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SENSITIVITY TO CHEMICAL COMPOSITION VARIATIONS AND HEATING/OXIDATION MODE OF THE BREAKAWAY OXIDATION IN M5® CLADDING STEAM OXIDIZED AT 1000°C (LOCA CONDITIONS)

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ABSTRACT

This paper deals with the influences of the chemical composition and the heating/oxidation mode on the breakaway oxidation of M5® cladding steam oxidized at 1000°C (Loss of Coolant Accident conditions). In order to study the sensitivity of the breakaway oxidation to chemical composition variations around the nominal specifications of the M5® alloy, one-side oxidation tests were performed at 1000°C under steam at nearly atmospheric pressure on samples with various contents of Nb (0.87 and 1.25 wt%), Fe (195 and 715 wt.ppm), O (500, 930 and 1680 wt.ppm), S (14 and 41 wt.ppm) and Hf (62 and 487 wt.ppm). Weight gains and hydrogen contents of the samples were measured after oxidation. It is found that the pre-breakaway oxidation kinetics and the time of occurrence of the breakaway transition are not significantly modified by chemical composition variations for the batches investigated: in all cases, the transition occurs at about 5000s, which corresponds to a weight gain of about 10 mg/cm² / one-side-oxidation. However, after the breakaway transition, some differences are observed on weight gains and hydrogen uptakes.

Moreover, the influence on the breakaway of both the heating and the oxidation modes were analyzed by comparing results obtained on M5® cladding samples one-side steam oxidized at 1000°C by the use of a resistance heating furnace and double-side steam oxidized by using an induction heating technique. The thicknesses of the oxide and $\alpha_{Zr}(O)$ layers were measured after oxidation. The occurrence of the breakaway oxidation does not appear to be affected by the heating mode and the oxidation type.

M5® is a trademark of AREVA NP

1. Introduction

During a postulated Loss of Coolant Accident, fuel claddings may be exposed to steam at high temperature until they are quenched by an Emergency Core Cooling System. Numerous studies demonstrated that at high temperature, the oxidation kinetics of zirconium alloys are mostly parabolic (or even cubic) and time-temperature oxidation correlation were derived from this [1,2]. The oxide formed is then sub stoichiometric, black and dense. However, in some cases, and especially around 1000°C, a sharp increase of the oxidation rate can be observed after an incubation period. Usually, the oxidation rate slows down a little just before the transition. A scalloped metal-oxide interface and intensive oxide cracking are usually observed after an oxidation in those conditions followed by a quench. After the transition, the zirconia becomes (at least locally) stoichiometric, usually whitish, yellowish or even pinkish (depending on the alloy), porous, and an oxide spalling is sometimes observed during the oxidation.

This increase in the oxidation rate coincides with a significant hydrogen uptake. This hydrogen uptake is often used as an early clue that the so-called "breakaway" phenomenon occurs. For instance in [3] the authors consider that a hydrogen concentration of 200 wt.ppm is the indication that a breakaway oxidation is in progress for double-side oxidation, as there

is usually no hydrogen pick-up observed during oxidation above 1100°C.[4].

The increase in the oxidation rate and the hydrogen pick-up can then induce an embrittlement of the cladding.

The breakaway mechanism is not very well known yet, even though as soon as in the early 1980s, Leistikow et al. [5, 6] proposed a scenario, based on the fact that the phenomenon appears for a temperature at which the high temperature (tetragonal) zirconia was susceptible to transform into monoclinic zirconia. Numerous factors are assumed to influence the incubation time and the breakaway oxidation: the oxidation temperature is the first order parameter, but also concerned the chemical composition of the alloy and/or its surface preparation for example. The discrepancies observed between some of the results reported in the literature illustrate this sensitivity. Some results previously obtained at CEA [7, 8] have shown that the breakaway transition of the standard M5® alloy occurs after about 5000-5500s at 1000°C under flowing steam atmosphere, at nearly atmospheric pressure. Furthermore, it was observed that, under those conditions, the occurrence of breakaway is not significantly modified by pre-hydriding or pre-oxidation under simulated in-service conditions. Zr-Nb or E110 alloys in particular were suspected to have a shorter incubation period than some results previously obtained on Zircaloy [9-11].

In this study, we focus on the influence of two parameters on the breakaway phenomenon. First the impact of small variations around the nominal composition of five chemical elements in M5® alloys and second the effect of the heating mode (resistive furnace heating versus induction heating) on the breakaway incubation time, oxidation rate and hydrogen pick-up of the alloy.

2. Material and experimental procedures

The material studied here are as-received AREVA NP commercial M5® cladding tubes, and cladding tubes variants with chemical composition around the nominal specifications (Tab 1).

Tab 1: Chemical composition of the studied M5 materials

	Hf (ppm)	Fe (wt%)	Nb (wt%)	O (wt%)	S (wt ppm)
M5®	54	0.034-0.037	1.0	0.118-0.148	13-26
High Nb			1.25		
Low Nb			0.87		
High Fe		0.071-0.072			
Low Fe		0.019-0.020			
High O				0.168	
Low O				0.093	
Ultra Low O				0.050	
Low S / High O				0.167	14
High S / Low O				0.134	41
Low Hf	50				
High Hf	500				

Two different CEA facilities were used. The first one, DEZIROX 1, already described in previous papers [7,8] used a vertical resistive furnace to heat the 150 mm long specimen, one-side oxidized in a steam environment (near atmospheric pressure) with an average steam flow rate (mass of condensed water divided by the test time and normalized to the cross-sectional area of the steam chamber) of about 70 mg/(cm².s). This is CEA standard apparatus for breakaway oxidation studies and the influence of the chemical composition was evaluated using this facility only.

The second one, CINOG BP [12], allows performing double side oxidation tests in a steam environment at nearly atmospheric pressure on 20 mm long specimens. Steam flows up through a quartz-tube chamber with a steam flow rate of about 40 mg/(cm².s).

The specimens oxidized in the DEZIROX 1 facility were water quenched (down to room temperature) after oxidation whereas the samples tested in CINOG BP were naturally cooled down to room temperature with an average cooling rate of about 100°C/s.

3. Results

3.1. Influence of the chemical composition on the breakaway oxidation

In order to check the chemical composition influence of alloying elements and main impurities on the breakaway oxidation phenomenon, the different materials were one-side oxidized in DEZIROX 1 at 1000°C, for three oxidation times (3270s, 5292s and 9500s) and directly quenched in water at room temperature. The results were compared to those obtained for numerous oxidation times on standard M5® and, for each (chemical element/oxidation time) couple. Post oxidation hydrogen content measurement was performed on the specimen with the highest weight gain. All the results are listed in the table 2.

Tab 2: Weight gain and post test hydrogen content results for all chemical variants tested

Chemical element investigated	Oxidation time (s)	Weight gain (mg/cm ²)	Post-test hydrogen content (wt.ppm)	Chemical element investigated	Oxidation time (s)	Weight gain (mg/cm ²)	Measured hydrogen content (wt.ppm)
M5®	50	0.77	-	930 ppm O	3270	6.30	42
	160	1.81	10		5292	10.17	271
	323	2.83	11		9500	9.57	-
	650	4.03	14		17.66	812	
	1060	4.27	-	1680 ppm O	3270	6.53	62
		4.62	11		5292	9.22	110
	1290	4.61	19		9500	8.61	-
	3270	6.71	-		15.24	-	
	5292	8.01	-	17.09	291		
		8.16	89	14 ppm S (1670 ppm O)	3270	6.37	52
	8.43	75	5292		8.16	-	
	7500	11.55	434		9500	9.07	96
	8600	11.69	286		17.78	521	
	9500	13.29	-	17.16	-		
10800	15.84	634	41 ppm S (1340 ppm O)	3270	6.65	58	
14551	22.2	923		5292	8.72	-	
0.87 % Nb	3270	6.83		49	9500	9.43	115
	5292	7.96		-	14.06	-	
	912	79	62 ppm Hf	3270	7.66	91	
	9500	16.62		535	5292	7.90	-
11.47	-	7.94	101				
1.25 % Nb	3270	6.50	58	9500	15.62	396	
	5292	9.66	141		11.51	-	
	8.91	-	487 ppm Hf	3270	7.10	65	
	9500	16.45		529	5292	8.24	110
14.32	-	9500	8.08	-			
193-195 ppm Fe	3270	6.77	50	14.30	324		
	5292	8.04	-	13.07	-		
	11.00	334	500 ppm O	3270	6.67	55	
	9500	15.10		-	5292	9.01	120
18.68	810	9500		7.76	-		
11.19	-						
713-715 ppm Fe	3270	6.55	40	11.82	200		
	5292	9.24	266	9500	11.19	-	
	8.87	-	18.48		588		
	18.48	588	17.69		-		
17.69	-						

Before the breakaway occurrence, the oxidation kinetics are expected to be nearly (sub-) parabolic at 1000°C, and that is exactly what is observed for the standard M5® and for all the chemical variants investigated for oxidation time up to 5292s. For this oxidation time, results become a little more widespread, as the breakaway oxidation appears. This dispersion is mostly observed in the post breakaway regime: significant differences in weight gains are observed after 9500s at 1000°C. The same can be said of the hydrogen pick-up: the hydrogen content measured remains below 100 wt.ppm (oxidation one side) after a 3270s oxidation (even below 50 wt.ppm in most cases) but increases suddenly at the onset of breakaway. After the transition, hydrogen pick-up appears to be more important in some cases, in particular for low Fe content (<200wt.ppm) and intermediate oxygen content (~900/1000 wt.ppm) (Fig 2.). Breakaway oxidation is linked to the spalling of the oxide layer: no significant spalling (less than 0.01g) is observed after 3270s at 1000°C and quenching, for

all tested materials, but some spalling appears at the onset of breakaway, after a 5292s oxidation, and significant and more scattered spalling appears for longer oxidation times (Fig 1.).

In summary, the results show that:

- the pre-breakaway oxidation kinetics and the time of occurrence of the breakaway transition are not significantly modified by chemical composition variations investigated. In all cases, the transition occurs at about 5000s corresponding to a weight gain of about 10 mg/cm²/single-side oxidation and less than 100ppm of hydrogen.
- after the breakaway transition, weight gains and hydrogen uptake data are scattered.

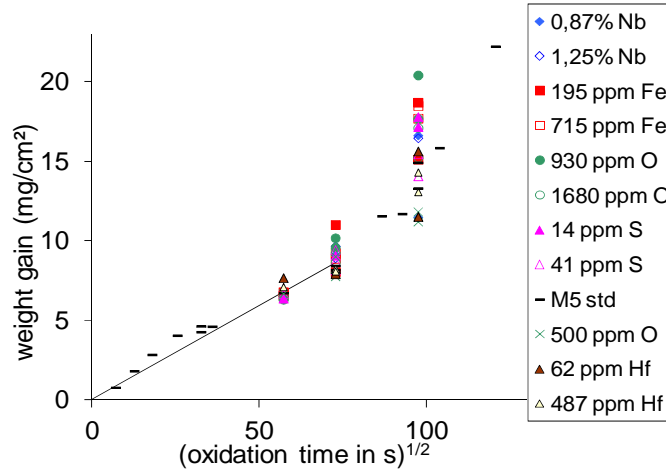


Fig 1. Weight gain as a function of oxidation time

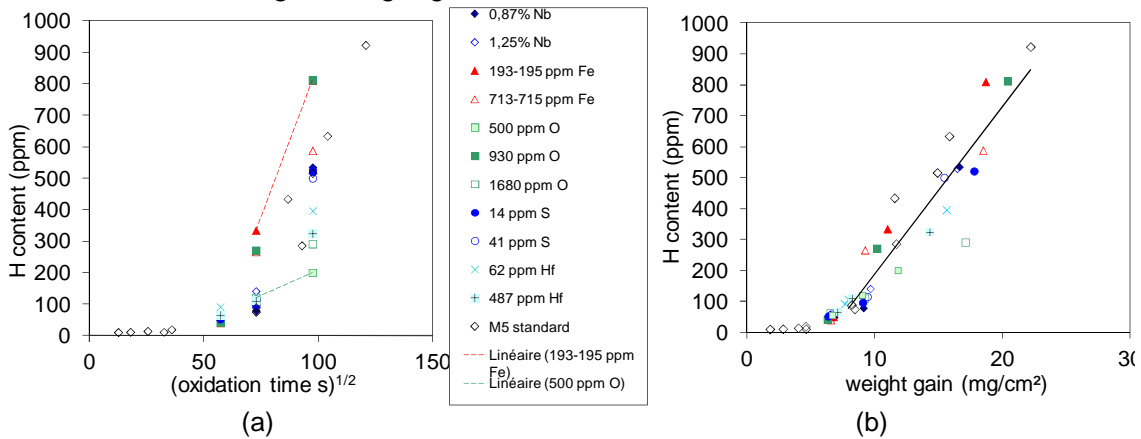


Fig 2. Post oxidation H content as a function of (a) oxidation time and (b) weight gain

3.2. Influence of the heating process on the breakaway oxidation

M5® was oxidized in both facilities, CINOG BP, double-side, induction heating (DS-IH) and DEZIROX 1, single-side, furnace heating (SS-FH), for different oxidation times at 1000°C. Transverse cross-sections of the oxidized samples were observed by Scanning Electron Microscopy (SEM) so that the thicknesses of the different layers (Fig 5.) and the fractions of the alpha(O) and prior-beta phases across the clad wall-thickness (Fig 4.) could be quantified by using image analyses. The results show no significant influence of the heating mode and the oxidation type on the hydrogen pick-up (Fig 3). The evolution as a function of oxidation time at 1000°C of the oxide, alpha(O) and prior-beta phase layers (Fig 5) or the morphology of the oxide-metal interface, which appears wavy (Fig 6.). In order to compare SS-FH and DS-IH phase layer thickness, the alpha-O and mixed alpha-O prior-beta phase layer thickness was first measured on SS-FH specimens (Fig 5a, left side). Then, this profile was duplicated symmetrically and convoluted to project what would have been obtained on DS-FH (Fig 5c). This convoluted profile was then compared (Fig 5d) to the actually measured profile obtained on DS-IH and the profiles appeared nearly identical. In other words, the occurrence of breakaway oxidation does not appear to be strongly affected by the heating/oxidation mode.

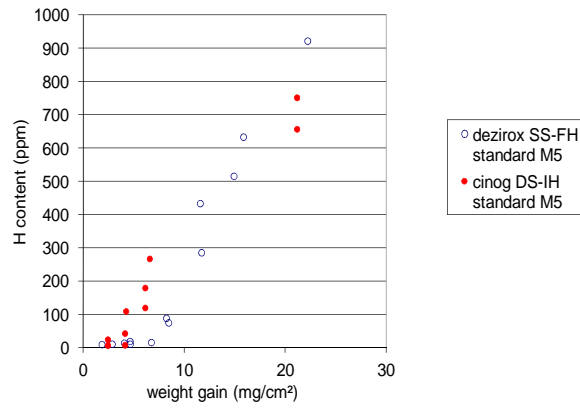


Fig 3. Post oxidation hydrogen content as a function of weight gain for Single-Side Furnace-Heated (SS-FH) and Double-Side Induction-Heated (SD-IH) specimens

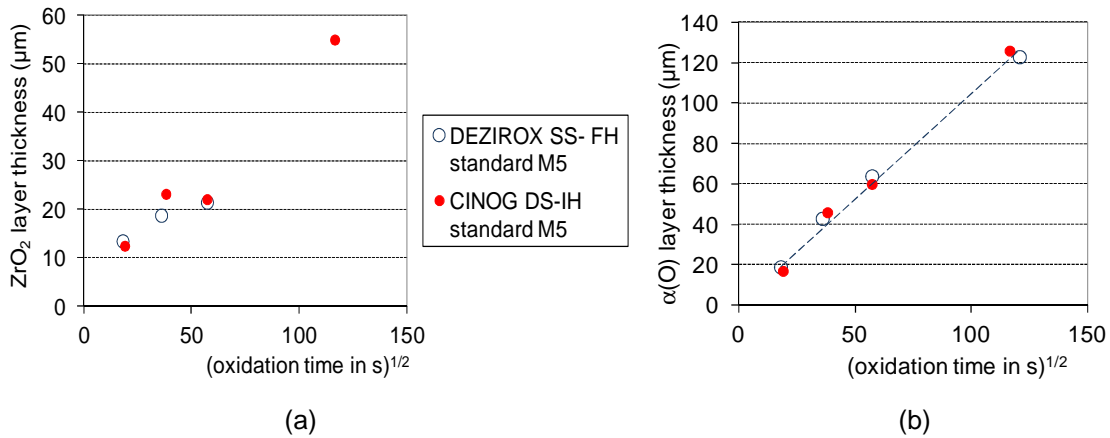
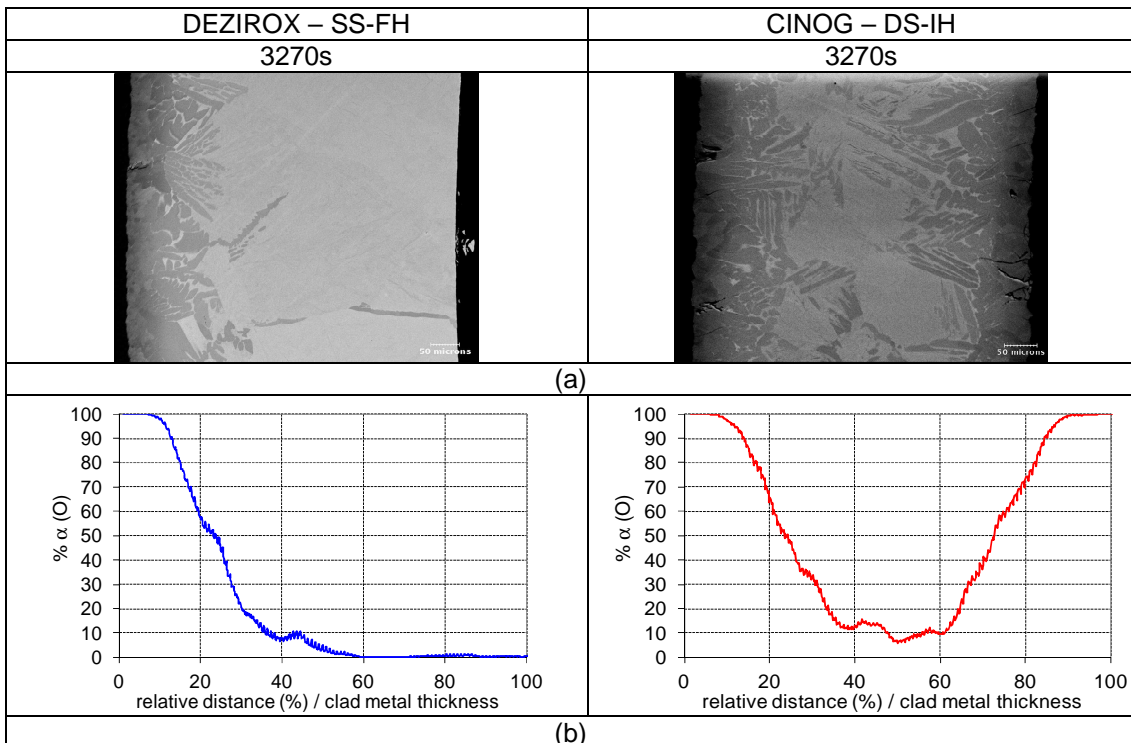


Fig 4. Zirconia phase layer thickness (a) continuous alpha(O) phase layer thickness (b) as a function of oxidation time for SS-FH and DS-IH specimens



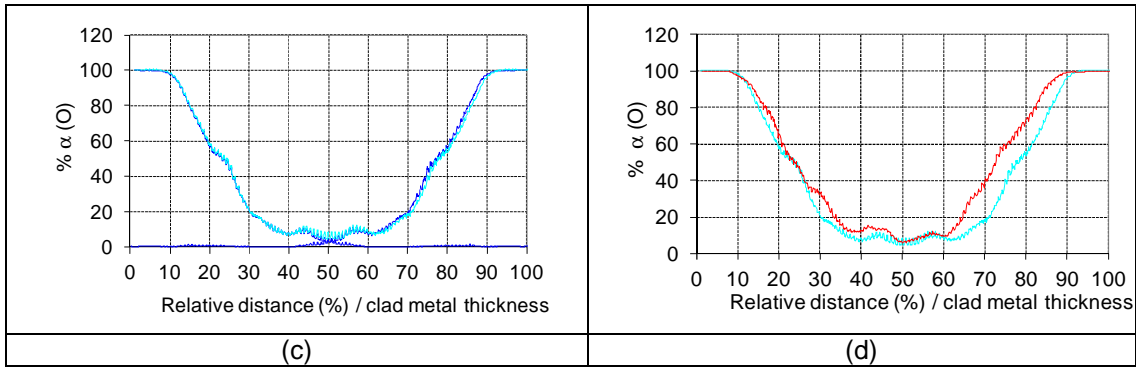


Fig 5. Comparison of the $\alpha(O)$ layer obtained after 3270s at 1000°C in SS-FH or DS-IH conditions; (a) SEM images; (b) % $\alpha(O)$ layer deduced from SEM images analysis; (c) projected DS-FH $\alpha(O)$ layer distribution; (d) comparison between measured DS-IH and projected DS-FH

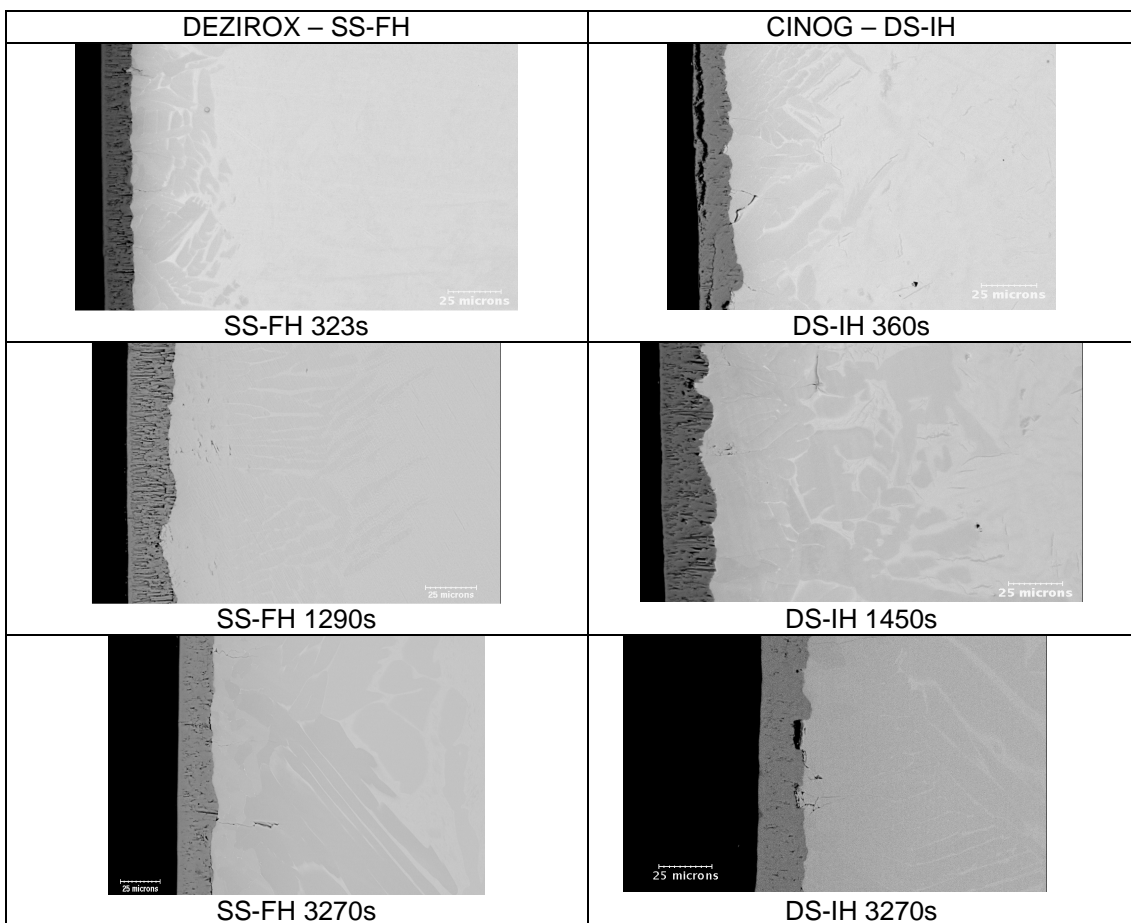


Fig 6. SEM illustrations of the waviness of the zirconia/ $\alpha(O)$ interface for SS-FH and DS-IH specimens for different oxidation times at 1000°C

4. Conclusions

No significant impact of the chemical composition variations investigated - Nb (0.87 and 1.25 wt%), Fe (195 and 715 wt.ppm), O (500, 930 and 1680 wt.ppm), S (14 and 41 wt.ppm) and Hf (62 and 487 wt.ppm) - was observed on breakaway incubation time, oxidation kinetics pre-breakaway, and hydrogen pick up as a function of the weight gain in post breakaway regimen.

No significant impact of the heating mode was observed on the breakaway incubation time, on pre-and post breakaway $\alpha(O)$ layer thickness or on oxidation kinetics or H pick up in post breakaway regimen.

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