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Progress in Surface Science 78 (2005) 101–184

Progress in SURFACE SCIENCE

www.elsevier.com/locate/progsurf

Review

Surface chemistry of zirconium

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Abstract

This article presents an overview of the surface chemistry of zirconium, focusing on the relationship of what is known from model studies and how this connects to current and future applications of Zr-based materials. The discussion includes the synergistic nature of adsorbate interactions in this system, the role of impurities and alloying elements, and temperature-dependent surface–subsurface transport. Finally, some potential uses of zirconium and its alloys for biomedical and nanolithographic applications are presented.

Keywords: Zirconium; Oxidation; Surface chemistry; Subsurface species; Diffusion; Water; Oxygen; Hydrogen; Nuclear materials; Alloys; Zircaloy

Contents

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0079-6816/$ - see front matter
doi:10.1016/j.progsurf.2005.07.001

1. Contextual overview

Zirconium has a unique combination of properties that historically led to its use as a structural material in nuclear fission reactors. Zirconium was chosen for this role since it provides desirable mechanical strength and processing characteristics common to other metals, but with a much lower thermal neutron absorption cross-section. Equally as important, it is corrosion resistant in service, which is intimately related to its surface chemistry. Refs. [1–4] provide excellent overviews of nuclear technology and the role played by zirconium-based materials in BWR and PWR applications.

An obvious question is "why are studies of surface chemistry relevant to such real-world environments?" The main reason is that unlike many metal alloy systems, zirconium alloys used in the nuclear industry are very pure and can almost be considered single-component systems. For example, nuclear-grade Zry-2 has a composition of roughly 98.1% Zr, 1.5% Sn, and less than 0.4% of Fe, Cr and Ni combined. Because of this we anticipate that for the Zr materials system, we will be able to connect surface science results with real-world observations better than has been possible in other systems.

Recently, the chemical and aerospace communities have begun to take advantage of the corrosion resistance of this class of materials. In addition, the biomedical community has also begun to use zirconium-based materials in prosthetics applications particularly due to their excellent wear characteristics. Chemical-grade, rather than nuclear-grade, materials are often used in these areas. The chemical-grade alloys have compositions similar to their nuclear counterparts, except that they are not depleted of the naturally occurring hafnium. Hafnium is considered chemically equivalent to Zr, but its neutron absorption characteristics are very different, requiring its removal for nuclear applications.

Many of the processes relevant to the environmental degradation of metals in service involve surface chemistry and localized transport phenomena. These can be studied, on model systems, by the methods discussed in this review. In addition to thermal cycling and gas/liquid exposures, we can also attempt to mimic radiation environments using electron bombardment and field-driven techniques. Again, since the industrially significant alloys are very nearly pure, it should be possible