $ZrTe_5$
8	873	25	100	$ZrTe_{2-x}$+ $ZrTe_3$
9	900	21	40	$ZrTe_{2-x}$+ $ZrTe_3$
10	1073	20	43	$ZrTe_{2-x}$
11	1073	4.6	40	$ZrTe_{2-x}$
12	1273	20	40	$ZrTe_{2-x}$+ ZrSiTe
13	1273	20	100	$ZrTe_{2-x}$+ ZrSiTe
14	1273	20	100 with 20K/hr	$ZrTe_{2-x}$+ZrSiTe

Table 3: Reaction of Zircaloy-4 cylinders with tellurium

number	$T_{Zircaloy-4}$ [K]	$P_{Tellurium}$ [atm.]	reaction time [hr]	reaction products
15	873	$10^{-3.5}$	20	$ZrTe_{2-x}$+ $ZrTe_3$
16	1073	$10^{-3.5}$	2	$ZrTe_{2-x}$
17	1073	$10^{-3.5}$	20	$ZrTe_{2-x}$
18	1073	$10^{-3.5}$	100	$ZrTe_{2-x}$
19	1273	$10^{-9.2}$	20	Zr_5Te_4
20	1273	$10^{-3.5}$	20	$ZrTe_{2-x}$+ ZrO_2
21	1273	$10^{-1.4}$	20	$ZrTe_{2-x}$+ Zr_5Te_4
22	1273	$10^{-3.5}$	heating transient	$ZrTe_{2-x}$+ZrO_2

5 Discussion

From the results it is evident that $ZrTe_{2-x}$ is the compound which is formed in most cases. Already at 673 K $ZrTe_5$ and $ZrTe_3$ are formed on the surface of the Zircaloy-4. At 873 K $ZrTe_5$ is not stable and from 1073 K $ZrTe_3$ is not present in the reaction products. Formation of $ZrTe_{2-x}$ occurs at temperatures between 723 and 1273 K. Zr_5Te_4 is found in a few experiments at high reaction temperatures, but as the only reaction product it is formed in experiment 19.
Although the compound Zr_3Te, which was reported by Matkovic et al.[10] was prepared in separate experiments in our laboratory by means of heating compacted mixtures of tellurium and zirconium powder, it was never observed in the zirconium telluride layer formed on the surfaces of Zircaloy-4 in the present experiments.
Apparently, the reaction temperature and the telluride vapour pressure determine the formation of zirconium tellurides. High temperatures generally lead to formation of $ZrTe_{2-x}$ on the surface of Zircaloy. However, when the tellurium vapour pressure is low or when all tellurium has reacted and heating is continued, formation of Zr_5Te_4 is observed. The formation of this more zirconium-rich compound can be ascribed to the effect, that at high reaction temperatures and low tellurium pressure the diffusional transport of zirconium towards- and inside the telluride layer is increased, while there is less transport of tellurium towards this layer.

Cordfunke and Konings[3] calculated the tellurium vapour pressure in the fuel-cladding gap at 1000 K as a function of the oxygen potential of the fuel. In a small range of oxygen potentials this pressure varies from 10^{-10} to 10^{-1} atmosphere. The present experiments show that formation of $ZrTe_{2-x}$ or Zr_5Te_4 will occur under these conditions. The present study shows that for calculation of the release behaviour of tellurium the formation of the compounds $ZrTe_{2-x}$ and Zr_5Te_4 during interaction of tellurium with the Zircaloy cladding, needs to be taken into account. This interaction will lead to retention of tellurium in the core in the initial stage of an accident. Thermochemical data of $ZrTe_{2-x}$ and Zr_5Te_4 are needed to accurately (re)calculate the tellurium speciation in Zircaloy-clad UO_2 fuel.

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[13] Powder Diffraction File, International Centre for Diffraction Data (Newtown Square Corporate Campus, Pennsylvania).

Figure Captions:

Figure 1: Tentative phase diagram of the Zirconium-Tellurium system.

Figure 2: Photographs of zirconium telluride formation on the surface of Zircaloy-4 at 723K, experiment 7.

2a: Zircaloy pellet before reaction.

2b: After 10 hours of reaction.

2c: After 30 hours of reaction.

2d: After 100 hours of reaction.

Figure 3: Photographs of zirconium telluride formation on the surface of Zircaloy-4 at 873K, experiment 8.

3a: After 30 minutes of reaction.

3b: After 1 hour of reaction.

3c: After 10 hours of reaction.

3d: After 100 hours of reaction.

Figure 4: SEM-picture of the cross section of the reacted pellet after 100 hours at 723K, experiment 7.

Figure 5a: SEM-picture of the cross section of the reacted Zircaloy pellet of experiment 13, 100 hours at 1273K.

Figure 5b and 5c: SEM/EDX-micrograph of the same cross section for Zr and Te

Figure 1

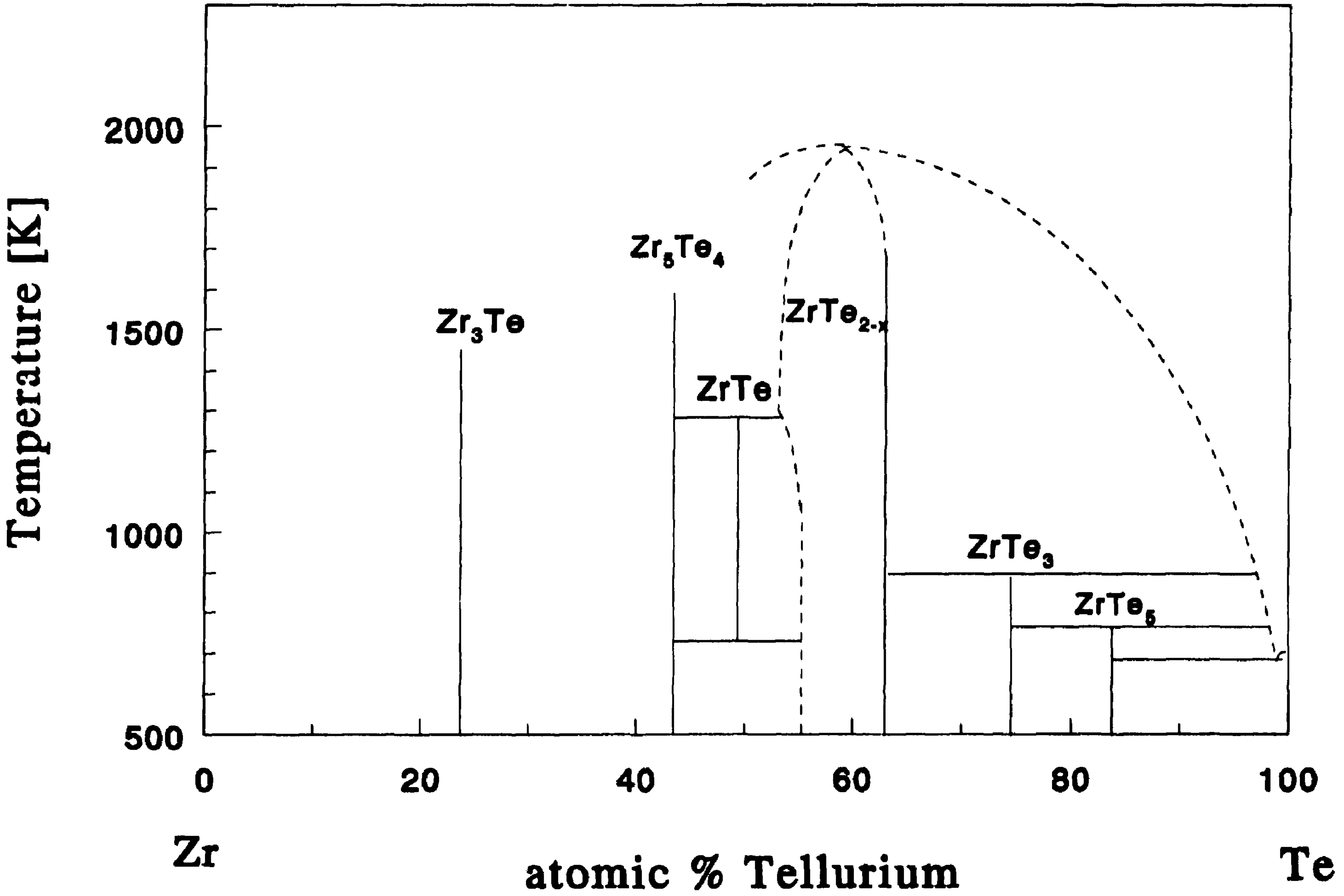

Temperature [K]
2000
1500
1000
500
Zr$_5$Te$_4$
Zr$_3$Te
ZrTe$_{2-x}$
ZrTe
ZrTe$_3$
ZrTe$_5$
0
20
40
60
80
100
Zr
atomic % Tellurium
Te

Fig. 2a

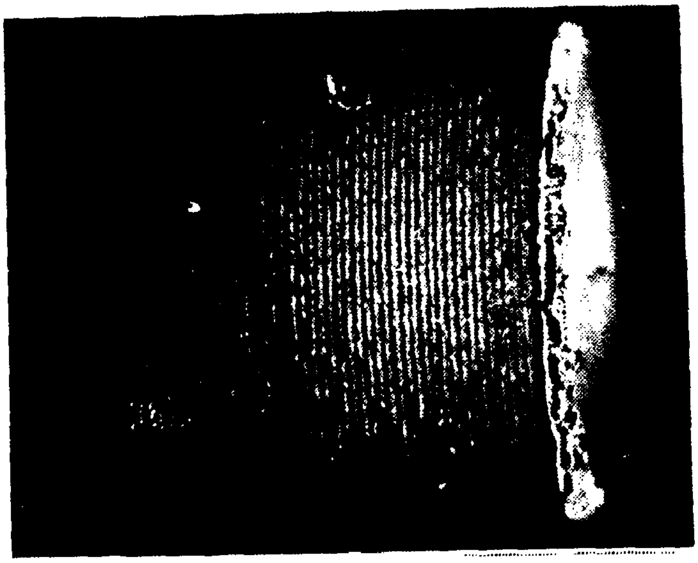


Fig.2b

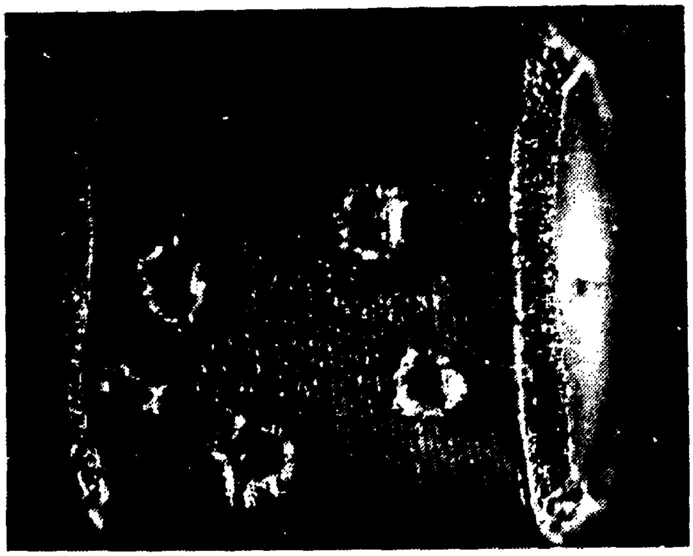


Fig. 2c

Fig. 2d

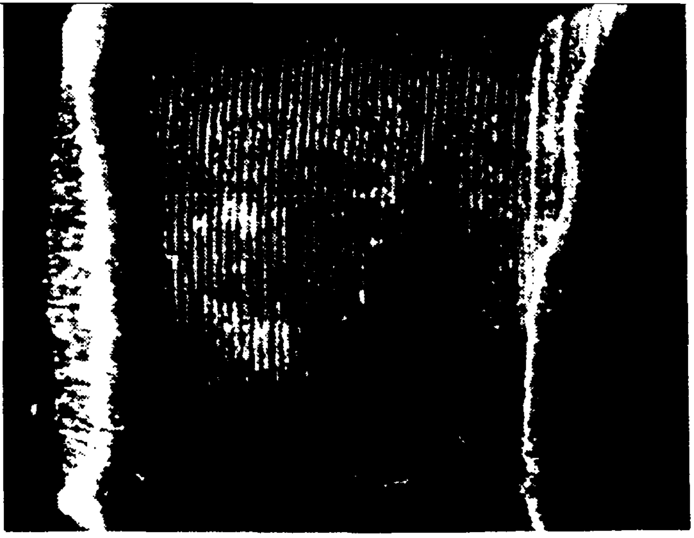


Fig. 3a

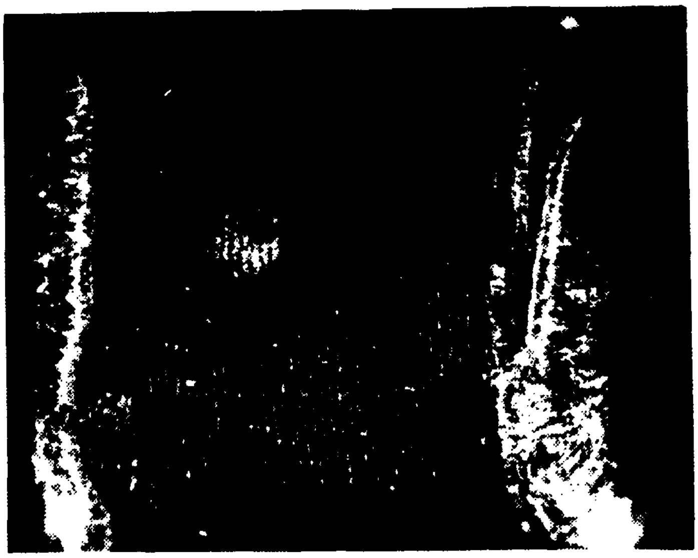
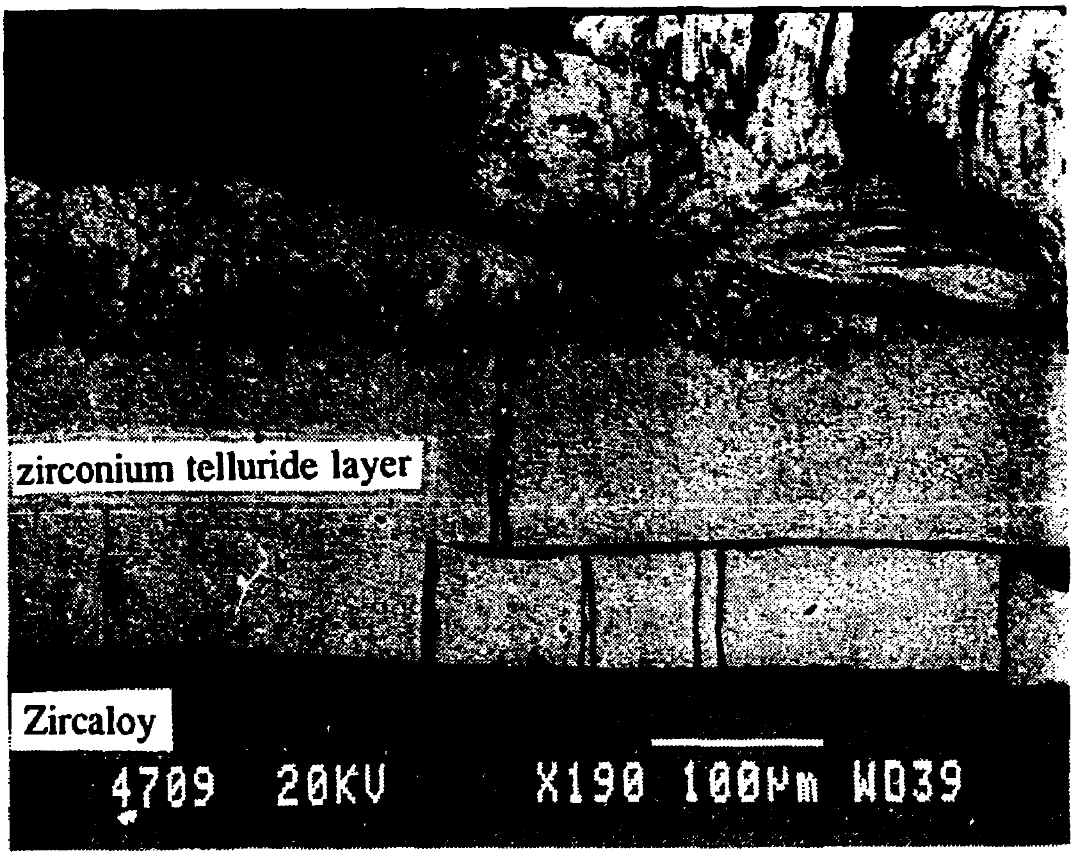


Fig. 3b

Fig. 3c

Fig. 3d

Figure 4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Zircaloy
4709 20KV X190 100Pm WD39

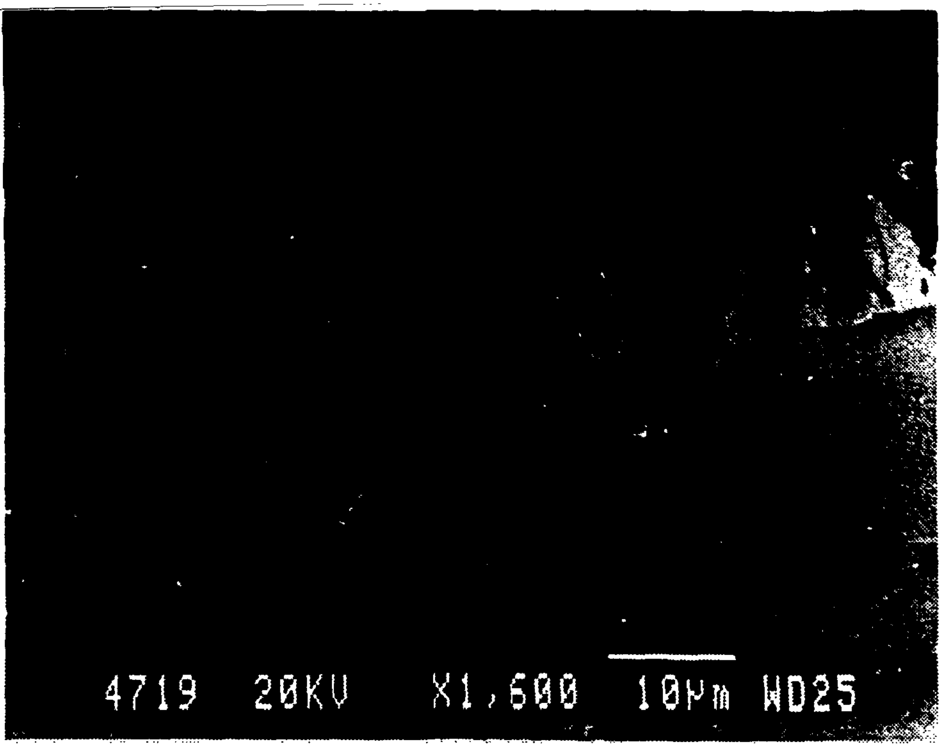

Fig. 5a

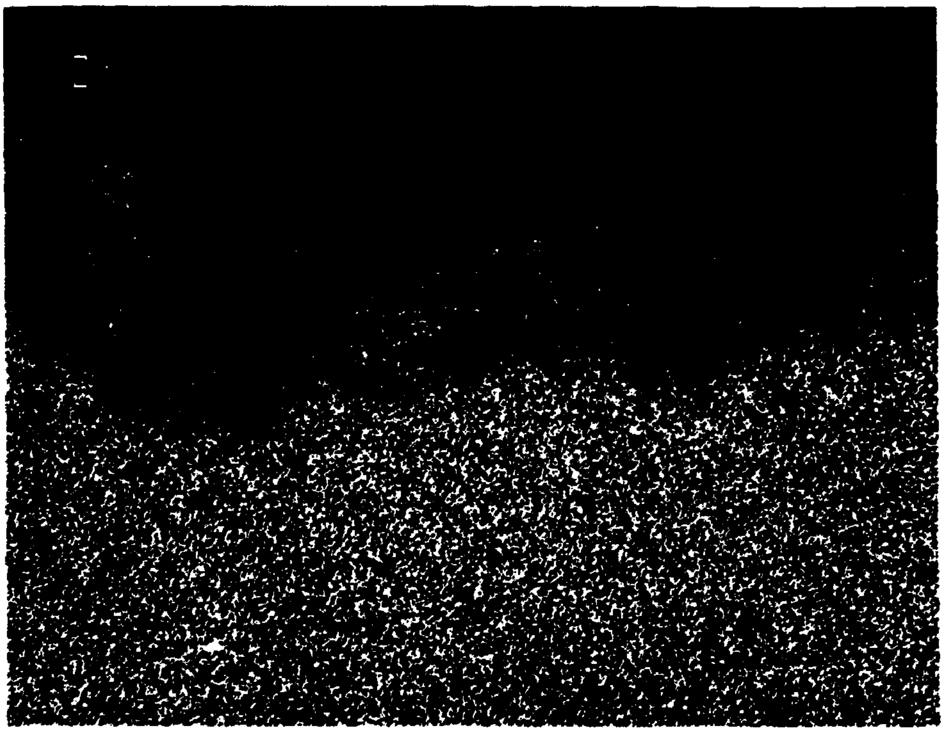

Fig. 5b

Fig. 5c