Preparation and Characterization of Pt/γ-Al2O3 Model Catalyst on NiAl Alloy

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Preparation and Characterization of Pt/γ-Al₂O₃ Model Catalyst on NiAl Alloy


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Numerous studies of heterogeneous catalysis systems clearly demonstrate that the metal nanoparticle (NPs)/support interaction is significant in determining the catalytic chemistry. Theoretical simulations have been performed to understand the metal/support interactions [1,2]. For example, theorists discovered that electronic and oxygen defects of γ-Al₂O₃ anchor the active particles [1]. Platinum NPs dispersed on γ-alumina is one of the most widely used heterogeneous catalysts and Pt performs extremely well as a catalyst for the oxygen-reduction reaction used in fuel cell industries. Hence, we chose Pt/γ-Al₂O₃ as a model heterogeneous catalyst system to investigate the metal NPs/support interface by electron microscopy methods with the ultimate goal of bridging the gap with theoretical simulations of the interfacial atomic and electronic structure. However, theoretical simulations assume single crystal, planar supports with no impurities, but commercial γ-Al₂O₃ is polycrystalline and irregular in shape [3]. Hence, we are producing a model catalyst support via oxidation of single crystal NiAl to create crystalline and planar γ-Al₂O₃.

We oxidized NiAl(110) from 823K – 1223K at oxygen partial pressures of 10⁻⁷ - 0.2 atm for 1 to 2 hrs within a controlled atmosphere furnace in order to discover the optimal oxidation conditions forming single crystal γ-Al₂O₃ with flat surface. The microstructure and crystallinity of the oxide films were characterized by X-ray diffraction (XRD) with 2Theta scan, Seemann-Bohlin scan and cross-section transmission electron microscopy (XTEM), Fig. 1, 2. The created γ-Al₂O₃ single crystal film follows a Stranski-Krastanov (SK) epitaxial growth, where NiAl[011][110]||γ-Al₂O₃(111)[211]. This relative orientation matches the Nishiyama-Wasserman (NW) orientation to accommodate 3% lattice mismatch at the NiAl∥γ-Al₂O₃ interface, Fig.2.

To deposit Pt NPs on the γ-Al₂O₃ film, Pt was e-beam evaporated onto the γ-Al₂O₃ (111); the particle size ranged from 2-4 nm. XTEM samples were made by using a dual-beam focused ion beam and Fischione Nanomill™, and the interface was characterized by high resolution TEM (HREM), Fig.3. Pt NPs were faceted with an epitaxial relationship of Pt(111)||γ-Al₂O₃ (111). The small Pt particles with less than 0.6 height to width ratio showed a 7% d(111) expansion parallel to the interface suggested strong support effects on the structure of NPs. In summary, γ-Al₂O₃ single crystal film has been prepared successfully via oxidation of NiAl; we will characterize the Pt/γ-Al₂O₃ interface by HREM and EELS and discuss these implications in relation to theoretical predictions [4].

References

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Fig.1 X-ray Diffraction scan of $\gamma$-$\text{Al}_2\text{O}_3$/NiAl(110) at various oxidation temperature, (222) $\gamma$-$\text{Al}_2\text{O}_3$ thin film on the surface; Seemann-Bohlin (alpha=1deg) scan confirm (111) orientation single crystal.

Fig.2 Cross-section HREM image of 850°C 1hr oxidized NiAl/Al$_2$O$_3$ interface, (a). Uniform $\gamma$-Al$_2$O$_3$ film grows on NiAl substrate. (b). SAD of $\gamma$-Al$_2$O$_3$ film, (c). Select area diffraction along interface.

Fig.3 Cross-section HREM image of Pt NPs deposited on $\gamma$-Al$_2$O$_3$(111) support