Alloys of platinum and gadolinium present significant activity enhancement over pure Pt for the oxygen reduction reaction (ORR), both in the form of extended electrode surfaces and nanoparticulate catalysts. The active phase consists of a compressed Pt overlayer formed on Pt5Gd electrodes upon exposure to the electrolyte by acid leaching. Here, we investigate the formation, strain and correlation lengths of the active Pt overlayer by using in situ synchrotron grazing incidence X-ray diffraction on Gd/Pt(111) single-crystalline electrodes. The overlayers form upon exposure to electrolyte under open circuit conditions; the compressive strain relaxes slightly upon repeated electrochemical cycling in the potential range 0.6 to 1.0 V versus the reversible hydrogen electrode (RHE). In addition, the strain relaxes strongly when exposing the electrode to 1.2 V versus RHE, and the thickness of the crystalline portion of the overlayers increases with potential above 1.3 V versus RHE.