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In situ quantification of electrochemical dissolution of hafnium-tantalum alloys in acidic media

Andrei Ionut Mardare *, Jan Philipp Kollender, Martina Hafner, Achim Walter Hassel

Christian Doppler Laboratory for Combinatorial Oxide Chemistry, Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, Linz 4040, Austria

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ABSTRACT

A thin film hafnium-tantalum combinatorial library with a compositional spread of over 70 at.% was used for electrochemical dissolution experiments in nitric acid. Surface microstructure analysis and crystallographic characterization of individual Hf–Ta alloys confirmed a hexagonal to tetragonal transition from pure Hf to pure Ta accompanied by a change in the surface grain structure. A flow-type scanning droplet cell microscope coupled to downstream analytics was used for the quantification of Hf and Ta dissolution rates along the entire compositional spread. Potentiostatically applying 3 V vs. SHE for 120 s for an electrolyte flow of 0.46 ml min^{-1} resulted in dissolution rates of pure Hf and pure Ta in the ng s^{-1} cm^{-2} and pg s^{-1} cm^{-2} range, respectively. For both species, the average dissolution rate was independent of the compositional gradient, indicating a dissolution enhancement of minor species. A decrease in their activation energy for dissolution triggered by a surface energy modification was the reason for the observed behavior.

1. Introduction

Both tantalum and hafnium valve metals are highly relevant for special applications requiring high melting points and remarkable mechanical properties and chemical stability such as superalloys for turbines and nuclear reactor components [1] or space applications requiring low aging embrittlement and good ductility at extremely low temperatures [2]. Due to their good biocompatibility, Hf and Ta are candidates for use in bio-medical alloys [3,4] where corrosion stability is crucial. The use of low-temperature co-deposition techniques in the Hf–Ta system presents the possibility of obtaining metastable or even amorphous phases while having a very high tendency to form undercooled solid solutions [5]. Moreover, excellent high-temperature oxidation resistance has been proven for Hf with 20 wt.% Ta while Hf represents one of the most promising candidates for improving Ta oxidation resistance [6]. Corrosion of these alloys represents a highly relevant aspect for all applications. Even though some studies about Hf and Ta dissolution in HF can be found [7–9], no data regarding their corrosion in non-fluorine containing acids are available. The present study offers a systematic investigation of electrochemical dissolution over a wide range of the Hf–Ta binary alloys, which may reveal relevant compositions with superior properties to those of the pure metals [10].

2. Materials and methods

A widespread Hf–Ta thin film combinatorial library was deposited using a co-sputtering system (Mantis Deposition) with a base pressure of 10^{-8} Pa and 130 mm deposition distance. Two opposite RF powered sputtering guns hosting a high purity Hf target (machined from plate of Hf 99.9% (Zr max. 2%) Hauner Metallische Werkstoffe) and a Ta target (99.95%, ITL-Vacuum-Components) were concomitantly operated for this purpose in 5×10^{-1} Pa Ar. Thermally oxidized Si wafers (100 mm diameter) were used as substrates. The thickness of the Hf–Ta compositional spread was 300 nm at the samples centre. Additionally, pure Hf and Ta thin films were deposited in identical conditions for serving as reference samples.

Microstructural investigation of the Hf–Ta library was done using a field emission SEM (Zeiss Gemini 1540 XB) with 20 kV acceleration voltage and in-lens detection. The chemical composition along the library was determined using energy dispersive X-ray spectroscopy (EDX, Oxford INCA). Crystallographic properties were studied using an X-ray diffraction (XRD) system (PANalytical X'pert Pro) with a Cu-Kα source without monochromator. The XRD measurements were done in either 1° grazing incidence geometry, which rendered a spot size width of 3 mm or in Bragg Brentano. The XpertHigh software was used for data analysis and peak identification.

A flow-type scanning droplet cell microscope (FT-SDCM) connected to an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Scientific, iCAP Q) was used for locally studying the electrochemical dissolution behavior of Hf–Ta alloys. A schematic description of the experimental arrangement along the compositional spread is provided in Fig. 1.

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* Corresponding author. Fax: +43 732 2468 8905.
E-mail address: andrei.mardare@jku.at (A.I. Mardare).

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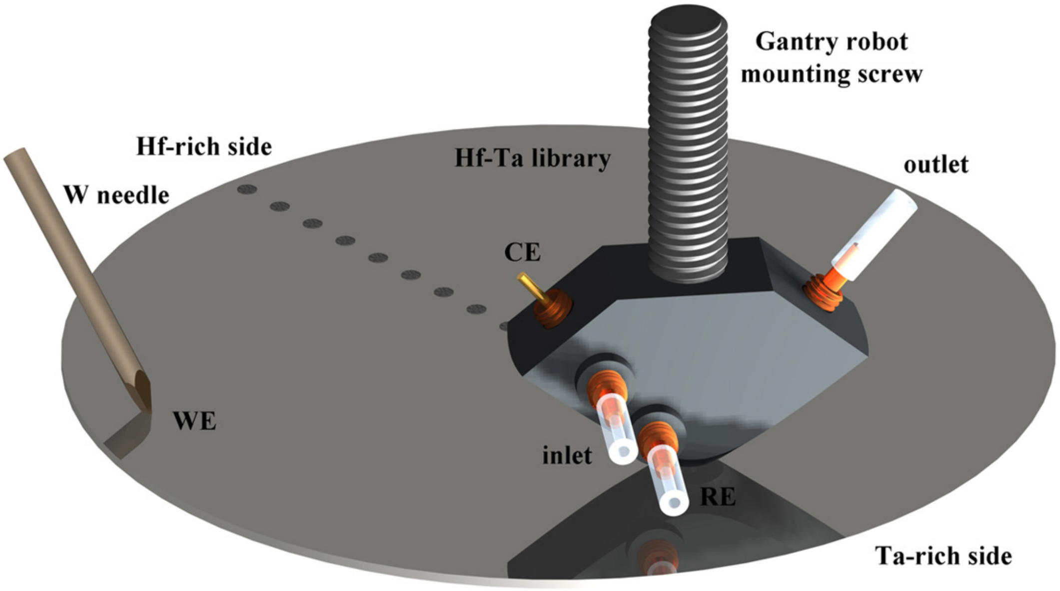

Fig. 1. Experimental setup illustrating the FT-SDCM during its Hf–Ta surface scanning procedure.

The FT-SDCM was attached to a Gantry robot via the indicated mounting screw, allowing automatic scanning/imaging of the investigated library surface by a controlled surface positioning combined with automatic constant force surface contacting. Manufacturing of the cell body was done using 3D printing [11]. The internal design of the flow channels ensures that the electrolyte is only locally wetting the surface of the material library (spot area of 1.91 mm^2), which enables addressing selected Hf–Ta compositions. Tygon tubes were used for connecting the FT-SDCM to the electrolyte reservoir and ICP-MS. An Au counter electrode and a small 3 M Ag/AgCl reference electrode (Metrohm, Switzerland) were used. The electrolyte flow direction was chosen as to avoid species being adsorbed on the surface of the counterelectrode. The used electrolyte (0.1 M HNO_3) was prepared from high purity nitric acid (Ultrapure, Merck) and ultrapure water (>18.2 MΩ cm, <3 ppb TOC, Millipore Q System). A peristaltic pump was used to transport the electrolyte and the dissolved species at a constant flow rate of 0.46 ml min^{-1} through the FT-SDCM and further into the ICP-MS. The electrical contacting of the Hf–Ta thin films was done using a sharp W needle. A potentiostat (Compactstat, Ivium Technologies) was used to perform the electrochemical dissolution experiments in strong oxidizing conditions in acidic environment by applying 3 V vs. SHE for 120 s for each addressed spot. Standard solutions for ICP-MS calibration were prepared from Ta (998 ± 4 μg ml^{-1}) and Hf (100.1 ± 0.46 μg ml^{-1}) stock solutions (Inorganic Ventures, USA).

3. Results and discussion

The Hf–Ta thin film combinatorial library mapped by EDX (not shown here) indicated an almost linear compositional gradient with a compositional resolution of 0.3 at.% mm^{-1}. The total obtained compositional spread of the Hf–Ta library under study ranged between Hf–20 at.% Ta and Hf–90 at.% Ta along the total library length. The surface microstructure evolution along the library was mapped via SEM (not shown here). A grain evolution identical with the one detailed described in a previous study was observed [12]. If the sputtered Hf surface typically shows two distinct types of grains (larger pyramidal ones protruding from a finer grained base layer), the addition of Ta dramatically changes this initial appearance. As a result, above 20 at.% Ta, the surface is only formed by small spherical grains with equivalent diameters in the range of 20 nm. Increasing the Ta amount in the library produces a continuous surface morphology change. A highly relevant fact (previously observed in the aforementioned study and confirmed here) is that the microstructure transition toward the features of pure Ta surface occurs through a compositional region around 60 at.% Ta, where the surface revealed elongated grains with extremely long grain boundaries.

The compositional evolution of the crystallographic features of the Hf–Ta library follows very well its microstructural changes. Sputtered pure Hf films have hexagonal symmetry while pure Ta films are tetragonal. During the increase of the Ta amount along the library, a transition from hexagonal to tetragonal symmetry is present, as expected. Due to a rather strong mismatch between both symmetries, a certain degree of amorphization was detected from XRD data (not shown here) confirming previous findings. Above 80 at.% of Ta, the initial hexagonal structure is completely converted to tetragonal. This symmetry transition via a quasi-amorphous state was previously found to have an impact on the basic electrochemical properties of the Hf–Ta alloys [12].

In order to relate the Hf–Ta composition, surface morphology and crystallography to the electrochemical stability of these alloys in acidic media, the entire library was scanned by the FT-SDCM, and dissolution rates of Hf and Ta were locally measured via ICP-MS. As reference, the dissolution rate of pure Hf and Ta films were first measured against Hf and Ta calibration standard solutions to determine area normalized dissolution rates. In Fig. 2, these are presented for both pure metals.

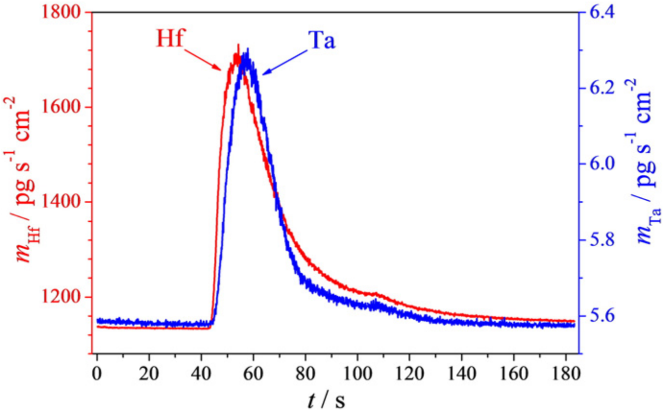

Fig. 2. Hf and Ta dissolution curves in acidic media quantified by ICP-MS.