ABSTRACT

Nanoscale Corrosion and Tribology Mechanisms in CoCrMo Alloys and Associated Systems

Alex Yu-Wei Lin

Early-stage oxidation and corrosion mechanisms of CoCrMo and NiCrMo alloys can be analyzed on the nanoscale by transmission electron microscopy. Both alloys are attractive for a broad array of applications such gas turbines and aircraft engine components as they are known for their excellent corrosion resistance and mechanical properties at elevated temperatures. Additionally, CoCrMo alloys are widely used in orthopedic implants such as total hip replacements, as they have low wear rates and high biocompatibility, resulting in long service lifetimes. Since corrosion and oxidation behavior and the resulting oxide layers on the alloy surfaces are very sensitive to the conditions employed, it is necessary to understand the relevant mechanisms at specific operating conditions. A thorough analysis of the crystallography and chemistry of nanoscale oxide layers formed on these alloys by transmission electron microscopy can provide fundamental insights on the thermodynamics and kinetics of oxide formation in very different environments.

Nonequilibrium oxide phases, which have unusual combinations of crystallography and chemical compositions, are observed in the early-stage oxidation and corrosion of CoCrMo alloys. An investigation of CoCrMo alloys oxidized at a moderate temperature and short time scale reveals that grain boundaries play a role in assisting the formation of oxides that contain solute capture. As cation and oxygen diffusion is rapid through high-energy grain boundaries, spinel oxides with Cr contents that exceed the thermodynamic limits are observed. An aqueous corrosion appraisal of CoCrMo alloys also shows that the oxide layer, which has predominantly rocksalt crystallography, contain a significant amount of Cr, exceeding the solubility described in thermodynamic data. The oxide layers on a CoCrMo

alloy corroded in model synovial fluids containing hyaluronic acid is somewhat different, as rocksalt crystallography is observed but does not have any solute capture, suggesting that there is a secondary process occurring as the alloy interacts with biomolecules in typical simulated synovial fluids. Further electrochemical analysis indicates that hyaluronic acid significantly prevented the formation of a protective layer by removing Cr cations from the oxide layer. Possible strategies to prevent this deleterious effect are currently under investigation.

In addition, tribological mechanisms at nanoscale contacts are shown both experimentally and theoretically. With *in situ* transmission electron microscopy, mechanical deformations such as compression and shear are observed in crumpled graphene, which is composed of intra-sheet links and graphitic nanocrystals. *In situ* sliding reveals that intra-sheet links are flexible and can fold and unfold reversibly while graphitic nanocrystals are rigid, demonstrating the origins of enhanced mechanical stability and wear resistance of crumpled graphene. By combining contact mechanics and flexoelectricity, the electromechanical couplings at contacting surfaces can modeled, explaining the thermodynamic driver behind tribocharge transfer. The link between flexoelectricity and triboelectricity is important for understanding the complex nature of localized electrical properties at nanoscale asperities and can lead to the better designs of surfaces to be tailored for specific applications.

Approved by

Professor Laurence D. Marks

Department of Materials Science and Engineering

Northwestern University, Evanston, IL 60208 USA