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## Modeling of liquid phase formation due to the solid zircaloy-4/solid stainless steel interaction

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**ABSTRACT:** A diffusion model that describes the eutectic interaction between both as received and oxidized Zry-4 and AISI 316 stainless steel at temperatures between 1000 to 1300 °C is presented. The instantaneous positions of the two solid/liquid interfaces, are input data. We calculate the interdiffusion coefficients in the melt and the solid/liquid interfaces concentration values for different temperatures.

### 1 INTRODUCTION

In recent experimental work (Hofmann 1990,1993) the formation of liquid phases in the Zircaloy-4 (Zry-4)/Inconel and Zry-4/AISI 316 Stainless steel (SS) systems due to eutectic interactions between the components is shown, at temperatures from 1000°C. As Zry-4 and SS are structural materials of the core of the reactor the Zry-4/SS system merits to be studied.

García (1992) presented a model to calculate the liquid phase formation in the Zry-4/Inconel system both for as received and oxidized Zry. In this work a different calculation scheme is developed. The required kinetic data are taken from experimental determinations. With these values we calculate the diffusion coefficient values in the melt for each temperature and the Zr and Fe concentration at the solid/liquid interphase boundaries.

At high temperatures the Zry oxidation reaction is very fast. Experiments indicate that the presence of the oxide layer delays the start of the interaction between Zry-4 and SS but does not avoid the formation of the liquid phase. The interaction starts, at a slower rate, after an initial delay period, during which the oxide layer dissolves. The model is also applied to simulate the experiments with pre-oxidized Zry-4 for different initial oxide thicknesses. A previously developed code (DISOL) (Piotrkowski 1993), able to simulate the oxidation of Zr and the dissolution of the oxide layer, was used to evaluate the delay time.

## 2 EXPERIMENTAL DATA

Annealing experiments were performed by Hofmann (1990, 1993). Oxide layers 10, 20 y 50  $\mu\text{m}$  thick were previously grown on some samples. The annealing temperatures ranged from 1000 to 1300°C. The maximum annealing times were of 900.

The parabolic rate constant, when an initial oxide layer is present, is defined as  $K=x^2/(t-t_0)$  where  $x$  is the reaction thickness and  $t_0$  is the delay time necessary to start the interaction. The kinetics proved to be always parabolic, indicating a diffusion controlled process.

## 3 OUTLINE OF THE MODEL

Figure 1 represents the system (plane geometry is considered) after some time of interaction at  $T \geq 1000^\circ\text{C}$ . SS is molten up to  $-x_1$  and Zry up to  $x_2$ . These distances are experimentally determined as functions of time for each temperature. The liquid formed is placed between  $-x_1$  and  $x_2$ . On the average this phase has the composition that corresponds to the involved volumes  $x_1S$  and  $x_2S$ , where  $S$  is the contact surface.

We assume that the total solid volume  $(x_1+x_2)S$  coincides with the volume of the formed liquid. It is further assumed that neither convection nor liquid movement takes place and that the only movement is related with diffusion of the major components, Fe and Zr, in the eutectic melt. Both diffusion processes are considered independent of each other. The second Fick's law can be applied:

$$(1) \quad \frac{\partial C^{Zr}}{\partial t} = D^{Zr} \frac{\partial^2 C^{Zr}}{\partial x^2}, \quad \frac{\partial C^{Fe}}{\partial t} = D^{Fe} \frac{\partial^2 C^{Fe}}{\partial x^2}$$

Zr and Fe diffusion in solid SS and Zry are neglected because we consider that the diffusion coefficients are small as compared with the liquid ones, that the number of solid phases is influenced by diffusion of the other components present in the melt, and the experimental work only reports the liquid phase kinetics. We also consider that although Fe diffusion coefficient in Zr takes very high values, both in  $\alpha$  phase (oxygen stabilized) (Hood 1988) and in  $\beta$  phase (Herzig 1987), Fe solubility in Zr is very low, about 0.03 in  $\beta$  phase at 1100°C (Arias 1988) and much lower in  $\alpha$  phase where besides the interstitial positions are blocked by the oxygen atoms (Forlerer 1994).

If  $C_1^{Fe}$  and  $C_2^{Fe}$  are, respectively, the maximum and minimum concentrations of Fe in the melt (Figure 1), Stefan's conditions in  $x_1$  and  $x_2$  for Fe are then:

$$(2) \quad C_2^{Fe} \frac{dx_2}{dt} = \left[ -D^{Fe} \frac{\partial C^{Fe}}{\partial x} \right]_{x=x_2}$$

$$(3) \quad (C_0^{Fe} - C_1^{Fe}) \frac{dx_1}{dt} = [-D^{Fe} \frac{\partial C^{Fe}}{\partial x}]_{x=x_1}$$

With the same hypothesis for Zr we have:

$$(4) \quad -C_1^{Zr} \frac{dx_1}{dt} = [-D^{Zr} \frac{\partial C^{Zr}}{\partial x}]_{x=x_1}$$

$$(5) \quad (C_0^{Zr} - C_2^{Zr}) \frac{dx_2}{dt} = [D^{Zr} \frac{\partial C^{Zr}}{\partial x}]_{x=x_2}$$

We define the adimensional coordinates of both interphases:

$$(6) \quad \gamma_1 = \frac{x_1}{2\sqrt{D^{Zr}t}} \quad , \quad \gamma_2 = \frac{x_2}{2\sqrt{D^{Zr}t}}$$

where  $\gamma_1$  and  $\gamma_2$  are positive constants. In terms of this variables the concentration of Zr in the melt is then:

$$(7) \quad C^{Zr} = C_1^{Zr} + \frac{C_2^{Zr} - C_1^{Zr}}{\text{erf}(\gamma_1) + \text{erf}(\gamma_2)} \left[ \text{erf}(\gamma_1) + \text{erf}\left(\frac{x}{2\sqrt{D^{Zr}t}}\right) \right]$$

and that of Fe is:

$$(8) \quad C^{Fe} = C_1^{Fe} - \frac{C_1^{Fe} - C_2^{Fe}}{\text{erf}(\gamma_1\phi) + \text{erf}(\gamma_2\phi)} \left[ \text{erf}(\gamma_1\phi) + \text{erf}\left(\frac{x}{2\sqrt{D^{Fe}t}}\right) \right]$$

where:

$$(9) \quad \phi = \sqrt{\frac{D^{Zr}}{D^{Fe}}}$$

Substituting the values of  $\partial C^{Zr}/\partial x$  and  $\partial C^{Fe}/\partial x$ , in the Stefan conditions, we obtain:

$$(10) \quad \frac{C_2^{Zr} - C_1^{Zr}}{C_1^{Zr}} = (\text{erf}(\gamma_1) + \text{erf}(\gamma_2)) \sqrt{\pi} \gamma_1 e^{\gamma_1^2}$$

$$(11) \quad \frac{C_2^{Zr} - C_1^{Zr}}{C_0^{Zr} - C_2^{Zr}} = (\text{erf}(\gamma_1) + \text{erf}(\gamma_2)) \sqrt{\pi} \gamma_2 e^{\gamma_2^2}$$

$$(12) \quad \frac{C_1^{Fe} - C_2^{Fe}}{C_2^{Fe}} = (\operatorname{erf}(\gamma_1 \phi) + \operatorname{erf}(\gamma_2 \phi)) \sqrt{\pi} \gamma_2 \phi e^{(\gamma_2 \phi)^2}$$

$$(13) \quad \frac{C_1^{Fe} - C_2^{Fe}}{C_0^{Fe} - C_1^{Fe}} = (\operatorname{erf}(\gamma_1 \phi) + \operatorname{erf}(\gamma_2 \phi)) \sqrt{\pi} \gamma_1 \phi e^{(\gamma_1 \phi)^2}$$

These equations can be put in terms of weight fractions,  $w$ , being  $C = w\delta^L$ , where  $\delta^L$  is the liquid density that can be calculated from the measured values of molten Zry-4 and SS, and their respective densities, assuming that the volume change between solid and liquid can be neglected.

Naming the weight fraction of elements different from Fe in the SS as  $w_{rest}^{Fe}$ , and supposing that the Zry-4 is only Zr, one can write  $w^{Zr} + w^{Fe} + w^{rest} = 1$  and naming  $M = w^{rest}/w^{Fe} = 0.351/0.649$ :

$$(14) \quad w^{Zr} = 1 - w^{Fe}(1+M) \quad w^{Fe} = \frac{1 - w^{Zr}}{1+M}$$

We assume that the  $M$  value in the liquid remains unchanged, this means that the diffusion coefficients of the rest elements in the liquid are approximately the same.

From the Stefan conditions, taking into account (13) and (14) we obtain a system of 4 equations and 4 unknowns:  $\gamma_2$ ,  $\phi$ ,  $w_1^{Zr}$  y  $w_2^{Zr}$ . With these we calculate the diffusion coefficients and the interphases concentrations.

As was already said, the delay for the beginning of the oxidized Zry-4/SS interaction is associated with the time required for the dissolution of the oxide layer. To calculate this delay time, the DISOL code, able to predict the times for the development and dissolution of oxide layers, was applied. For an oxide layer of thickness  $X(\mu\text{m})$ , which remains at a constant temperature  $T(K)$ , the dissolution time  $t_0(s)$  can be calculated with the equation:

$$(15) \quad t_0 = 2.53 \cdot 10^{-8} X^2 e^{221120/RT}$$

#### 4 RESULTS AND DISCUSSION

We determine the volume fraction of Zry-4 (or Zr) in the melt at each temperature, from the experimental work, and with these values we calculate the weight fraction of Zr in the melt,  $w_L^{Zr}$ :

$$(16) \quad w_L^{Zr} \approx w_L^{Zry} = \frac{\rho^{Zry}}{a\rho^{SS} + \rho^{Zry}}$$

with  $a = x_1/x_2 = \sqrt{K^{SS}/K^{Zry}}$ . By checking the interfaces concentrations we always found  $w_1^{Zr} < w_L^{Zr} < w_2^{Zr}$ , as expected. Table 1

shows the calculated boundaries concentrations. The value of  $\phi$  in all the calculations was about 0.90. The liquid diffusion problems with infinite dilute solutions can be described in terms of an interdiffusion coefficient, this means  $\phi=1$ . In this problem we have a finite dilution so  $\phi \neq 1$ , but as  $\phi \sim 1$ , we define an interdiffusion coefficient by means of a regression of all the values for Fe and Zr.

The calculation was performed for the as-received and the pre-oxidized cases.

The measured delay times for the interaction in Zry-4, with different initial oxide layers, are compared with the values calculated with the DISOL code. For 20 and 50  $\mu\text{m}$  a good fit is obtained between calculated and measured values considering the accuracy of the experiments. For 10  $\mu\text{m}$  DISOL predicts times longer than the measured ones. This can be explained taking account of another mechanism, besides the oxide layer dissolution, which reduces the delay time. This could be fast diffusion through different short circuits across the oxide layer, such as grain boundaries and cracks, which contributes to form liquid at each side of the oxide layer. This hypothesis is corroborated by experimental observation of an oxide layer between liquid.

Figure 2 shows the calculated diffusion coefficients, for initial oxide layers of 0, 10, 20 and 50  $\mu\text{m}$ . Empty markers:  $D^{\text{Zr}}$ , full markers:  $D^{\text{Fe}}$ . Figure 3 shows the delay for the reaction start as a function of the inverse temperature on the Zry-4 side. Thin line: calculated with DISOL code, thick line: measured.

## 5. CONCLUSIONS

The eutectic interaction between both as received and oxidized Zry-4 and AISI 316 stainless steel at high temperatures (1000 to 1300°C) is well described by a diffusion model that only takes into account the displacement of the major components of each alloy through the liquid layer. The solid/liquid interfaces concentrations, and the interdiffusion coefficient in the liquid, representing the as-received Zry-4/SS and the oxidized Zry-4/SS interactions, for initial oxide layers of 10, 20 and 50  $\mu\text{m}$  are obtained. The model also describes the delay for the interaction initiation when an oxide layer is present on Zry-4, by solving a previously developed code that computes the time for the dissolution of a given oxide layer into the Zry-4 matrix.

## 6. REFERENCES

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Table 1.  
Calculated Zr boundaries concentration values.

Oxide ( $\mu\text{m}$ )	T ( $^{\circ}\text{C}$ )	w <sub>2</sub> Zr	w <sub>1</sub> Zr
0	1000	0.9275	0.9132
	1100	0.9165	0.8992
	1150	0.9105	0.8931
	1200	0.9053	0.8863
10	1100	0.8141	0.7719
	1150	0.8213	0.7915
	1200	0.8292	0.8100
20	1050	0.8040	0.7630
	1100	0.7898	0.7678
	1200	0.7808	0.7572
	1250	0.7474	0.6914
	1300	0.7082	0.6735
50	1100	0.7494	0.6976
	1200	0.7753	0.7616
	1250	0.6716	0.5958
	1300	0.5584	0.4253

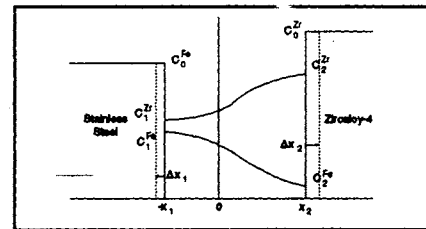


Figure 1

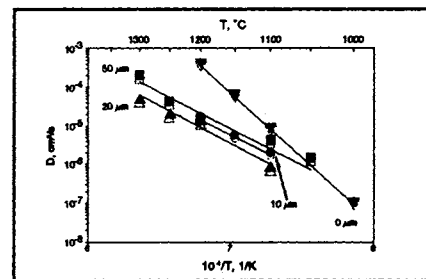


Figure 2

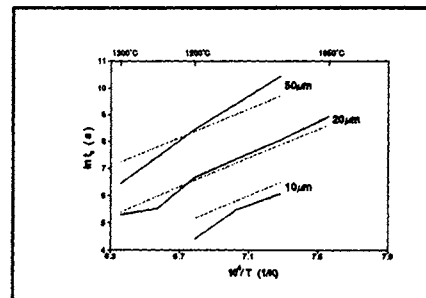


Figure 3