The Correlation of Subsurface Oxygen Diffusion with Variations of Silver Morphology in the Silver–Oxygen System

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Abstract

Silver undergoes pronounced morphological changes following high-temperature treatment in various gas atmospheres. SEM analysis shows that high-temperature treatment in oxygen leads to pronounced facetting of the silver surface. *In situ* XRD shows a strong texturing of the polycrystalline bulk and an expansion of the unit cell resulting from the dissolution of oxygen. Two distinctly different forms of subsurface oxygen have been identified and the influence of morphological changes on the mechanism leading to their formation clarified. The first of these species is Oβ. It is bulk-dissolved oxygen which diffuses via an interstitial mechanism through low-resistance diffusion paths such as grain boundaries and open crystalline planes. Temperature programmed desorption spectroscopy analysis reveals that high-temperature oxygen pretreatment results in the formation of crystalline surfaces exhibiting different oxygen diffusion barriers. At elevated temperatures, pure thermal reordering dominates over oxygen-induced restructuring of the silver bulk and surface. The near-surface region is, therefore, comprised primarily of close-packed crystalline planes at elevated temperatures. The barrier for interstitialcy diffusion is overcome at temperatures in excess of 923 K, allowing bulk-dissolved, atomic oxygen to (Oβ) segregate into these low-indexed planes. This likely occurs via an interstitialcy diffusion mechanism where oxygen substitutes for silver atoms in the lattice. This oxygen species is referred to here as Oγ. Analysis of ISS depth profiling of silver foils treated under various conditions shows that the diffusion coefficient is a positive function of the oxygen concentration. This is a direct result of the oxygen-induced recrystallization of the silver resulting in a lowered barrier to diffusion. *In situ* XRD shows that oxygen located in octahedral holes of silver preferentially diffuses in the [110] direction. This requires the anisotropic displacement of silver atoms. The resulting strain culminates in a slight expansion of the silver unit cell and the preferential growth of crystals in the shape of needles. STM imaging of the surface shows the macroscopic silver facets to be composed of smaller, columnar crystallites, thus confirming the validity of the model based on the XRD data.