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# Chemical interaction between Zircaloy-4 and Inconel 718

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ABSTRACT: Isothermal reaction experiments were performed in the temperature range of 1000-1300 °C in order to determine the chemical interactions between Zircaloy-4 fuel rod cladding and Inconel 718 spacer grids of Pressurized Water Reactor (PWR) under severe accident conditions. It was not possible to apply even higher temperatures since fast and complete liquefaction of the components occurred as a result of eutectic interactions during heatup. The liquid reaction products formed enhance and accelerate the degradation of the material couples and the fuel elements, respectively. Only small amounts of Inconel are necessary to liquefy large amounts of Zircaloy.

Thin oxide layers on the Zircaloy surface delay the beginning of the chemical interaction with Inconel but cannot prevent them. In this work the reaction kinetics have been determined for the system as-received and pre-oxidized Zircaloy-4/Inconel 718. The interactions can be described by parabolic rate laws; the Arrhenius equations for the various interactions are given.

## 1 RESULS

The chemical interaction between Zircaloy and Inconel is a diffusion controlled process and can therefore be described quantitatively by Arrhenius equations. Besides the identification of the reacting species, phases, and temperature of onset of liquid phase formation, one of the main results was the determination of the reaction kinetics, which may by used in a code system to predict the material behavior at high temperature.

### 1.1 Chemical behavior

The chemical interaction between Zircaloy-4 and Inconel 718 shows that a liquid reaction zone develops at temperatures as low as 1000 °C. The melting points of Inconel 718 and Zircaloy-4 are 1335 and 1760 °C respectively.

Although many elements are involved in the Zry/Inconel chemical interaction, the binary phase diagrams offer a reasonable explanation of low temperature liquid phase formation. The (Ni-Zr), (Fe-Zr) and (Cr-Zr) phase diagrams indicate that eutectic interactions occur in these binary system. The cross-sections of the Zry-Inconel reaction specimens after annealing at 1000, 1100, 1150 and 1200 °C for various reaction times are shown in figure 1. The cross-section of both as received and pre-oxidized Zry/Inconel reaction specimens (initial oxide layer of 10 μm) are presented for comparison. The eutectic interactions, which occur at 1000 °C and higer, result in the formation of liquid reaction products and voids form as some of the molten material relocates.

Although the crucibles specimens were annealed in the upright position, the reaction zones of the as-received Zry are not symmetrical around the circumference. Apparently very small forces are sufficient to induce asymmetric reaction zone in the Zry-4 wall. First interactions have been noticed at 1000 °C after annealing times longer than 5 minutes. In all cases, the reaction in the Zry-4 was much stronger than in Inconel. This may be explained by phase diagram considerations. Only small amounts (≥ 5wt. %) of Ni,Fe or Cr are necessary to liquefy large quantities of Zr. Also, since the eutectic temperatures in the (Ni-Zr), (Fe-Zr), and (Cr-Zr) systems are lowest on the Zr-rich side, Zr can be liquefied at much lower temperatures than Ni,Fe, or Cr.

The solidified reaction zones were examined with SEM/EDX. Besides the determination of the element distribution, quantitative measurements were performed.

The molten reaction zone consists of two layers formed due to the eutectic reaction, the morphology of the reaction zone was observed in the whole range of temperature and time examined. The element distribution shows Cr enrichment and Ni depletion in the thinner reaction layer I adjacent to the Inconel. In the reaction layer II, Zr, Ni and Fe are uniformely distributed, Cr is connected with precipitates in this zone.

The integral chemical analysis of the solidified melt of reaction layer I shows the following chemical composition: about 56 wt.% Zr, 23% Cr, 9% Fe, 5% Ni, 5% Mo,2% Nb. The integral.analysis for the reaction layer II reveals: 82 wt.% Zr, 12% Ni, 3% Fe, 2% Cr, 1% Sn, which is very similar to the chemical composition of the eutectic point on the Zr-rich side in the (Ni-Zr) system. From the binary (Ni-Zr) and (Fe-Zr) phase diagrams and the chemical composition of the reaction zone it is clear that the diffusion of Ni and Fe into Zry is initially responsible for the low-temperature liquefaction of Zircaloy. The further liquefaction of Zry may then occur faster by dissolution of the Zr in the liquid reaction product.

The metallic (Zr,Ni,Cr) melts in the two reaction layers decompose into various phases on cooldown.

During the isothermal interaction the liquid phase formed due to the (Ni-Zr) eutectic interactions penetrates along the grain boundaries of the $Zr(Cr, Fe)_2$ phase, which develops in the reaction layer I (Cr enriched zone) due to the diffusion of Zr into Inconel. This liquid / solid interaction dissolves to a certain extent the $Zr(Cr, Fe)_2$ phase; the amount and size of this phase decrease with increasing distance from the Inconel/liquid interface. In the reaction layer II, which is liquid at the reaction temperature, the $Zr(Cr, Fe)_2$ phase is present only in a very limited amount. During cooldown the liquid alloy of reaction layers I and II starts to solidify and decomposes into the β-$Zr_2(Ni, Fe)$ phases. The $Cr_2(Zr, Fe)$ phase was observed only in the reaction layer I at temperatures above 1150 °C.

## 1.2 Reaction kinetics

The behavior of the solid / solid contact interface of Zircaloy / Inconel in the temperature range 1000 - 1200 °C shows the pronounced damage of Zircaloy, which is indicated by the extended thickness of the liquid reaction zone resulting from the chemical interactions. To be able to determine the reaction kinetics between Zry-4 and Inconel 718, the thicknesses of the reaction zones were measured as a function of the reaction time. The isothermal growth of the reaction zone (dissolution of Zry and Inconel) is a linear function of the square root of time (parabolic rate law) for all temperatures examined, indicating a diffusion - controlled process.

Ni and Fe diffuse into solid Zry and initiate Zry liquefaction as soon as the solid/liquid phase field has been reached, small amounts of Inconel dissolve large amounts of Zry. Above about 1250 °C complete liquefaction of the specimens occurs.

The reaction zone growth rates for the Zry/Inconel interactions are plotted as a function of the reciprocal temperature in Figure 2.

The growth rate equations determined for the temperature range of 1000 to 1200 °C are:

for Zircaloy-4

$$\boxed{x^2/t\ (cm^2\ /\ s) = 4.435\ .\ 10^4\ .\ \exp\ (-252093\ /\ RT)}$$

for Inconel

$$\boxed{x^2/t\ (cm^2\ /\ s) = 2.884\ .\ 10^5\ .\ \exp\ (-294962\ /\ RT)}$$

These equations can be extrapolated to lower temperatures, but not to higher temperatures since fast and complete liquefaction of the materials take place at about 1250 °C.

### 1.3 Influence of an oxide layer on Zircaloy - Inconel interaction

The chemical interaction between pre-oxidized Zircaloy-4 and Inconel 718 (initial $ZrO_2$ layer thicknesses: 20 and 45 um) indicate that the oxide layer delays the beginning of the interaction and reduces the reaction rate, but cannot prevent interaction. The cross section of Zry/Inconel reaction specimens annealed at 1000, 1100, 1150 and 1200 °C for various reaction times are shown in Figure 1. The cross section of both as-received and pre-oxidized specimens (initial $ZrO_2$ layer thickness 10 µm) are presented for comparison. Inconel does not interact with stoichiometric $ZrO_2$, but the oxide layer will be dissolved by Zry, while forming oxygen-stabilized α-Zr (O) during a time-dependent incubation period, $t_o$. The delay in interaction (liquid phase formation) is determined by the time which is necessary for the oxygen to diffuse from the $ZrO_2$ layer into Zry forming a "metallic" oxygen-stabilized α-Zry(O) phase which can then interact with Inconel.

The experimental results with the pre-oxidized Zry specimens have shown that the liquefaction of the specimens has shifted to higher temperatures. The chemical reaction rate was slower compared with the specimens tested in the as-received condition. The protective character of the $ZrO_2$ layer on the Zry surface, which acts initially as a barrier for the Zry/Inconel interactions, depends on the temperature, initial oxide layer thickness and time. Liquid phase formation starts before the oxide layer has completely disappeared, a thin porous oxide layer remains in the liquid reaction zone; the same effect was seen in the chemical interaction between Zry-4 and 1.4919 ss (AISI 316) (Hofmann and Markiewicz 1994). The oxygen from the $ZrO_2$ layer diffuses into Zry, stabilizing the α-Zry(O) phase, and forms a substoichiometric $ZrO_{2-x}$ oxide layer. In this way, Zr from the oxide layer can interact with Ni and Fe, producing a liquid phase on the Inconel side which penetrates through the cracks of the brittle oxide layer reaching the α-Zry(O) phase.

The calculated isothermal growth rates for the initial $ZrO_2$ thicknesses of 20 and 45 µm are plotted versus the reciprocal temperature in Figures 3 and 4. The growth rate equations and '$t_0$' values have been determined from the $x^2$ versus t correlation of the experimental data.

The results indicate that a $ZrO_2$ layer delays the chemical interaction between Zry and Inconel. However, the protective effect of the oxide layer could be inhibited at the contact point of both materials if the interaction took place in an oxidizing atmosphere. To clarify this point, a few experiments were done in steam atmosphere. The interaction was demonstrated by several molten zones on the external surface of the Zry tube in the regions of contact. A cross section of a sample heated at 1150 °C for 3 min. is shown in Figure 5. Liquid phase formation due to the chemical interactions is not prevented under conditions of unlimited steam oxidation.

## 2 DISCUSSION

The main purpose of this work has been to determine the kinetics of reaction between Zircaloy and Inconel with a view of understanding and describing analytically the chemical interactions between the Zircaloy-4 fuel rod cladding tubes and Inconel 718 spaçer grids in integral experiments like the CORA test (Hagen, Hofmann, Schanz and Sepold 1989). Although some interaction experiments have been described by Daniel and Nichols (1985), Nagase and Uetsuka (1990), no Arrhenius equation had been previously been developed from the data. In all cases, the maximun thickness of the reaction zone was used in the evaluation of the kinetic data to obtain conservative results.

In the Zry/Inconel system, a considerable amount of liquid phase is formed around 1000 °C; the amount of liquefied material increases with increasing temperature and time. The nickel-zirconium and iron-zirconium phase diagrams show that due to eutectic interactions early melt generation has to be expected which initiates melt progression within the fuel assembly at low temperatures.

The results of the present single-effect tests are in agreement with results of integral tests (CORA experiments) where fuel rod bundles were heated to temperature of about 2000 °C (Hagen, Hofmann, Schanz and Sepold 1989). In all cases, damage to the bundle was initiated by Zircaloy/Inconel and Zircaloy/stainless steel interactions. Localized liquefaction of these components started at around 1200 °C. The low temperature melt formation initiates bundle damage and causes the chemical attack of the fuel rods dissolving the cladding tubes and part of the $UO_2$ fuel. By this process, molten fuel formation and relocation as well as early fission product release can take place even well below the melting point of Zry. The melts relocate towards cooler regions of the core where they may cause coolant channel blockages upon solidification.

Thin oxide layers on the Zry surface can delay the chemical interactions with Inconel, but cannot prevent them. $ZrO_2$ interacts with metallic Zr while forming oxygen-stabilized $\alpha$-Zr(O) resulting in a sub-stoichiometric $ZrO_2$. $\alpha$Zr(O) is capable of interacting with the Inconel alloy components. The oxygen dissolved in the Zry lattice exerts influence on the diffusion and/or dissolution processes; the reaction rates are slower. In all other cases, the reaction of Zry with oxygen or steam is more favorable thermodynamically than the reactions with Inconel, but as the integral bundle meltdown experiments show, a steam environment cannot prevent the chemical interaction between Zry and Inconel.

The chemical analysis of the reaction zone in the single-effect tests showed a great similarity in the chemical composition of some phases (developed during the chemical interactions) compared with the analysis of integral CORA experiments and chemical analysis on selected samples from the TMI-2 reactor core (Kleykamp and Pejsa 1991) for example the phases $Zr_2$ (Ni, Fe) and $\beta$-Zr.

The chemical interactions which take place during the integral fuel bundle tests could be explained only by the single-effects tests results. The complexity of a severe reactor accident scenario with the resulting multitude of materials interactions make a complete interpretation of the many possible chemical interactions extremely difficult and in some cases even impossible.

## 3 SUMMARY AND CONCLUSIONS

- Inconel 718 in contact with Zircaloy gives rise to chemical interactions which can be described by a parabolic rate law.

- As a result of eutectic interactions at temperatures as low as 1000 °C, the liquid phase causes a fast and complete liquefaction of both components of the reaction couple at about 1250 °C.

- Only a small amount of Inconel is necessary to liquefy large amounts of Zry.

- Thin $ZrO_2$ layers on the Zircaloy surface delay liquid phase formation and reduce the rates of reaction, but cannot prevent the chemical interaction.

- In experiments of short durations, the $ZrO_2$ layers shift the liquefaction temperature to higher values; the incubation period depends on the initial oxide layer thickness and on the temperature.

- Liquid phase formation due to the chemical interactions at low temperatures is not prevented under unlimited steam oxidation conditions.

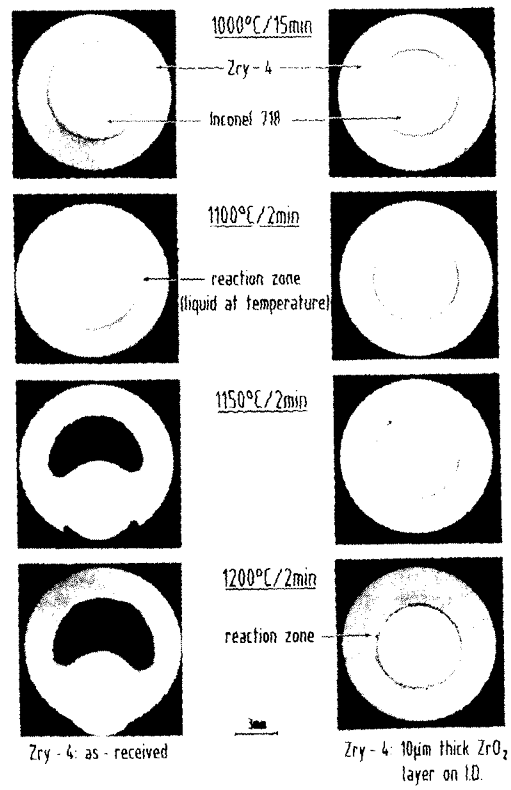


**FIG.1**: Chemical interactions between Zircaloy-4 and Inconel 718 at different temperatures; influence of a thin $ZrO_2$ layer on the reaction behavior (right column of pictures).

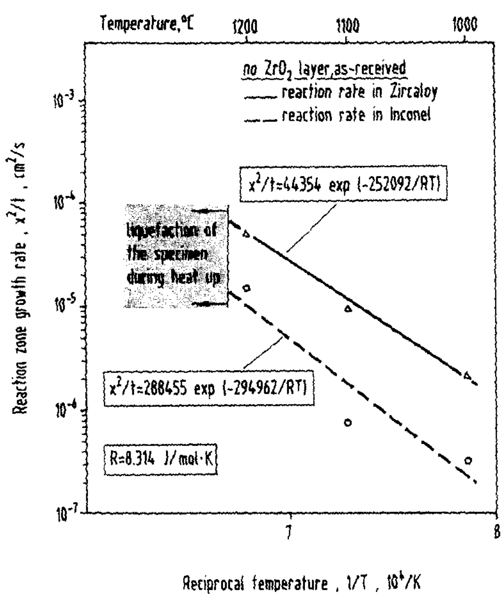


**FIG.2**: Reaction zone growth rates for the Zircaloy-4/Inconel 718 reaction system

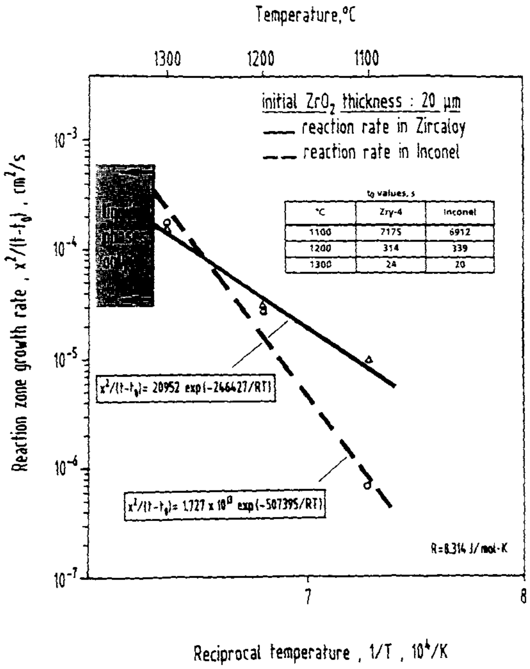


**FIG.3:** Reaction zone growth rates for the pre-oxidized Zircaloy-4/Inconel 718 system; initial $ZrO_2$ layer thickness: 20 µm

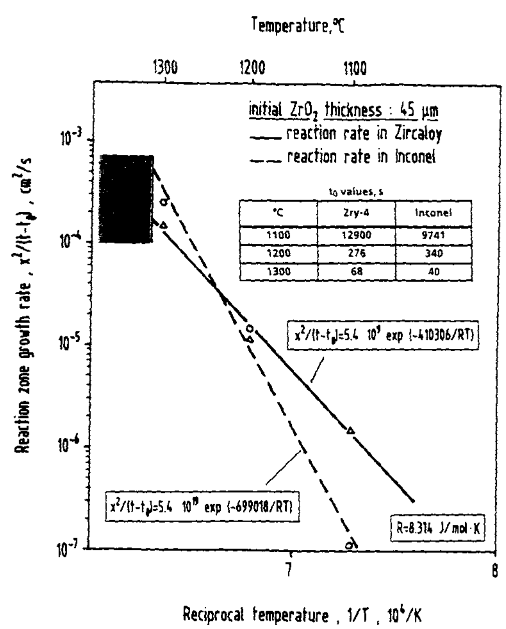


**FIG.4:** Reaction zone growth rates for the pre-oxidized Zircaloy-4/Inconel 718 system; initial $ZrO_2$ layer thickness: 45 µm

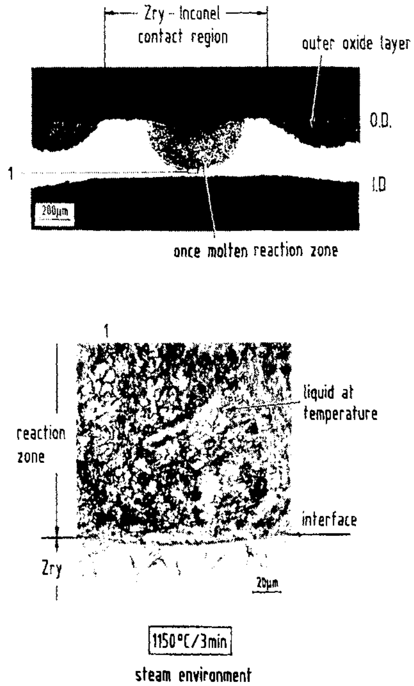


FIG.8: Chemical interactions between Zircaloy-4 tube and Inconel 718 after 3 min at 1150°C in steam atmosphere.

## REFERENCES


Daniel, B. Nichols, A. 1985. The liquefaction of alloys identifield with structural materials in a PWR core. AEEW-M 2250.

Hagen, S. Hofmann, P. Schanz, G. Sepold, L. 1989. Results of the severe CORA fuel damage experiments. KfK 4376.

Hofmann, P. Markiewicz, M. 1994. Chemical interaction between Zry-4 and stainless steel. KfK 5106.

Kleykamp, H. Pejsa, R. 1991. Chemical and X-Ray diffraction analysis on selected samples from TMI-2. KfK 4872.

Metals Handbook 1990 ASM International, Materials Park, OH, USA

Miller,. G. 1986. Zirconium; Academic Press Inc., Publisher 111, N.Y.

Ngase, F. Uetsuka, H. 1990. Interaction between Zry tube and Inconel spacer grid at high temperature. JAERI-M 90-165.