Applied Surface Science 258 (2011) 1514–1518

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Surface geometry of pure iridium oxidized at 1373 K in air

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ARTICLE INFO

Article history:
Received 20 May 2011
Received in revised form
26 September 2011
Accepted 26 September 2011
Available online 2 October 2011

Keywords:
Iridium
Surface structure
Faceting
Oxidation

ABSTRACT

The surface microstructure of a polished Ir sample during isothermal heat treatment at 1373 K in air was characterized. Various surface morphologies including triangular pits and terraces, "pyramid"-like plateaus and striated edges were observed. Changes in surface geometry were highly dependent on the original grain orientation. Most grains were confirmed to possess or partly exhibit a geometric configuration of {1 1 1} faceting habit, while periodic bond chain (PBC) vectors played an important role in determining the ultimate surface morphology. The mechanism and process of how these distinct surface morphologies formed are discussed.

1. Introduction

Favored for its superior chemical stability, high melting point (2716 K) and excellent high-temperature strength, Ir is used in several essential applications such as in catalysts [1], spark plugs [2] and protective coatings [3,4]. For instance, this metal is indispensable for coating the combustion chambers of nuclear power plants, ensuring combustion at temperatures above 2530 K [5]. Another particular application of Ir is to serve as catalyst boosting reactions producing hydrogen gas from methane [6], methanol [7–9] and ethanol [6,10], etc. Since most applications are fulfilled at high temperatures, Ir must cope with oxidation in environments containing oxygen. In addition, the increasing demand for efficient use of fossil fuels in automobile engines also generated a more severe and complex combustion atmosphere for ignition spark plugs, for which Ir has proven its potential serving as the sparking electrode. Therefore, it is important to evaluate the oxidation behavior of this promising metal.

In the 1960s and 1970s, many studies, especially those supported by the U.S. Atomic Commission, investigated the high-temperature performance of Ir [11–13]. The results revealed a variety of oxide forms (e.g., IrO_3, IrO_2 and Ir_2O_3) at different volatilities upon exposure of Ir to oxygen-containing environments above 1369 K. These pioneering studies focused on quantitatively specifying the iridium oxide species of volatilization, disregarding the fact that an almost bare surface would result from the transpiration of gaseous Ir oxides. As a result literature reporting the surface geometry of Ir after thermal exposure was not available at that time when powerful electron microscopy had yet not to be developed.

Actually, there are always concerns to use high-melting VIB (Cr, Mo and W) and Pt group (Pd, Rh, Pt, Ru, Ir and Os) metals in oxidative atmospheres because most of them form volatile oxides. In the case of Ir, its solid oxide IrO_2 is stable up to 1369 K at 1 atm, above which the metal enters the regime of forming volatile oxide species (mainly IrO_3) until 1773 K [14,15]. The growing process and mechanism for Ir oxide formation were discussed in our previous research [16], and in this unique follow-up study we concentrate on the consequences of IrO_3(g) evaporation induced by the co-effects of heating and reaction under the laws of chemical etching [17,18]. By investigating the surface microstructure diversification process, the growth mechanism of the characteristic surface morphology of Ir during oxidative thermal exposure can be understood.

2. Material and methods

Pure iridium elemental powder (>99.99 mass%) was used to prepare a button ingot by the arc melting method. In order to mitigate splash loss during operation, the powder was precompressed to make dwarf cylinders. Before melting, the chamber of the arc melting furnace was flushed three times with Ar and then pumped to below 3×10^{-3} Pa. The button ingot was inverted and remelted five times to ensure homogeneity, followed by a successive solution treatment at 2273 K in vacuum ($<2 \times 10^{-3}$ Pa) for 24 h to further eliminate voids and enhance uniformity. After that the ingot was

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doi:10.1016/j.apsusc.2011.09.121

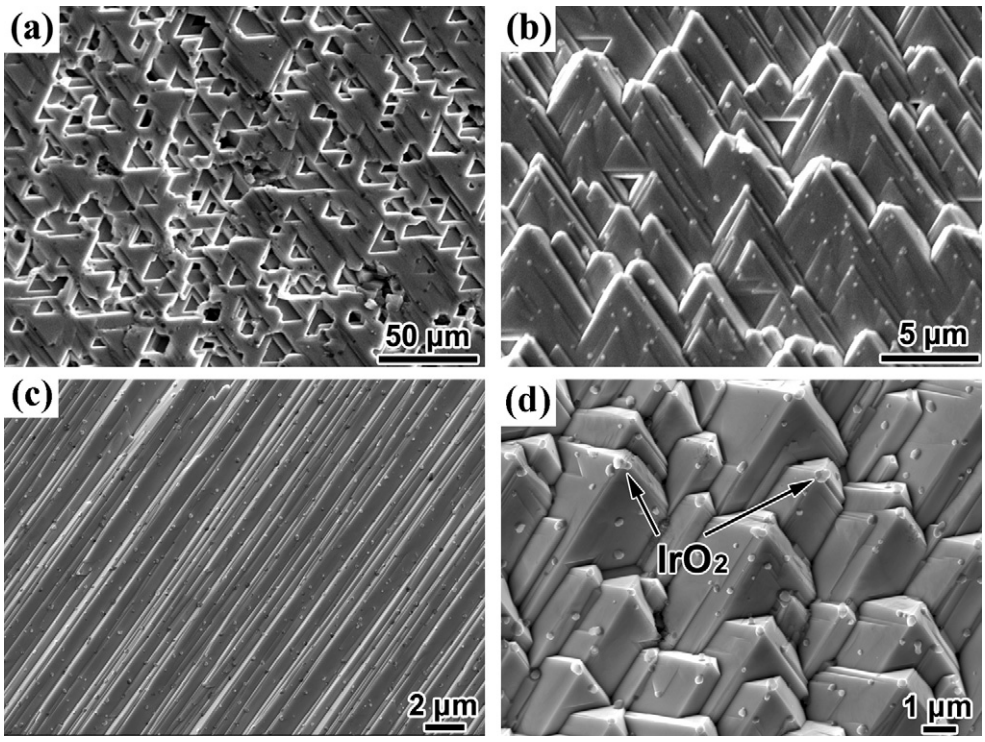

Fig. 1. Diverse views of Ir surface morphology after 360 min of isothermal exposure at 1373 K in air (a: triangle pits, b: layered triangular terraces, c: striated edges, d: columns with pyramid top).

cut into plates with dimensions of 3 mm × 3 mm × 1 mm using a wire electric discharging machine (Wire-EDM).

The isothermal exposure test of a mirror-polished Ir sample was performed at 1373 K within a muffle furnace. Note that repeated SEM/EDS inspections were directly implemented on the same Ir specimen at exposure intervals. For electron backscattered diffraction (EBSD) characterization, an orientation imaging microscopy (OIM) system (EDAX/TSL) attached to a field-emission SEM (JEOL 7001F) was used to explore a large surface area (1500 μm × 1500 μm) at a step size of 4 μm to determine the initial orientation of the selected grains.

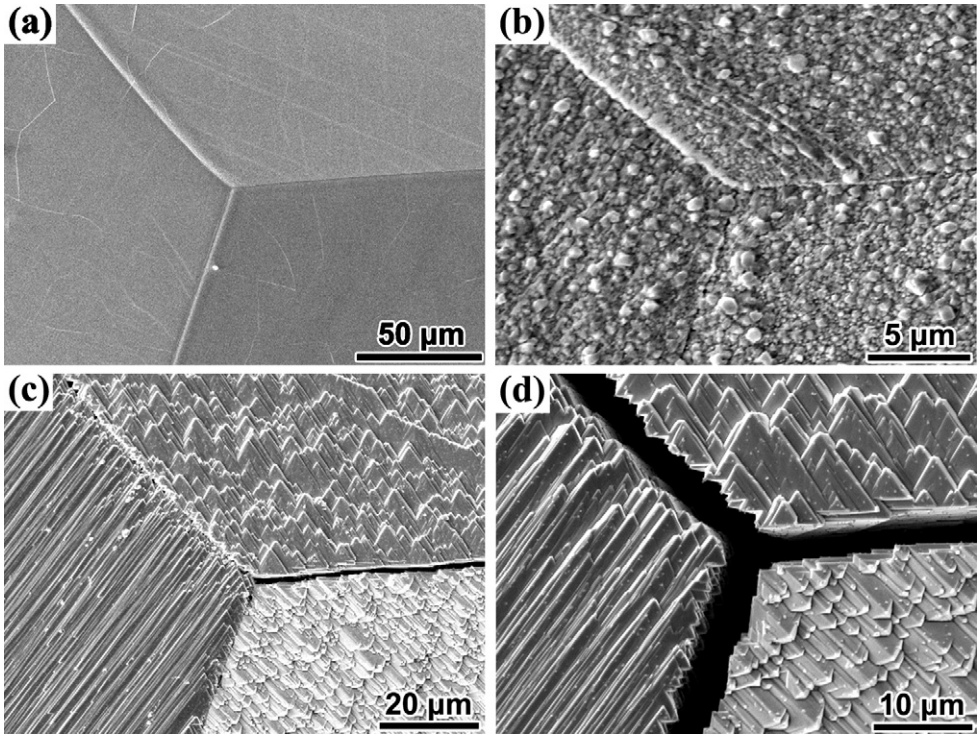

Fig. 2. Surface morphology evolution of a pure Ir specimen during thermal exposure at 1373 K in air (a: 0 min, b: 5 min, c: 60 min, d: 360 min).