

# MODELING THE EFFECT OF HYDROGEN ON CREEP BEHAVIOR OF ZIRCALOY CLADDING

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**Abstract:** During dry storage of used nuclear fuel, creep is the most likely degradation mechanism for the zirconium alloy fuel cladding. The cladding integrity during dry storage depends on the internal fuel rod pressure, the temperature, the amount of oxidation, irradiation hardening and the content of hydrogen which has been taken up during in-reactor operation. In this paper, the effect of hydrogen on the creep behavior of zirconium alloy cladding material was investigated at the temperature of 400°C. Depending on temperature, hydrogen can be found in the material under the form of solid solution and/or precipitated hydride. To capture this phenomenon, a numerical mesoscale model of the hydrogenated material has been built using the Finite Element (FE) method. The numerical setup explicitly describes the hydrides as an inclusion in a hydrogenated matrix. The matrix creep behavior follows combined Norton-Bailey creep rules whereas the hydrides are considered to be elastic material. The creep law was defined in FE Code ABAQUS using the user subroutine CREEP. The comparison of predicted creep behavior obtained from FE showed good agreement with the results reported in literature. Particularly, our model is able to seize the competition between the creep strain rate enhancement induced by hydrogen in solid solution and its reduction due to precipitated hydrogen.

## 1 INTRODUCTION

Zirconium alloys are used as cladding material for nuclear fuel in Light Water Reactors (LWRs) because of the low thermal neutron capture cross section of zirconium, the good mechanical properties and limited corrosion. The fuel cladding is the first barrier against release of radionuclides and its integrity is therefore essential. In order to maintain the integrity, assessment of all relevant degradation and failure mechanisms need to be considered (Rosen and O'Connell, 1994). Dry storage is the solution used by many facilities worldwide in order to increase their storage capacity while awaiting a perennial storing solution. During dry storage creep is one of the degradation mechanisms for used fuel cladding, as an excessive creep strain may lead to an eventual ductile fracture (Blackbum et al., 1978). The creep strain is limiting the possible life time, during dry storage as well as dictating the maximum allowable temperature in order to maintain the integrity of the cladding. Therefore the integrity of used fuel cladding during dry storage has been evaluated by predicting its creep behavior. Mayuzumi and

Onchi (Mayuzumi and Onchi, 1990) proposed an empirical creep model, which covers a wide temperature range to be used under long-term storage conditions. In the reactor environment, hydrogen is generated in coolant water due to oxidation of Zry-4 or radiolysis, and diffuses into the cladding material. Depending upon the temperature i.e. Terminal Solid Solubility for Dissolution (TSSD), hydrogen can be found in the material under the form of solid solution or/and precipitated hydrides. For example the solubility limit of hydrogen in Zry-4 is about 170 ppm at 400°C (Rui and Xiaoxue, 2009) and excess hydrogen forms zirconium hydrides. In the framework of continuum mechanics, hydrides precipitates in the  $\alpha$ -Zr can be viewed as a metal-matrix composite.

Among the different variations of zirconium alloys, the so-called Zircaloy-4 (Zry-4) is used as cladding material for fuel in Pressurized Water Reactors (PWRs). The creep strain rates of Zry-4 under annealed condition (annealed at 650°C for 4 hours) show an increase when hydrogen is in solid solution and a decrease when part of the hydrogen precipitates as hydrides (Rupa et al., 2002). Setoyama and

Yamanaka (Setoyama and Yamanaka, 2004) studied the effect of hydrogen on creep behavior of zirconium and Zry-4 using the indentation technique. They observed an increase in the creep rate with the addition of hydrogen when hydrogen is in the form of solid solution. In addition, they stated that the creep exponent is independent of hydrogen content and the increase in creep rate is due to the change in the Young's modulus with hydrogen Yamanaka et al., 2002).

Since the Zry-4 cladding material is subjected to stress for long periods of time at elevated temperatures, a thorough knowledge of creep behavior is required for their engineering applications. However, costly and time consuming creep experiments make it difficult to experimentally assess the creep behavior of the cladding. Therefore, the development of analytical and/or numerical approaches for predicting the creep behavior is indispensable. However, the analytical models cannot directly represent the actual creep behaviors of the heterogeneous materials, because the local state of stress and strain in the matrix is highly heterogeneous in nature.

On the other hand, numerical methods such as the FE Method enable to evaluate the micro-mechanical/meso-mechanical behaviors during the creep of the heterogeneous materials, since they can successfully model the time-dependent problems and local stress field. Numerous reports can be found in the literature explaining the numerical studies related to the creep behavior of heterogeneous materials (Dragone and Nix, 1992, Sørensen et al., 1993 and Sabbah and Essam, 2007). Dragone and Nix, Sørensen et al. developed numerical frameworks for stress analysis and prediction of creep behavior of metal matrix composites by using unit cell modeling. The creep behavior of magnesium alloys reinforced with short fibers was numerically determined by Sabbah and Essam, using simple idealization of the composite material. In their work, modeling was carried out using three relationships describing separately the three stages (i.e. primary, secondary and tertiary) of the creep behavior of magnesium alloys.

The present paper focuses on the influence of hydrogen in solid solution and hydrides precipitates at 400°C on the creep behavior of Zry-4 using a numerical modeling approach. The Zry-4 is considered as annealed and in sheet form. Thus, the resulting behavior may differ from that of typical Zry-4 tubes being used as cladding material and exhibiting high deformation and thus residual stresses.

## 2 NUMERICAL MODELING

### 2.1 Creep Constitutive Law

The creep constitutive law for describing the creep behavior of the Zry-4 matrix is similar to the one used for magnesium alloys (Sabbah and Essam, 2007). An empirical relationship is applied for each creep stage of the creep curve (primary, secondary). A mathematical relationship for the description of the creep behavior up to the secondary stage could be achieved by combining these two relations as follows:

$$\dot{\epsilon}_{c,eff} = mA_p \sigma_v^{n_p} t^{m-1} + A_s \sigma_v^{n_s} \quad (1)$$

where  $\dot{\epsilon}_{c,eff}$  is the effective creep strain rate,  $\sigma_v$  is the von Mises stress,  $t$  is the time, and  $m$ ,  $A_p$ ,  $A_s$ ,  $n_p$  and  $n_s$  are material constants. The first term (Norton-Bailey) on the right-hand side of equation (1) represents the primary creep and the second term (Norton) describes the secondary state creep strain.

According to Setoyama and Yamahaka, the change in creep strain with presence of hydrogen in the form of solid solution is due to change of Young's modulus. The change in Young's modulus of Zry-4 as function of hydrogen content up to the TSSD is given by the equation (2) by Yamanaka et al. (Yamanaka et al., 2002) as follows:

$$E_H = (1 - 2.518 \times 10^{-4} \cdot C_H) E, \quad (2)$$

where  $E_H$  is Young's modulus of Zry-4 with hydrogen in the form of solid solution at the content  $C_H$  (ppm), and  $E$  is Young's modulus of the material without hydrogen.

Thus, the creep coefficients as a function of hydrogen content  $A_{pH}$  and  $A_{sH}$  can be written as follows:

$$A_{pH} = A_p \cdot [(1 - 2.518 \times 10^{-4} \cdot C_H)]^{n_p-1}, \text{ and} \quad (3)$$

$$A_{sH} = A_s \cdot [(1 - 2.518 \times 10^{-4} \cdot C_H)]^{n_s-1}.$$

To predict the creep behavior of Zry-4 with the presence of hydrogen in the form of solid solution, in the present work, equation (1) with the modified creep coefficients according to the equation (3) is used. While for further increase of hydrogen content (hydrogen is precipitated in form of hydrides), a numerical mesoscale model of the hydrogenated material has been built using the FE method. The numerical setup explicitly describes the hydrides as an inclusion in a hydrogenated Zry-4 matrix. The creep behavior the hydrogenated Zry-4 matrix follows a combined Norton-Bailey and Norton creep rule equation (1) and its creep strain coefficients are

defined according to the equation (3), whereas the hydrides are considered to be elastic material. The creep law was implemented in FE code ABAQUS using the user subroutine CREEP.

## 2.2 Details of Hydrided Zircaloy-4 a - Finite Element Modeling.

Hydrided Zry-4 consists of the idealized, untextured hydrogenated matrix (i.e. hydrogen up to TSSD limit dissolved in Zry-4 matrix) and precipitated hydrides. The size of the hydrided Zry-4 considered in the present work is  $600\ \mu\text{m} \times 600\ \mu\text{m}$  as the thickness of the cladding material is approximately  $600\ \mu\text{m}$ . The distribution of hydrides is assumed to follow the symmetries about the radial and transverse axes, hence in the present work, one quarter of the hydrided Zry-4 was modeled ( $300\ \mu\text{m} \times 300\ \mu\text{m}$ ). It was also assumed that all the hydrides are  $\delta$  type (Daum et al., 2009) and that the bonding between hydrides and Zry-4 matrix is perfect. The orientation and length distribution of hydrides have been taken from scaling the measured real hydride distribution in a cladding tube (Valance et al., 2010). The thickness of the hydrides considered is  $0.5\ \mu\text{m}$ . The FE simulation code ABAQUS was used to carry out the finite element modeling and analysis. The hydrided Zry-4 was discretized, using four-noded plane stress solid elements with reduced integration (CPS4R). After checking for convergence, approximately 45000 elements and 65000 nodes were used in the FE mesh. The hydrogenated Zry-4 matrix was considered as elasto-plastic with creep, while hydrides were considered as elastic bodies. The material properties of non-hydrogenated Zry-4 matrix were taken from the literature (Puls et al, 2005). The elastic properties of the hydrides were assumed to be the same as for Zry-4 matrix, as reported in the literature (Nho et al., 1989), at room temperature the mechanical properties of solid hydrides remain about the same as the original zirconium alloy and decrease with temperature at about the same rate as the zirconium alloy. The Young's modulus and Poisson's ratio at  $400^\circ\text{C}$  are  $74.78\ \text{GPa}$  and  $0.346$ , respectively. The creep parameters used here for non-hydrogenated Zry-4 are  $A_p = 4.06 \times 10^{-14}\ \text{MPa}^{-n_p}\text{hr}^{-1}$ ,  $A_s = 9.16 \times 10^{-19}\ \text{MPa}^{-n_s}\text{hr}^{-1}$ ,  $n_p = 5.2$ ,  $n_s = 6.97$  and  $m = 0.34$  obtained experimentally in this study (not reported here). The Young' modulus  $E_H$  and creep coefficients ( $A_{pH}$  and  $A_{sH}$ ) for the hydrogenated Zry-4 matrix were estimated according to the equations 2 and 3.

In order to predict the creep behavior, finite ele-

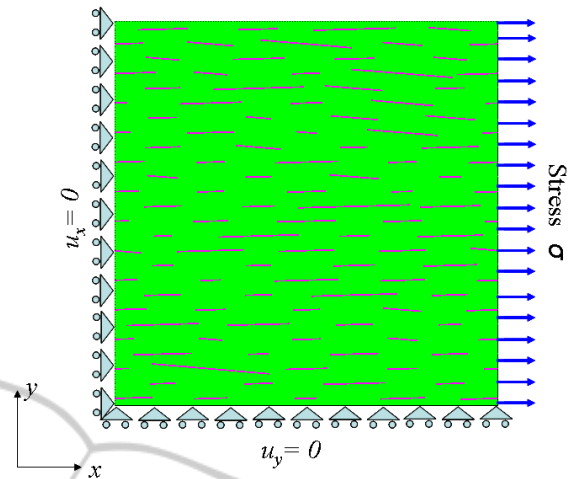


Figure 1: Hydrided Zry-4 (hydrogen content = 500ppm) with boundary conditions.

ment calculations were performed in two steps: first, the stress field in the hydrogenated Zry-4 matrix and hydrides is calculated for a given initial tensile stress in terms pressure (equal to the stress) using a nonlinear elastic-plastic calculation at time  $t = 1 \times 10^{-10}$  hour. The stress is then kept constant and subsequent time-dependent creep analyses were performed. The large strain FE model is employed by invoking the NLGEOM option within ABAQUS. Figure 1 illustrates the boundary condition for the FE analysis. The average creep strain versus time curve was computed by taking the ratio of average elongation at the load application region (see Figure 1) to the original length of microstructure.

## 3 RESULTS AND DISCUSSION

Figure 2 depicts the von Mises stress distribution of hydrogenated Zry-4 matrix for a hydrogen content of 500 ppm initially and after 250 hours at  $400^\circ\text{C}$  under a stress of  $120\ \text{MPa}$ . From this figure it can be observed that the von Mises stresses are reduced in the matrix as a consequence of the compressive stresses induced in the matrix during creep. Though there is a slight increase in local stresses ( $131\ \text{MPa}$  to  $147\ \text{MPa}$ ) the reduction in stress around the hydrides is much higher. The von Mises stress in the matrix around the hydrides was initially about  $115\ \text{MPa}$  for an applied stress of  $120\ \text{MPa}$ , and is reduced to  $58\ \text{MPa}$  after 250 hours. The reduction in stress is about 50%. As the equivalent stress level is decreased, the creep strain rate decreases. The magnitude of stress depends on the distribution and quantity of hydrides in the hydrogenated matrix.

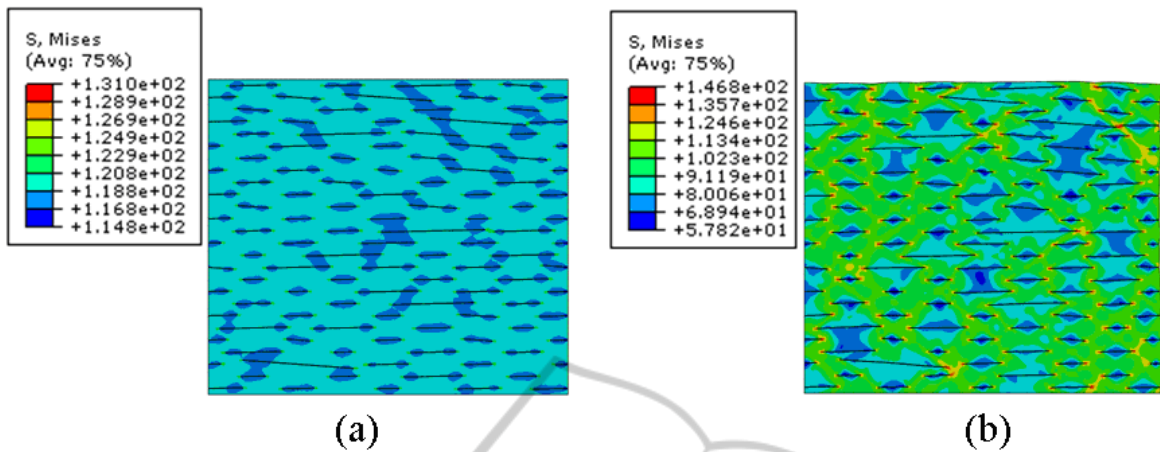


Figure 2: von Mises stress distribution of sample with a 500 ppm loaded under 120MPa at 400°C; (a) initially and (b) 250 hours von Mises stress field (stress direction according to figure 1).

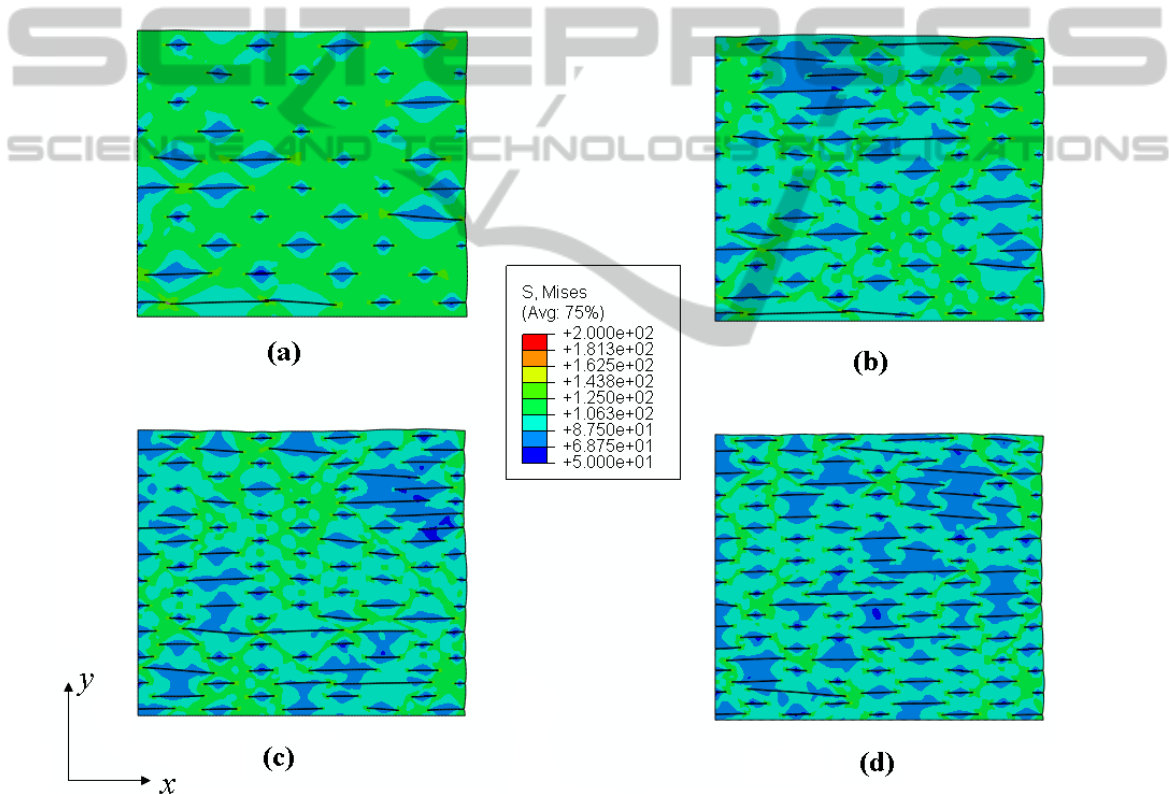


Figure 3: von Mises stress distribution at 250 hours, creep duration for different hydrogen contents, (a) 300 ppm, (b) 400 ppm, (c) 450 ppm and (d) 500 ppm (stress direction according to figure 1).

and the creep strain dropped to 4.05% when the hydrogen content was 500 ppm. The comparison of creep strain without hydrogen and with 170 ppm hydrogen content shows a relative increase of creep strain by 28%, whereas the creep strain without hydrogen and with 500 ppm hydrogen content shows a relative decrease of 51%. At a hydrogen content of 240 ppm, the same creep strain as for a Zry-4 with

out hydrogen was predicted.

Figure 3 shows the von Mises stress after 250 hours at 400°C and under a stress of 120 MPa for different hydrogen contents. From this figure it can be seen that the von Mises stress in the matrix decreases with increase of hydrogen content, which leads to a reduction in creep strain.

The overall creep strain as a function of time for

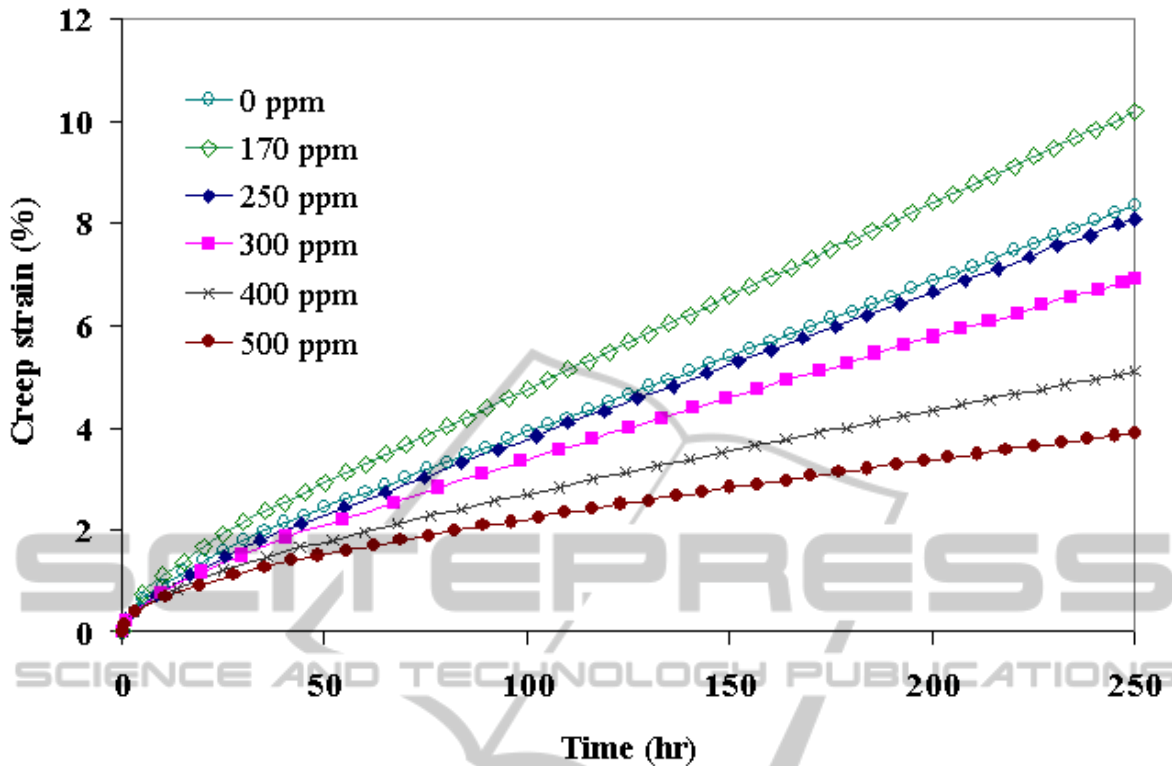


Figure 4: Creep strain versus time for different hydrogen contents.

different hydrogen content and creep strain after 250 hours is shown in figure 4. The creep strains increases with the increase of hydrogen content up to the TSSD, thereafter decreases for further increase of hydrogen content. Similar behavior was reported in the literature by Rupa et al., 2002. After 250 hour the maximum creep strain was found to be 10.23% when the hydrogen content was 170 ppm (corresponding to TSSD for temperature 400°C),

A similar trend in creep behavior is observed for the other stress levels studied in this work. The creep strains (on log scale) at 250 hours at a temperature of 400°C and under different applied stresses (80 MPa, 100 MPa, 120 MPa and 130 MPa) are shown in figure 5. The creep strain increases with stress magnitude, however, the hydrogen content at which the creep strain equals the one for Zry-4 without hydrogen decreases with an increase of the applied stress (indicated by the small circles in figure 5). The hydrogen content at which this is the case is 442 ppm at 80 MPa, 302 ppm at 100 MPa, 262 ppm at 120 MPa and 251 ppm at 130 MPa.

Figure 6 shows the variation of the steady state creep rates as a function of hydrogen content for different applied stress values. The curves show that, as expected for all the hydrogen contents below the solubility limit, the steady state creep strains are

higher for higher applied stresses.

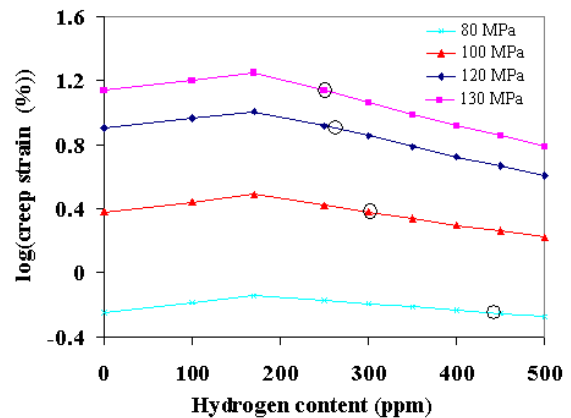


Figure 5: Creep strain (on log scale) at 250 hours as a function of hydrogen content for different applied stresses; the circles indicate the hydrogen contents for the same creep strain as without hydrogen.

It can also be observed that the drop in steady state creep rate is higher for higher applied stress when the hydrogen content increases from 250 ppm to 500 ppm. For a stress of 130 MPa, the drop in steady state creep rate is about 68%, whereas the drop is about 33% for a stress of 80 MPa. From

these steady state creep rates, the equivalent steady state creep parameters are estimated. The equivalent steady state creep parameters as a function of hydrogen content are depicted in figure 7. The stress exponents decrease linearly with the increase of the hydrogen content, while the creep coefficients show an exponential increase with hydrogen content.

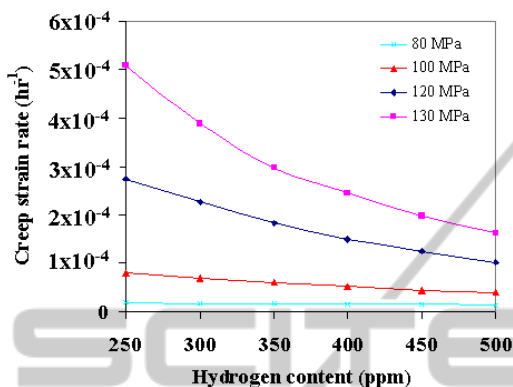


Figure 6: Steady state creep strain rate as a function of hydrogen content.

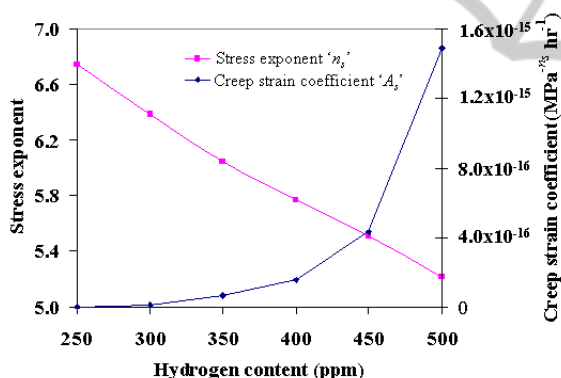


Figure 7: Steady state creep stress exponent ( $n_s$ ) and creep strain coefficient ( $A_s$ ) as a function of hydrogen content.

#### 4 COMPARISON OF PRESENT RESULTS AND LITERATURE

In order to validate the present model, it is attempted to compare the calculated creep curves for Zry-4 with hydrogen contents of 180 ppm and 500 ppm with those published by Rupa et al., 2002. Figure 8 reveals a good agreement of the creep curves obtained in this present work and from literature.

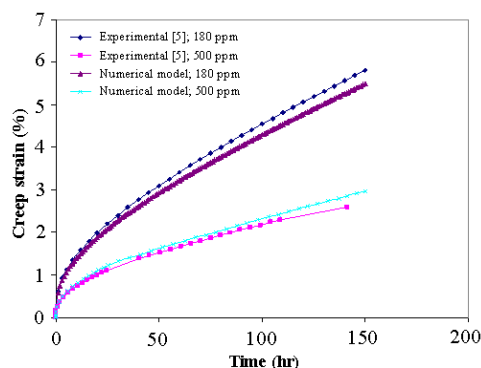


Figure 8: Comparison of creep strain versus time curves obtained by present work and literature Rupa et al., 2002 for two hydrogen contents.

#### 5 CONCLUSIONS

In this paper a numerical model was proposed to investigate the effect of hydrogen on the creep behavior of Zry-4. This zirconium alloy being used as tube cladding for nuclear fuel, the material has been considered here as texture-free and in sheet form. The creep behavior of hydrided Zry-4 is analyzed by the Finite Element Method.

For all applied stresses, the creep strain increases with increase of the hydrogen content up to TSSD, and decreases for a further increase of the hydrogen content. As the level of applied stress increases, the hydrogen content for the same creep strain without hydrogen decreases.

The stress exponent decreases linearly with increase of hydrogen content, while the creep coefficient value shows an increase exponentially with increase of hydrogen content. A comparison of predicted creep curves obtained from the present work with the creep curves reported in literature showed good agreement.

#### REFERENCES

- Rosen, R. S., O'Connell, W. J., 1994. *Lawrence Livermore National Laboratory, Livermore, CA 94550 USA.*
- Blackburn, L. D., Ferwick, D. G., Fields, S. R., James, L. A., Moen, R. A., 1978. *Hanford Engineering Development Laboratory Report, HEDL-TME 78-37.*
- Mayuzumi, M., Onchi, T., 1990. *Journal of Nuclear Materials. 171 381-388.*
- T. Rui, T., Xiaoxue, Y., 2009. *International Journal of hydrogen energy. 34 7269-7274*
- Rupa, N., Clavel, M., Bouffieux, P., Domain, C., A. Legris, A., 2002. *Zirconium in the Nuclear Industry 13th*

- International Symposium, ASTM STP 1423, ASTM International, West Conshohocken, PA, (2002) 811-836*
- Setoyama, D., Yamanaka, S., 2004. *Journal of Alloys and Compounds*, 379(2004)193-197.
- S. Yamanaka, S., M. Kuroda, M., Setoyama, M., 2002 *Trans. Atomic Energy Soc. Japan. 1 4 (2002) 323-328.*
- Dragone, T. L., Nix, W. D., 1992. *Acta Metall. Mater.* 40(12)(1992) 2781-2788.
- Sørensen, N. J., 1993. *Acta Metall. Mater.* 41 (10) (1993) 2973-2982.
- Sabbah, A., Essam, E., 2007. *Computational Materials Science* 39 (2007) 155-159
- Daum, R. S., Chu, Y. S., Motta, A.T., 2009. *Journal of Nuclear Materials* 392 (2009) 453-463
- Valance, S., Bertsch, J., Alam, A. M., 2010. *Journal of ASTM International (JAI)* (2010) – accepted/in press
- Puls, M. P., San-Qiang Shi., Rabier, J., 2005. *Journal of Nuclear Materials* 336 (2005) 73-80
- Nho, K., Choi, S., Lee, B., 1989. *Journal of the Korean Nuclear Society* 336 (1989) 111-122

