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OXIDATION KINETICS AND HYDROGEN UPTAKE OF TITANIUM ALLOYS IN PRESSURIZED WATER REACTORS (PWR) PRIMARY WATER

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Extended Abstract : As used for many years by the former Soviet Union, and still up to now, as structural materials for the on-board nuclear reactors found on ice-breakers, titanium alloys were assumed to be good candidates for possible future nuclear reactors. In that optic, the first qualification steps of such materials in PWR primary water environment involve a better understanding of the oxidation kinetics and mechanisms. The hydrogen uptake associated with the reduction reaction will be addressed as well.

In this framework, two titanium alloys have been studied: commercially pure titanium T40 (alpha phase), Ti-6Al-4V (10% beta phase). Dedicated coupons were then sequentially exposed to a medium representative of PWR primary water (hydrogenated, 290°C, 150 bars, reductive conditions and neutral-to-basic pH) for various periods of time in a corrosion loop: 0, 163, 500 and 1000 hours. After exposure, the oxide layers developed on the coupons were analysed using scanning and transmission electron microscopy, Raman spectroscopy, XPS (X-ray Photoelectron Spectroscopy) and GD-OES (Glow Discharge – Optical Emission Spectroscopy) in order collect information on the structure of the oxide layers, their thickness and their composition. Hydrogen content was measured after each oxidation sequence by total fusion technique (catharometry).

Despite the difference in their chemical composition and their microstructure, both alloys showed similar oxidation features. A few tens of nanometer thick continuous anatase film developed on the

materials surface during exposition to PWR primary water environment, covered by much larger (micrometric) anatase crystallites. The size of these crystallites increased with the exposure time and reached a few micrometers at 1000 hours. No alloying element was found in the oxide layers (GD-OES), except after 1000h exposure where some Al(+III) – from XPS profiles – was found in the oxide at the oxide/alloy interface for TA6V alloy, as present in the initial native nanometric oxide layer, suggesting a cationic growth mechanism. Gold markers-type experiments are under process in order to precise/confirm this growth type.

The oxidation (both growth rates of inner continuous layer – figure 1a – and outer discontinuous layer equivalent thickness) and hydrogen uptake kinetics – figure 1b – seemed approximately linear, suggesting an interface reaction control. Moreover, GD-OES depth profiles revealed an accumulation of hydrogen in the alloy in the vicinity of the oxide/alloy interface, suggesting possible trapping of hydrogen in this area, probably in correlation with a local higher vacancies density due to the oxide formation mechanisms.

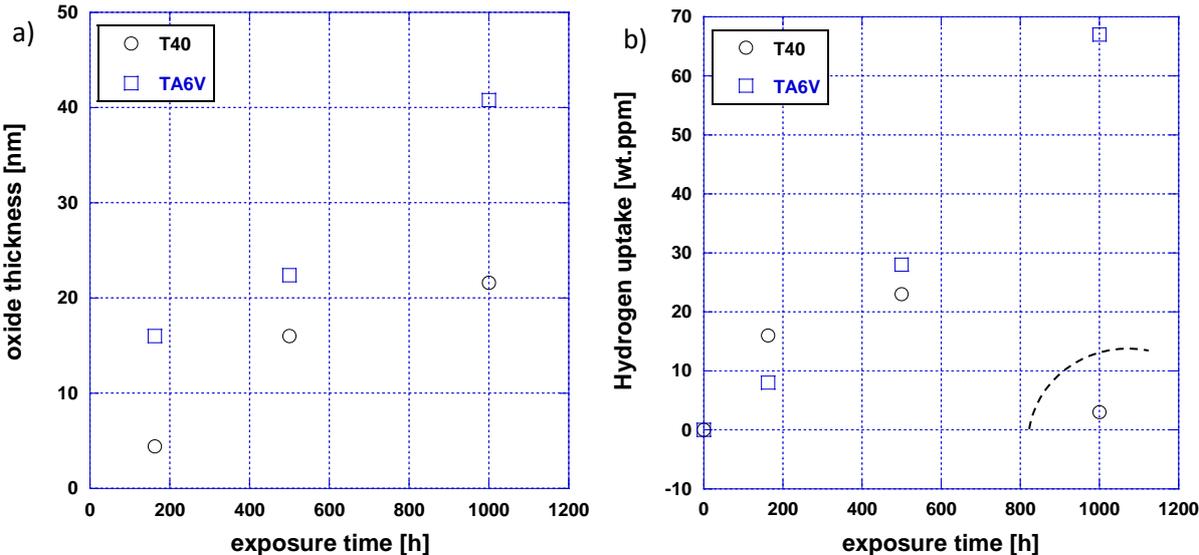


Figure 1 : Evolution of a) the inner continuous anatase layer with exposure time for the two Ti-base alloys T40 and TA6V, and b) the associated global hydrogen uptake.