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Microstructural changes due to anodic polarisation of palladium and silver films on YSZ

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ABSTRACT

Palladium and silver films with different microstructures were prepared on (111), (110), (100) and (311) orientated YSZ (yttrium stabilised zirconia) substrates. Subsequently, the as-prepared films were anodically polarised at 400 °C or only annealed at the polarisation temperature. As results of the annealing and polarisation, we observed i) oxidation of the palladium films, ii) grain growth in the case of silver films on (111) orientated YSZ and iii) de-wetting in the case of silver films on the other YSZ substrates. The comparison of the annealing and polarisation results revealed a modification of the oxidation process of palladium and a significant increase of de-wetting of silver films. Additionally, we observed different indications that the oxygen built-out occurred notably at grain boundaries within the metal films. These indications were: an increased polarisation resistance due to a decrease of suitable grain boundaries by oxidPd and Ag films on differently orientated YSZ (yttrium stabilised zirconia) were anodically polarised at 400 °C or only annealed at this temperature. We observed i) oxidation of the palladium films, ii) grain growth of silver films on (111) orientated YSZ and iii) de-wetting of silver films on the other orientated YSZ substrates. The comparison of the annealing and polarisation results revealed a modification of the oxidation process of palladium and a significant increase of de-wetting of silver films. Additionally, we observed different indications that the oxygen built-out occurred notably at grain boundaries within the metal films.

1. Introduction

The electrochemical cell metal|YSZ|metal [YSZ: yttrium-stabilised zirconia] can be used for solid fuel cells, oxygen sensors and in electro-catalytic processes. Due to electrical or chemical polarisation, oxygen is transported from one metal side to the other through the YSZ membrane. At the anodic side oxygen is removed and at the cathodic side, oxygen is built in. The oxygen exchange occurs mainly at the triple phase boundary between metal, YSZ and the gas phase, but it is also possible at lattice defects of the metal. Accordingly, it has been shown that in platinum and palladium films with twins as the only defects, these twins are the location of oxygen built-out due to bubble formation and bubble cracking [1]. In platinum films with other grain boundaries it had been found that these grain boundaries are also oxygen permeable [2,3].

The metal in the electrochemical cell metal|YSZ|metal should be catalytically active. Depending on the application it has to be an oxidation catalyst and/or a reduction (and/or hydrogenation) catalyst. In solid fuel cells the metal on the anodic side is mostly hydrogenation catalyst nickel [4]. In oxygen sensors (especially the lambda sensor) and in electrocatalytic processes, platinum (which is an oxidation and reduction catalyst) is mainly used [5]. However, platinum is very expensive and rated as critical [6,7]. Therefore, there are research activities to substitute platinum in many applications and for some applications substitutions are already used. Particularly in automobile catalysts palladium, which is also an oxidation and reduction catalyst, is now often used instead of platinum, or palladium is admixed with platinum to reduce the amount of platinum. Accordingly the price of palladium has increased in the last few years [8]. In addition, palladium is in principle similarly as critical as platinum, since it is mined and processed from the same ores as platinum. Additionally, for some applications palladium is too reactive, since it is much more reactive than platinum, especially for oxidation [9–12]. Silver could be a better substitute for platinum because it is not as reactive as palladium for oxidation, cheaper and rated much less critical than platinum and palladium [7]. But silver as a catalyst is less active (it is a good oxidation catalyst, but is not as good as a reduction catalyst). It also has a much lower melting point and therefore it could dewet in some applications, which work at high temperatures [13].

In the here presented study the anodic polarisation behaviour of palladium and silver films with different microstructures has been investigated. For that purpose the metal films were prepared by pulsed laser deposition on differently orientated YSZ substrates, since in former works a relevant influence of the substrate orientation on the microstructure of the metal film had been found [14–16]. The microstructural changes within the palladium and silver films during polarisation have also been compared to the annealing behaviour of the films. Accordingly,

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microstructural changes due to oxygen removal could be separated from annealing effects. In addition, the development of the polarisation resistance was studied. The results of this study will help for a more detailed understanding of the processes in the applications of such cells. They will also allow an assessment of a possible substitution for platinum by palladium or silver in such applications.

2. Experimental

2.1. Preparation of the palladium and silver films

The metal films were deposited by pulsed laser deposition (PLD), which was performed by a KrF laser ($\lambda = 248$ nm) with a repetition rate of 6 Hz, a pulse energy of 450 mJ and argon ($p = 2$ Pa, purity 99.95%) as background gas. In the deposition chamber the cylindrical and polished palladium or silver target (purities 99.95%) was placed at a distance of 4.5 cm to the substrate. The substrates were commercially polished (111), (100), (110) and (311) orientated YSZ single crystals with a diameter of 20 mm and a thickness of 0.5 mm. The yttrium content was 8 mol%. The substrate temperature was 200 °C. Films with a thickness of about 500 nm were prepared with a mean growth rate of about 1 μm/h. To obtain a specific geometry of the metal films (6 mm diameters) we used a metallic mask during deposition.

2.2. Annealing experiments

The annealing experiments were performed in a heating chamber (DHS900, Anton Paar, Austria) of the D8 X-ray diffractometer (Bruker AXS, Germany). Accordingly, it was possible to determine a possible oxidation by in-situ X-ray 2Theta-scans. The annealing temperature was 400 °C (heating and cooling rate: approximately 2 °C/min) and the annealing times were 10 min up to 24 h. For the annealing temperature, we chose the polarisation temperature, in order to compare the annealing results with the polarisation results. We annealed one selection of all types of prepared silver and palladium films on the differently orientated YSZ substrates. We checked the reproducibility in the case of silver films on (111) and (311) YSZ. In the case of palladium films we had investigated the reproducibility of the annealing behaviour in detail in former studies [1,17].

2.3. Polarisation experiments

The prepared metal films were the working electrode in the electrochemical cell metal|YSZ|Pt-paste during the anodic polarisation experiment. We used a three point method. The Pt-paste was the counter electrode and an extra Pt-paste circle on the substrate side of the working electrode was used as the reference electrode (for more details see [1]). The electrochemical measurements were performed with a VersaSTAT measurement device (Princeton Applied Research) at 400 °C and 10 mV, 100 mV as well as 600 mV each for 10 min. We chose this polarisation temperature, because pre-experiments (at 200 °C and 300 °C) showed that the resistance of the oxygen-ion conductor YSZ is too high at lower temperatures and there were problems with strong de-wetting of the silver films at higher temperatures (at 500 °C) [17]. The polarisation resistance of the working electrode was determined from the current–time-curves. We also checked these values by impedance measurements before and after the polarisation. The reproducibility of the polarisation experiments was checked with three samples of the silver films on (111) and two on (311) orientated YSZ as well as with one palladium film on (100) orientated YSZ.

2.4. Characterisation methods

The metal films were characterised before and after polarisation (or after annealing) by scanning electron microscopy (SEM; field emission microscope: Zeiss, Supra 55 VP) and by texture investigations [electron backscatter diffraction (EBSD) investigations by an additional equipment for the SEM microscope of Crystal, Oxfords Instruments and X-ray pole figure measurements by a D5000 Siemens diffractometer]. We measured the {111} pole figure of the metal films and of the YSZ substrate through the metal films. By EBSD measurements we obtained the local orientations within the metal films (in a step size of 100 nm). From these local orientations the local misorientations were calculated and shown in a grain boundary map and in a misorientation distribution graphic.

An important difference in the texture analysis by pole figure and EBSD investigations is the size of the investigated area. In the case of the XRD measurements with the used 2 mm aperture, an area of about 4 mm in diameter (the absolute size depends on the tilt angle)

Table 1
Grain boundary angles and sizes of palladium and silver films on differently orientated YSZ substrates.

YSZ orientation	Metal	Grain boundary angles	Grain sizes [nm]
(111)	Pd	60° and a few 3°	3000
(100)	Pd	All, 60° preferred	300
(110)	Pd	All, 60° preferred	300
(311)	Pd	All, 60° preferred	400
Polycrystalline	Pd	All, 60° preferred	200
(111)	Ag	All, mainly 3° and 60°	250
(100)	Ag	All, mainly 3°, 30° and 60°	200
(110)	Ag	All, 60° preferred	100
(311)	Ag	All, 60° preferred	100
Polycrystalline	Ag	All, 60° preferred	100

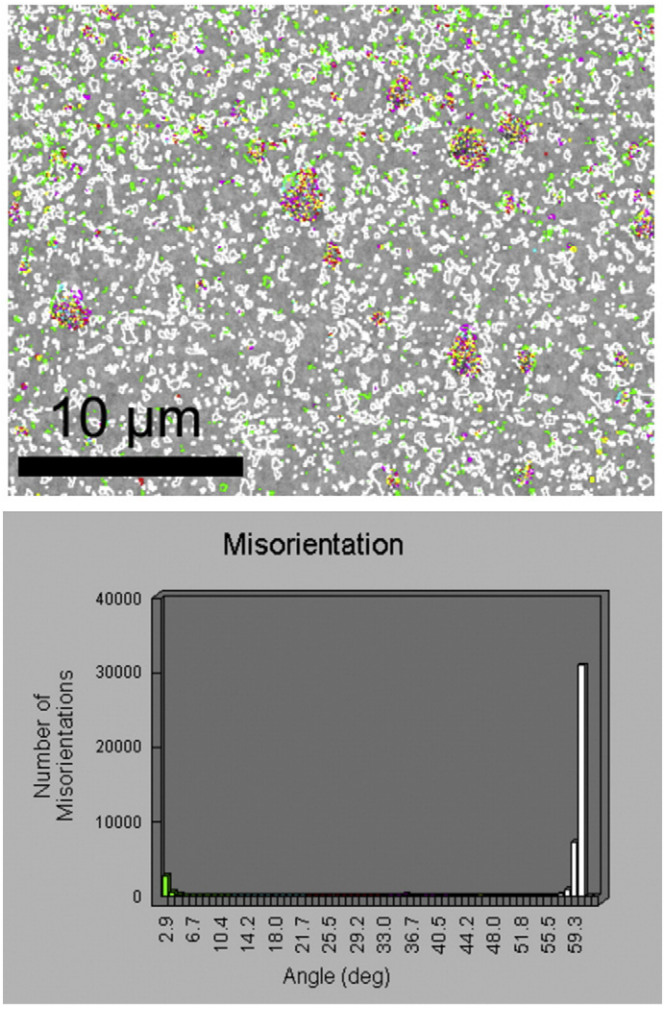

Fig. 1. Grain boundary map of an as-prepared palladium film on (111) orientated YSZ (top) and grain boundary (or misorientation) distribution graphic (bottom). Accordingly, mainly white 60° twin grains and a few green small angle grain boundaries are found.