The influence of impurities in Zr-2.5Nb on oxygen and deuterium pickup at 573 K in D2O

R. Ploc

► To cite this version:

R. Ploc. The influence of impurities in Zr-2.5Nb on oxygen and deuterium pickup at 573 K in D2O. Journal de Physique IV Proceedings, 1993, 03 (C9), pp.C9-763-C9-770. 10.1051/jp4:1993979 . jpa-00252421

HAL Id: jpa-00252421

<https://hal.science/jpa-00252421>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The influence of impurities in Zr-2.5Nb on oxygen and deuterium pickup at 573 K in D₂O

R.A. Ploc

Atomic Energy of Canada Limited, Research Chalk River Laboratories, Station 55, Chalk River, Ontario K0J 1J0, Canada

Abstract. — Short term corrosion tests in D₂O at 573 K (pH = 10.5) of Zr-2.5wt% Nb containing small, deliberate additions of impurity elements have shown that elements such as Sn, Fe, Cr, V and Si lead to total weight gains lower than a set of Zr-2.5Nb controls. Low total weight gains did not always convert to low deuterium pickups. Low Cr and Fe additions resulted in relatively low deuterium uptakes but high Fe and Sn, in any concentration, caused high deuterium uptake values. Ni additions resulted in high specimen to specimen variability and high percent theoretical deuterium uptakes.

1. Introduction.

This publication discussed results from an investigation into the relative importance of individual impurities found in Zr-2.5Nb in conferring or reducing the alloy's ability to resist hydrogen isotope absorption. The present data are insufficient to confirm, deny or modify existing theories [1].

2. Experimental.

An impurity element, X, at a concentration of x , (ppm by wt) was added to Zr-2.5Nb to form the ternary Zr-2.5Nb- x X. Some elements, such as Fe, were already present in the Zr-2.5Nb stock material at significant concentrations and this was accounted for in the final determination of x . Control specimens were fabricated using the same melting, heating and homogenization route as the ternary alloys. Both the alloys and the controls were corroded in autoclaves at 573 K, 8.6 MPa in D₂O at a pH (pD) of 10.5 (room temperature). Specimen preparation, details of the corrosion environment, weighing procedures and other details were reported previously [2].

3. Results and discussion.

The alloy microstructure is an important factor in determining the corrosion rate and is likely to influence the amount of deuterium absorbed. Some elements are α -Zr stabilizers (such as oxygen and tin) while others (such as Nb) stabilize the metastable β -Zr phase. Therefore, depending on the impurity addition, microstructures can radically change. Figure 1 shows six microstructures. For Fe, random and small precipitates can be detected for an addition

of 800 ppm Fe (7820 ppm at), the precipitate distribution appears to be random, neither favouring the α - or β -Zr phases (or the boundaries). The effect, if any, of these precipitates on the weight gain data of figure 2 is small, (10 to 15% maximum). For an as yet unknown reason, Fe additions reduce the average corrosion rate relative to the controls.

Fig. 1. — Zr-2.5Nb alloys containing: a) 800 and b) 4800 ppm Fe; c) 400 and d) 4500 ppm Cr; e) 1000 ppm Mn and f) 1000 ppm P. a = alpha and b = beta phases, p = precipitate. Magnification marker = 10 μ m.

Fig. 2. — Total weight gain after 40 days of corrosion in D₂O at 573 K and pH = 10.5. Each bar is labelled with the impurity and its ppm concentration.

The total weight gained by a specimen during corrosion arises from two sources; oxygen pickup (in the form of an oxide film) and absorption of deuterium in the bulk of the alloy. The two components have been resolved in this study, however, some ambiguity exists since only single specimens can be analyzed. Tests begin with approximately 30 specimens per batch. As the exposure history increases, the number of specimens decreases since on each occasion that the corrosion test is interrupted for weight gain measurements, one coupon is withdrawn for destructive analysis. The decreasing number is not a problem if each specimen performs identically. Unfortunately, significant variability often exists and the investigator must decide which specimen to use for analysis. Ni additions result in much variability, sometimes by an order of a magnitude. After 119 days of exposure the Zr-2.5Nb-4000 ppm Ni batch contained specimens with total weight gains of 40, 390 (average) and 600 mg/dm². In such extreme cases all three specimens were analyzed and the "average" value used as a data point. The high and low values were also analyzed for the Percent Theoretical Pickup (PTP, discussed later) and compared with the average.

Figures 3 and 4 give the percent deviation from the average control specimen behaviour. At 40 days the weight gain variation for the controls was approximately 25%. The variation for deuterium and oxygen pickups is unknown, only one to three specimens are analyzed at any given exposure. The average control specimen values at 40 days were 49 and 0.18 mg/dm² for oxygen and deuterium, respectively.

Examination of figures 3 and 4 indicates that some ternaries included in the latter are not represented in the former. The reason is oxide spalling of the 1000 ppm Al and 4000 ppm Si ternaries. Deuterium pickup values were not available for the 4500 ppm Cr and 250 ppm Mn ternaries. The deuterium weight gain for the 4000 ppm Ni ternary was too large (16 mg/dm²) for inclusion in figure 4.

Fig. 3. — Percent deviation of the oxygen weight gains from the average control specimen behaviour at 40 days exposure.

Fig. 4. — Percent deviation of the deuterium weight gains from the average control specimens behaviour at 40 days exposure.

The relative behaviour of the various ternary alloys is similar in both figures 2 and 3. For example, < 1000 ppm V reduces oxidation, i.e., alloys with different concentrations cannot be distinguished from each other by their weight gains. Sn additions are uniformly beneficial in reducing oxygen pickup. Ni ternaries are particularly reactive, peaking at about 300 ppm. The largest total weight gain is for 3600 ppm Mn (excluding 4500 ppm Cr for which oxygen pickup data was not available) closely followed by 300 ppm Ni. The relative importance of Ni and Mn are reversed in the oxygen pickup data which suggests that 3600 ppm Mn has a large deuterium component in the total weight gain. This is confirmed in figure 4. Based on figure 3, alloys containing < 1000 ppm Si, P or V, Cr with < 500 ppm, Fe up to the tested maximum of 5000 ppm, or Sn up to 10000 ppm significantly reduced the overall corrosion rate relative to the Zr-2.5Nb controls.

In figures 2 to 4, the Zr-2.5Nb-800 ppm V alloy appears to be out of sequence. The pickup values for this alloy are higher than those with both less and with more vanadium. The reason for this unexpected behaviour is unknown, but a likely explanation is incorrect chemical analyses or alternatively, inhomogeneous mixing.

For in-reactor usage, the total weight gain and oxygen pickup values are not as important as the amount of deuterium absorbed by an alloy. Figure 4, gives this detail. When compared with figures 2 and 3, it can be seen that oxygen pickup is not strongly dependent on Fe concentration; however, deuterium absorption continuously increases up to 4000 ppm at which point the alloy and controls behave the same. Sn additions (for at least the first 40 days) significantly increase deuterium absorption. The short-term nature of our results do not indicate whether Sn will continue to absorb greater than normal amounts of deuterium. Experience with CANDU⁽¹⁾ nuclear reactors [3, 4] has indicated that Zircaloy-2, which contains 1.2 to 1.7 wt% Sn, is more susceptible to deuterium pickup than Zr-2.5Nb.

A common method used in the nuclear industry to display deuterium pickup data is to plot the Percent Theoretical Pickup (PTP) as a function of corrosion time. For PTP, one assumes that the corrosion process results from the break up of a water molecule into one atom of oxygen and two atoms of hydrogen. One hundred percent theoretical pickup corresponds to two hydrogen atoms being absorbed by the alloy for every oxygen atom incorporated into the oxide. The PTP values in figure 5 were derived from figures 3 and 4.

The nickel ternaries are an example of when the PTP should not be used to assess the susceptibility of an alloy to deuterium absorption. For most nickel ternaries, the PTP is less than 1% (see Fig. 5), which suggests a better performance than the controls specimens for which the PTP is 1.5%. However, the nickel alloys, because of their high corrosion rates absorb undesirable amounts of deuterium (Fig. 4). The same argument is true for the 3600 ppm Mn ternary. An opposite trend exists for most of the vanadium ternaries, a small amount of deuterium is absorbed but the PTP is high.

During the first few days of corrosion, when the oxide film is thin, the passage of a deuterium ion through the oxide film is enhanced by a high electric field, i.e., the corrosion potential is fixed but the film is thin so the field is high. The positive deuterium ion is attracted by the negative potential at the oxide/metal interface. The passage of the deuterium ion is further enhanced by pitting-type dissolution of the oxide film by the lithiated D₂O. When the oxide is thicker, the field strength is lower and small amounts of localized dissolution are not significant. Hence, after several days of corrosion most of the alloys display approximately the same PTP, see figure 6.

On a long term basis, deuterium absorption is likely controlled by a constant thickness barrier or an interface reaction. The more or less constant ingress rate of 1 to 5% is indicative

(¹) CANDU: Canada Deuterium Uranium. Registered trademark.

Fig. 5. — Percent Theoretical Pickup (PTP) of deuterium after 40 days exposure. Data correspond to the deuterium weight gain information implicit in figures 3 and 4.

Fig. 6. — Percent Theoretical Pickup (PTP) of deuterium vs. duration of corrosion for several Zr-2.5Nb-xX ternaries.

of a barrier layer of constant, or slightly increasing thickness. Such layers are known to exist next to the oxide/metal interface [5]. Alternatively, the same effect could be achieved by control at either the outer or inner interfaces, i.e., by the rate of reduction of the water molecule or the rate of incorporation of the deuterium ion into the metal. Our data are insufficient to answer the question of whether control is by an interface but, if it was, we would favour the outer interface and the water reduction process being modified by the composition of the oxide (impurity ions modifying local potentials or conductivities).

Fig. 7. — Percent Theoretical Pickup, deuterium and oxygen weight gains vs. corrosion time for the 800 ppm V ternary. The deuterium values have been multiplied by a factor of 10.

Our preference is to assume that long term deuterium ingress is controlled by an inner barrier layer. As shown in figure 7, when the 800 ppm V ternary experienced a sudden increase in the oxidation rate (at 10 days), the PTP dropped from 2.6 to 0.85%. The sudden decrease in the PTP is reasonable and totally explainable if the rate of deuterium incorporation remains constant but the rate of oxide growth is accelerated, i.e., the barrier to oxide film growth was removed but the barrier to deuterium ingress remained constant. It is the lack of an immediate and large response in the ingress rate which suggests control by a constant thickness barrier layer.

Sn additions to Zr-2.5Nb lead to high deuterium ingress rates which decay to more acceptable levels after a few months of corrosion. The high rates may reflect the proposed ingress mechanism. For example, Sn suppresses oxide film growth which means that field assisted diffusion of the deuterium ion will be operational longer than for the other ternaries. Further, dissolution effects of the lithiated D₂O will also be more important. In the Zircaloy's, which have high Sn concentrations, it has been reported that the inner barrier layer is very thin or non-existent. This is perhaps why the Zircalloys are susceptible to deuterium pickup.

Because of the very high or sudden increase in deuterium pickup values as a function of concentration (see Fig. 4), it is suspected that precipitate formation may be occurring at critical concentrations for the Si, V, and Mn ternaries. This has yet to be investigated. For Sn, there are no obvious precipitates but the PTP is higher than for most other alloys (Fig. 6).

4. Conclusions.

Total weight gains from short out-reactor corrosion tests of Zr-2.5Nb- x X type alloys cannot be used to determine relative resistances to deuterium ingress. PTP's are also an unreliable guide. In some instances, where PTP's are low (Ni additions) the corrosion rate is high and this leads to large deuterium pickups. Our data show that PTP values should not be used to rank an alloy's susceptibility to deuterium pickup. The only useful measure is the obvious: deuterium weight gain as a function of exposure. It is suggested that Zr-2.5Nb-low Cr, V or Fe alloys should have a superior resistance to deuterium ingress than standard Zr-2.5Nb. Sn additions lead to higher than usual deuterium pickup values.

References

- [1] COX B., Atomic Energy of Canada Limited report, AECL-8702 (January, 1985); Presented at the 1984 Fall meeting of the Materials Research Society (Boston, November 26-30, 1984).
- [2] PLOC R.A., AMOUZOUVI K.F., Turner C.W., Proc. 24th Annual Conf. Int. Met. Soc. (Monterey, California, August 29-31, 1991).
- [3] URBANIC V.F., COX B., FIELD G.J., ASTM STP 937 (ASTM, Philadelphia, 1987) pp. 189-203.
- [4] URBANIC V.F., WARR B.D., MANOLESCU A., CHOW C.K., SHANAHAN M.W., STP 1023 (ASTM, Philadelphia, 1989) pp. 20-34.
- [5] GODLEWSKI J., GROS J.P., LAMBERTIN M., WADIER J.F., WEIDINGER H., ASTM STP 1132 (ASTM, Philadelphia, 1991) pp. 416-434.