Letter to the Editor

Comments to papers of J.H. Kim et al. [1] and M. Große et al. [2] recently published in JNM "On the hydrogen uptake of Zircaloy-4 and M5™ alloys subjected to steam oxidation in the 1100–1250 °C temperature range"

1. Introduction

During a postulated Loss-Of-Coolant-Accident (LOCA), the nuclear fuel cladding tube materials should experience High Temperature (HT) steam oxidation for prototypical times ranging from a few minutes up to ∼15 min, before reflooding of the core (i.e., water quenching). During the last ten years, there has been a huge international effort to study the Post-Quench (PQ) residual mechanical properties of fuel cladding tube modern alloys, after HT steam oxidation [3–12]; one of the objective of the underlying R&D programs was to focus on potential high "Burn-Up (BU) effects". It is now well admitted that, after HT oxidation, the residual cladding mechanical properties and especially the quenching resistance and the Post-Quench (PQ) ductility/toughness depend on:

(1) the quantity of oxygen which has diffused into the sub-oxide metallic layer, especially within the residual prior-β phase layer – for a given material, this parameter is directly fixed by the HT oxidation time/temperature conditions;
(2) the hydrogen material uptake which may come from:
  – the "classical" in-service corrosion behaviour of the material; at high BU, the overall cladding tube hydrogen content may reach a few hundred of weight-ppm for Zircaloy-4, while for some modern high corrosion resistant materials the "end-of-life" hydrogen content should be limited to lower values (i. e., ∼100 wppm for M5™ [11]),
  – a possible hydrogen uptake during the HT oxidation itself.

Concerning this last point, in two recent papers [1,2], the authors have shown some results concerning the hydrogen uptake after high temperature steam oxidation of different zirconium alloys including Zircaloy-4 and M5™ grades (for initial as-received conditions). For Zircaloy-4 alloy oxidised for 300 s at temperatures ranging from 1100 °C up to 1250 °C, Fig. 6 of [1] shows a significant hydrogen absorbed content, ranging from ∼150 up to ∼500 wppm. Moreover, after oxidising for 1 h at 1100 °C, Table 2 of [2] displays hydrogen content values of 1.76 at.% for Zircaloy-4 and up to 6.63 at.% for the M5™ alloy.

In fact, within the 1100–1250 °C[1] oxidation temperature range, it is generally admitted that oxidising under steam at the atmospheric pressure (with no local steam starvation) promotes the growth of stable tetragonal ("black") dense and protective oxide layer up to high oxidation levels. Moreover, it is generally observed that there is no significant hydrogen pick-up into the sub-oxide metallic part of the cladding tube associated with such a stable oxide layer growth. Then, compared to data from CEA and from most other institutes obtained after steam oxidation at 1100 °C and higher, the hydrogen uptake results published in [1,2] seem to us "unusual" and need further discussion, as this problem of potential hydrogen pick-up during steam oxidation at high temperature should be a crucial point with regard to the LOCA embrittlement criteria.

2. Short discussion from open literature and (unpublished) CEA data

First of all, it has to be mentioned that an overview of the past R&D programs devoted to fuel behaviour under LOCA and, especially on the HT "Cladding Oxidation, Resistance to Quench and Post-Quench Loads" can be found in a recent IRSN Technical Report [12]. Some of the references cited here have been picked-up from this quite exhaustive report.

2.1. The particular case of (old grade) Russian E110 (Zr–1%Nb) alloy

For this particular alloy, in a previous paper, Böhmert et al. [13] have shown high hydrogen uptake during HT steam oxidation, even for short oxidation times, which was linked to early occurrence of the "breakaway" phenomenon together with the formation of non protective (unstable) zirconia oxide. More recently, some extensive studies have been conducted by Yegorova et al. [3] on the one hand, and by Billone et al. [4] on the other hand, to get a better insight into the E110 alloy particular HT oxidation behaviour. From these studies it has been observed that the manufacturing process and the final cladding tube surface polishing play a major influence on the early occurrence of breakaway on a Zr–1%Nb alloy such as E110.

2.2. Behaviour of Zircaloy-4 and M5™ alloys upon HT steam oxidation in the 1100–1250°C temperature range

The appendix summarizes typical tabulated values of hydrogen analysis measurements performed on both materials after HT

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[1] For oxidation temperatures below 1100 °C, especially for temperatures close to 1000 °C which correspond more or less to the zirconia phase transformation temperature range, breakaway phenomena occurs after a certain "incubation" time. After breakaway occurrence, one can observe a rapid hydrogen uptake. From 1-side HT oxidation CEA data already published in [8,9] and for both Zircaloy-4 and M5™ alloys, a significant hydrogen uptake is only observe for oxidation time higher than ∼1 h. It has to be mentioned that these CEA data are quite consistent with the ANL [4] and KFKI [5] ones at this particular oxidation temperature.

steam oxidation tests. Some of these values have been extracted from ANL [4] and KFKI [5] recently reported studies, and are consistent with the data from JAEA/JAERI studies [6]. The unpublished CEA data here presented correspond to:

(1) one-side "Dezirox" steam oxidation experiments [10];
(2) two-side "Cinog" steam oxidation tests [17].

On Figs. 1 and 2, we have plotted all the hydrogen concentration data mentioned above versus the oxidation times at 1100, 1150, 1200 and 1250 °C. On these figures, we have added the KAE-RI [1] and FZK [2] data. It is obvious that these last ones are different from those of the other institutes. As mentioned previously, to our knowledge and with the exception of the particular behaviour

of the (old grade) E110 alloy, under an environment of pure steam at nearly the atmospheric pressure with no local starvation and for (quite short) LOCA prototypical oxidation times, oxidising in the 1100–1250 °C temperature range promotes the growth of a stable (protective) tetragonal zirconia oxide layer without significant hydrogen uptake.

2.3. Some parameters potentially influencing/destabilising the oxide growth, which could promote HT hydrogen uptake

Beyond some potential chemical impurities effects [3,4], at least two additional experimental procedure parameters should influence the growing oxide layer stability, and thus the hydrogen uptake upon steam oxidation at high temperature:
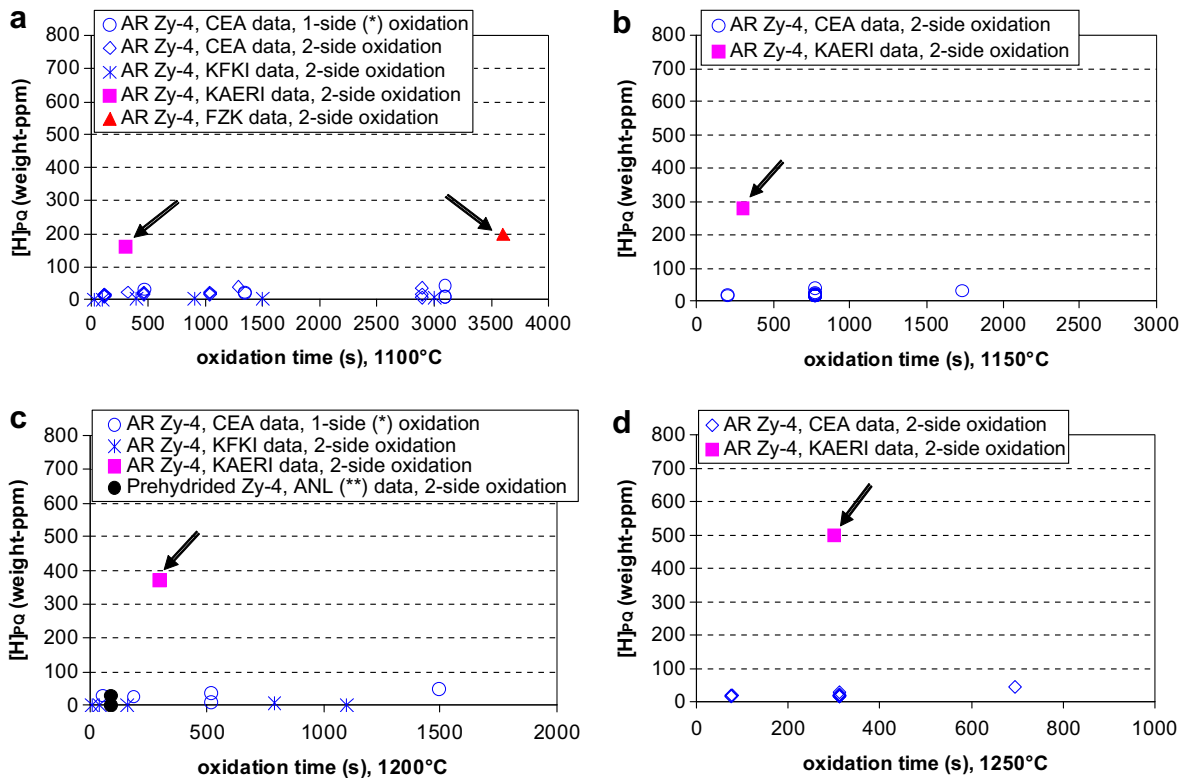

Fig. 1. Hydrogen cladding contents measured after HT steam oxidation of Zircaloy-4.
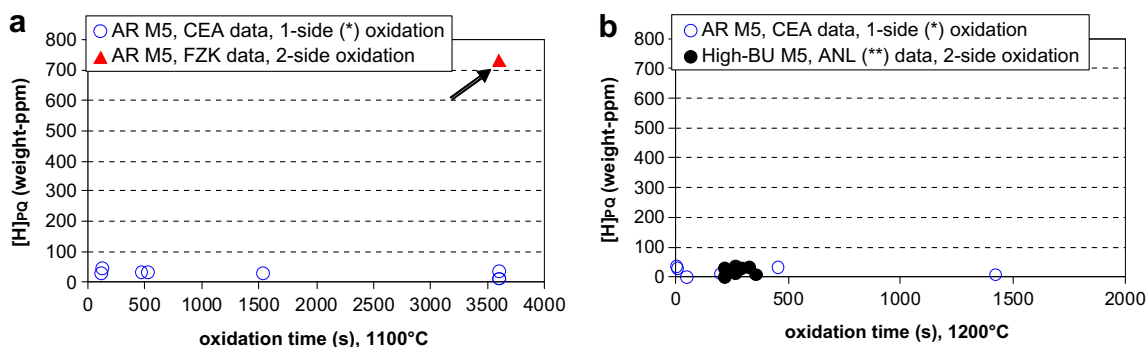

Fig. 2. Hydrogen cladding contents measured after HT steam oxidation of M5™. (*) The hydrogen contents plotted corresponding to 1-side "Dezirox" CEA oxidation tests have been multiply by a factor of two, to be able to compare with 2-side oxidation data, assuming that the hydrogen pick-up should be the same for both internal and external clad surfaces. (**) For ANL data, which correspond to pre-hydrided or high BU materials, the difference between initial and post-HT-oxidation-test hydrogen contents measured has been considered.

Table 1
CEA one-side "Dezirox" oxidation (unpublished) data.

Materials	Oxidation temperature (°C)	Oxidation time (s)	Post-quench hydrogen content (wppm)
As-received Zy-4	1100	467	16
		1349	11
		1349	9
		3098	5
		3098	21
		3098	5
	1200	55	14
		187	13
		520	18
		520	5
		1492	24
As-received M5™	1100	117	14
		132	22
		467	15
		529	16
		1529	14
		3606	5
		3606	5
		3606	18
	1200	51	14
		202	17
		455	16
		1422	27

(1) recent studies from ANL [18] have shown that, as apparently done and reported by Kim et al. in their paper [1], using HF-acid-mixture etching to clean the samples before HT oxidation test promotes a rapid breakaway occurrence. These recent ANL results confirm so far the significant influence of the final cladding tube surface polishing process on the occurrence of breakaway phenomena, as already pointed out on the E110 alloy [3,4];

(2) upon the HT oxidation process itself, the "quality"/efficiency of the steam flowing around the samples is another potential parameter which could be responsible for apparent HT oxidation data discrepancies. From previous JAEA/JAERI quite exhaustive studies performed on Zircaloy-4 [14–16], within the high oxidation temperature range, hydrogen uptake is observed for stagnant or flowing hydrogen enriched steam conditions when the volume fraction of hydrogen in the mixture of steam + hydrogen exceeds a certain threshold (∼0.4 typically).[2]

3. Conclusion

For Zircaloy-4 and M5™ alloys and from the data presented above, one can conclude that, beyond the potential discrepancy between experimental data (which can be sensitive to many parameters of the experimental procedure), the results mentioned in [1,2] are questionable and, at least, the authors should have discussed their unusual hydrogen pick-up results in comparison with other published data on Zircaloy-4 and M5™ alloys, especially after oxidising at 1100 °C and above. However, because hydrogen is now recognised as a major parameter influencing the cladding materials PQ mechanical properties after high temperature oxidation prototypical of LOCA transients, this "comments" letter has not to be considered as a negative appreciation of the data published in [1,2] but as an encouragement to the authors to bring a better knowledge of the origin of their apparent "unusual" hydrogen uptakes.

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[2] Such a situation is representative of secondary hydriding phenomena which can occur inside the balloon of a failed cladding tube [4,6].

Appendix A. Tabulated values of hydrogen analysis measurements after HT steam oxidation tests

See Tables 1–6.

Table 2
As-received Zircaloy-4 – CEA two-side "Cinog" oxidation (unpublished) data.

$T_{oxid.}$ (°C)	Oxidation time (s)	Post-quench hydrogen content (wppm)
1100	322	21
	1288	37
	2898	35
	116	10
	116	14
	116	13
	464	15
	464	18
	1043	16
	1043	21
	116	15
	464	23
	1043	19
	2898	8
	116	16
	2898	16
1150	198	15
	768	15
	768	16
	768	17
	768	17
	768	16
	768	15
	768	18
	768	25
	768	16
	768	38
	768	18
	768	16
	768	20
	768	18
	768	17
	768	18
	198	18
	768	21
	1737	31
1250	78	18
	312	29
	695	43
	76	17
	76	19
	312	18
	312	17
	312	17
	312	18
	312	21
	312	19
	312	19
	312	20
	312	17
	312	18

Table 3
KFKI data [5].

Materials	Oxidation temperature (°C)	Oxidation time (s)	Post-quench hydrogen content (wppm)
As-received Zy-4	1100	27	1
		102	1
		398	3
		900	2
		1500	2
		3000	5
	1200	10	1
		40	1
		163	1
		790	5
		1100	1

Table 4
ANL data [4].

Materials	Oxidation temperature (°C)	Oxidation time (s)	Initial hydrogen content (wppm)	Post-quench hydrogen content (wppm)
Pre-hydrided Zy-4	1200	92	442	471
		92	543	535
High-BU M5™	1200	220	101	88
		265	101	111
		325	101	133
		360	108	116
		295	108	137
		265	108	142
		220	108	135

Table 5
KAERI data [1].

Materials	Oxidation temperature (°C)	Oxidation time (s)	Post-quench hydrogen content (wppm)[b]
As-received Zy-4[a]	1100	300	~160
	1150	300	~280
	1200	300	~370
	1250	300	~500

[a] As mentioned previously, HF-acid-mixture etching has been used to clean the samples before HT oxidation testing.
[b] The hydrogen concentration values have been roughly estimated from a graphic plot (Fig. 6 of [1]).

Table 6
FZK data [2].

Materials	Oxidation temperature (°C)	Oxidation time (s)	Post-quench hydrogen content (wppm)[a]
As-received Zy-4	1100	3600	~200 (1.76 at.%)
As-received M5™	1100	3600	~730 (6.63 at.%)

[a] The authors mentioned that, thanks to the use of neutron radiography, the tabulated hydrogen contents correspond to the residual metallic part of their HT oxidised samples. Thus, the hydrogen content values corresponding to the global wall thickness of the tested cladding tubes should be significantly lower than the tabulated ones. However, even if normalising the hydrogen content tabulated values to the wall clad thickness, the measured hydrogen uptake is still significant, especially for the M5™ alloy oxidised for 1 h at 1100 °C.

References

[1] J.H. Kim, Myoung H. Lee, B.K. Choi, Y.H. Jeong, Journal of Nuclear Materials 362 (2007) 36–45.
[2] M. Große, E. Lehmann, M. Steinbrück, G. Kühne, J. Stuckert, Journal of Nuclear Materials 385 (2009) 339–345.
[3] L. Yegorova, K. Lioutov, N. Jouravkova, A. Konobeev, V. Smirnov, V. Chesanov, A. Goryachev, Experimental Study of Embrittlement of Zr–1%Nb VVER Cladding under LOCA-Relevant Conditions, NUREG/IA-0211/IRSN 2005-194/NSI RRC KI 3188 Report, 2005.
[4] M. Billone, Y. Yan, T. Burtseva, Cladding Embrittlement during Postulated Loss-of-Coolant Accidents, ANL NUREG/CR-6967 Report, ML082130389, 2008-07-31.
[5] Z. Hozer, C. Gyori, L. Matus, M. Horvath, Journal of Nuclear Materials 373 (2008) 415–423.
[6] F. Nagase, T. Fuketa, Journal of Nuclear Science Technology 42 (2) (2005) 209–218.
[7] J.-C. Brachet, J. Pelchat, D. Hamon, R. Maury, P. Jacques, J.-P. Mardon, Mechanical behavior at room temperature and metallurgical study of low-tin Zy-4 and M5™ (Zr–NbO) alloys after oxidation at 1100 °C and quenching, in: Proceeding of TCM on Fuel behavior under Transient and LOCA Conditions Organised by IAEA, Halden, September 10–14, 2001.
[8] L. Portier, Th. Bredel, J.-C. Brachet, V. Maillot, J.-P. Mardon, A. Lesbros, Journal of ASTM International 2 (2) (2005). Paper ID JAI12468.
[9] J.-P. Mardon, J.-C. Brachet, L. Portier, V. Maillot, T. Forgeron, A. Lesbros, N. Waeckel, Influence of hydrogen simulating burn-up effects on the metallurgical and thermal–mechanical behavior of M5™ and Zircaloy-4 alloys under LOCA conditions, in: 13th Int. Conf. on Nuclear Engineering, Beijing, China, May 16–20, 2005, Proceeding ICONE13-50457.
[10] J.-C. Brachet, V. Vandenberghe-Maillot, L. Portier, D. Gilbon, A. Lesbros, N. Waeckel, J.-P. Mardon, Journal of ASTM International 5 (5) (2008). Paper ID JAI101116.
[11] D. Kaczorowski, V. Chabretou, J. Thomazet, P.-B. Hoffmann, H.-J. Sell, G. Garner, Corrosion behavior of alloy M5™: experience feedback and understanding of phenomenological aspects, in: Proceeding of 2008 Water Reactor Fuel Performance Meeting, October 19–23, 2008, Seoul, Korea.
[12] C. Grandjean, G. Hache, A State-Of-The-Art-Report of Past Programmes Devoted to Fuel Behaviour Under Loss-Of-Coolant Conditions – Part 3 – Cladding Oxidation, Resistance to Quench and Post-Quench Loads, DPAM/SEMCA 2008-093 IRSN Technical Report, June 2008.
[13] J. Böhmert, M. Dietrich, J. Linek, Nuclear Engineering and Design 147 (1993) 53.
[14] T. Furuta, S. Kawasaki, Journal of Nuclear Materials 105 (1982) 119–131.
[15] H. Uetsuka, T. Furuta, S. Kawasaki, Journal of Nuclear Science and Technology 19 (2) (1982) 158–165.
[16] H. Uetsuka, T. Otomo, Journal of Nuclear Science and Technology 26 (2) (1989) 240–248.
[17] J.-C. Brachet, L. Portier, D. Hamon, Ph. Trouslard, S. Urvoy, V. Rabeau, A. Lesbros, J.-P. Mardon, Quantification of the Alpha(O) and Prior-Beta phase fractions and their oxygen contents in high temperature (HT) oxidised Zr alloys (Zy-4, M5™), in: Proceeding of the SEGFSM-Topical Meeting on LOCA, May 24–26, 2004, Argonne National Lab., Chicago, USA.
[18] M. Billone, Private communication – Data to be published (available upon request), ANL, 2009.

J.-C. Brachet
CEA Saclay,
DEN, Serv. Rech. Met. Appl.,
F-91191 Gif-Sur-Yvette,
France
E-mail address: jean-christophe.brachet@cea.fr

V. Vandenberghe
CEA Saclay,
DEN, Serv. Rech. Met. Appl.,
F-91191 Gif-Sur-Yvette,
France