

Nanostructure and local properties of oxide layers grown on stainless steel in high temperature water

Vincent Maurice, Toni Massoud, Lorena H. Klein,
Antoine Seyeux, Philippe Marcus
Laboratoire de Physico-Chimie des Surfaces, Chimie
ParisTech - CNRS (UMR 7045)
Ecole Nationale Supérieure de Chimie de Paris, 11 rue
Pierre & Marie Curie, 75005 Paris, France

One of the major materials challenge for continued safe, reliable and cost-effective utilization of water-cooled nuclear reactors for electricity production is development of improved understanding of the synergistic fundamental mechanisms responsible for corrosion and stress corrosion cracking degradation of austenitic steels and nickel base alloys [1]. In this work, surface analysis techniques, Atomic Force Microscopy (AFM) and Conducting Probe AFM, have been applied to study oxide films formed by interaction of 316L stainless steel with PWR primary water at 325°C. The objective was to characterize the nanometer scale structure of the oxide films providing corrosion resistance to the substrate and to get new knowledge on the relationship between nanostructure and local properties of the film that is a key aspect for local failure of the protection.

Exposure at 325°C of the specimens to PWR primary water was performed at EDF. The exposure times were varied from 2 to 6000 min.

AFM performed in intermittent contact (Tapping®) mode revealed a granular morphology of the oxide film at the nanometer scale. The mean lateral size of the grains was measured to increase from 19 to 48 nm for oxidation times between 2 and 6000 min. The grain size dispersion and the surface roughness were also measured to increase with exposure time, showing the development of a microstructure of the oxide film becoming less homogeneous with increasing oxidation time. The mean depth of the grain boundaries increased from 3.9 to 6.7 nm with exposure time but remained in all cases inferior to the oxide film thickness measured by ToF-SIMS depth profile analysis. The measured depth of the grain boundaries is consistent with oxide films fully covering the 316L substrate but their presence demonstrate the presence of local heterogeneities of the film thickness thought to impact the corrosion protection at the nanoscale.

Conducting Probe AFM coupled to a Resiscope module was used to measure simultaneously topography and electrical resistance of the oxide film-covered surface at the nanoscale. For imaging, the sample surface was scanned in contact mode at a constant minimal force. The topography and the contact resistance R were simultaneously acquired measuring respectively the vertical cantilever deflection D and the tip/sample current I. The current I was measured by the Resiscope module when applying a constant sample bias voltage V (V = -1 V) between the sample and the conducting tip. The local tip/sample contact resistance R is calculated as V/I.

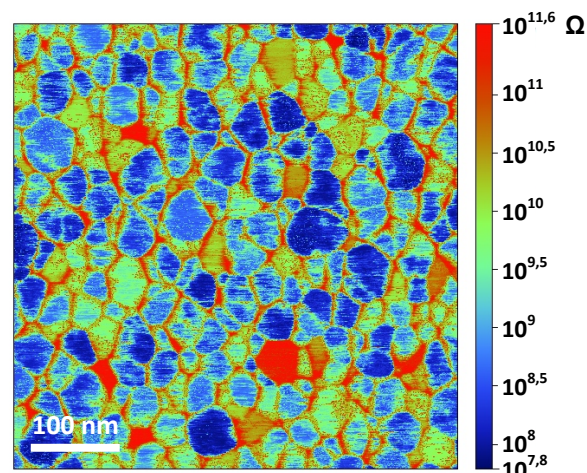


Figure 1 Surface electrical resistance image for 316L stainless steel exposed to PWR primary water at 325°C for 2 min.

The topography measured in Tapping® mode could be reproduced and the surface electrical resistance maps (Figure 1) revealed local heterogeneities at the nanoscale of the granular morphology of the oxide films. The mean resistance was found to increase with oxidation time in ratio consistent with thickness increase of the oxide film. Variations of R could be systematically measured at the boundaries joining the grains but also on grains of similar dimension and height. At grain boundaries, the resistance was systematically measured to be higher than on grains. This was assigned to the reduction of the contact geometry (i.e. contact area) between tip and oxide film surface and thus was not considered as revealing the heterogeneity of the resistance of the oxide film itself. On the grains with similar topography, the measured resistance could be found to vary by up to two orders of magnitude. Although variations of the contact geometry between tip and oxide film surface cannot be fully excluded, these local heterogeneities strongly suggest that the oxide grains themselves differ in composition, thickness and possibly epitaxy so as to exhibit significantly different properties of electrical conduction that may impact locally the corrosion protection provided by the oxide film.

Acknowledgments

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References

[1] S.J. Zinkle, G.S. Was, Acta Mater, 61, 735 (2013).