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Crystallization behavior of arc-deposited .ceramic barrier coatings

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Abstract

Al_2O_3 and Er_2O_3 were deposited by plasma-assisted physical vapor deposition using a filtered vacuum arc device. Varying the deposition conditions with respect to the substrate temperature and bias voltage, the crystallization behavior of these films was investigated by X-ray diffraction. In the case of alumina, when a bias voltage of −200 V is applied, crystallization of metastable crystal phases starts around 500 °C; the growth of the thermodynamically stable α-phase starts above 600 °C. This has to be compared with the thermodynamic phase transformation temperature of 1100 °C. For erbia, crystallization of the cubic crystal phase occurs at room temperature, when a bias voltage of −100 V is applied. Without exceeding the upper service limit, structural low activation materials can therefore be coated with stable ceramic barrier coatings. Deuterium permeation experiments performed with these types of coatings yield a permeation reduction factor of 40 in the case of alumina and 200 for erbia, respectively.

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1. Introduction

The safe operation of a future fusion power plant will require a thorough control of the on-site inventory of radioactive tritium. Hydrogen isotopes in general diffuse into and through metals. Thin ceramic coatings may be employed to control the diffusion of tritium into and through metallic structural materials of fusion power plants. In tritium breeder blanket concepts, production and qualification of radiation resistant tritium permeation barriers to limit tritium permeation are required [1]. In the case of self-cooled liquid metal blanket concepts, such coatings must, in addition, satisfy the requirements of high electrical resistivity and corrosion resistance. Al_2O_3 can be employed for T control [2–5], Er_2O_3 could even show sufficient corrosion resistance in contact with liquid lithium [6].

Alumina exists in many forms depending on its preparation [7]. As the aqueous mineral Boehmite, AlOOH, is heated, γ-Al_2O_3 is produced. Subsequently, other metastable transition crystal phases occur. Each phase has a unique crystal structure with respect to the positions of the Al atoms in the lattice. Since the O atoms remain stationary in an fcc-lattice in all of these crystal phases, their density is relatively constant at 3.60 g/cm^3. Upon heating above 1100 °C, the thermodynamically stable α-Al_2O_3 (corundum) phase is formed, in which the O atoms move to a hcp-lattice structure, with a density of 3.98 g/cm^3. This change of density corresponds to a shrinkage of the lattice. For thin films, this particular phase transition would therefore lead to crack formation.

For erbia mostly cubic crystal phases are reported in the literature [8]. However, also a hexagonal crystal phase has been identified [9]. In PVD deposition experiments cubic phases are reported [10].

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In addition to the importance of the crystal structure, particular attention must be given to the microstructure of the coatings. Since hydrogen diffusion in materials is often governed by imperfections, high-quality films without significant void fractions or impurity contents are required. In order to achieve such a high film quality, we employ a filtered vacuum arc device for the deposition of thin ceramic films. Because the deposited film is generated from an ionized plasma, the application of a bias voltage allows to control the energy of the incident particles. By varying this energy and the substrate temperature, the crystal structure as well as the microstructure of the deposited coatings can be controlled.

In this contribution, we report results about the crystallization behavior of Al_2O_3 and Er_2O_3 thin films and their respective permeation barrier performance.

2. Experimental

Employing a filtered vacuum arc facility, we deposit films with thicknesses up to several microns. A vacuum arc discharge on a solid metal cathode produces a metal plasma, and together with oxygen added from a gas inlet an oxide ceramic coating is deposited onto the substrate. The arc discharge, however, also produces droplets of molten material, which would significantly reduce the performance of the films as permeation barriers if they were incorporated into the coating. A very effective method of avoiding this drawback is to prevent the droplets from reaching the substrate by employing a 90° magnetic toroidal filter system. On the laboratory scale, a substantial decrease of droplet contamination of the coatings can be achieved by this method while sustaining high deposition rates. A schematic view of our setup is displayed in Fig. 1.

In this plasma-assisted PVD process, we can vary the substrate temperature as well as the substrate bias voltage. With our setup, we can apply RF-induced bias voltages up to −300 V which transforms directly into kinetic energy of the particles impinging onto the growing film.

In our setup, heating of the samples up to 800 °C is performed by means of an infrared heater behind the substrate. In the presence of a bias voltage, the impinging flux of energetic particles represents a non-negligible heat source leading to a time-dependent temperature increase during the coating process. Therefore the substrate surface temperature is monitored in situ using a pyrometer. Further details about the vacuum arc facility can be found in [11].

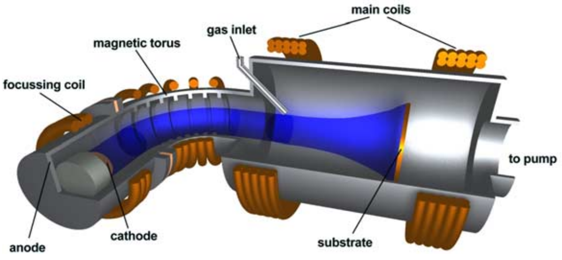

Fig. 1. Vacuum arc setup with toroidal filter system.

The stoichiometry of our metal oxide ceramic coatings was determined by means of Rutherford Backscattering measurements using a 1.5 MeV ^{4}He beam at a scattering angle of 165°. From the obtained spectra, the film composition was evaluated using the program SIMNRA [12].

The crystal structure analysis was performed using a 7-axis Seifert XRD 3003 X-ray diffractometer with Cu K_α radiation. Phase determination was done on the basis of the ICDD powder diffraction file data base, release 2000.

The hydrogen permeation experiments were performed with our setup described in detail in [13]. The sample divides the vacuum system into two parts. Sealing of the sample is done using gold O-rings on both sides. The inlet pressure can be actively controlled in a range from 10^{-3} mbar to 1 atmosphere. Measurement of the permeated flux is performed using a flux-calibrated mass spectrometer, Balzers QMA 125. The base pressure of the detector side is 10^{-9} mbar. The operating temperature ranges from room temperature to 600 °C.

3. Results and discussion

Rutherford Backscattering Spectroscopy showed that the films contained no traces of impurities. Concerning the composition of our coatings, we obtained stoichiometric Al_2O_3 and Er_2O_3 within an error margin of 2 at.%. It was found that this was always true, when the oxygen gas flow was sufficiently high. Excess oxygen at high gas flows was never observed. An example of a 1.5 MeV ^{4}He backscattering spectrum is shown in Fig. 2. By Scanning Electron Microscopy, it was verified that the films had a very smooth structure with a complete coverage of the substrate surface.

By varying the substrate temperature and bias voltage, the crystal structure of the alumina films can be controlled. In the special case of reactive vacuum arc deposition, the thermodynamically stable corundum phase can be obtained at a temperature of 800 °C. By applying a bias voltage of −150 V, this temperature can be decreased to a value of 650 °C. The kinetic energy of the impinging particles is dissipated in the surface layer and therefore increases the mobility of adatoms. An increase of the bias beyond this value is not accompanied by a further reduction of the critical temperature. A further increase of the bias voltage, however, is not desirable anyway, since at some point physical sputter-

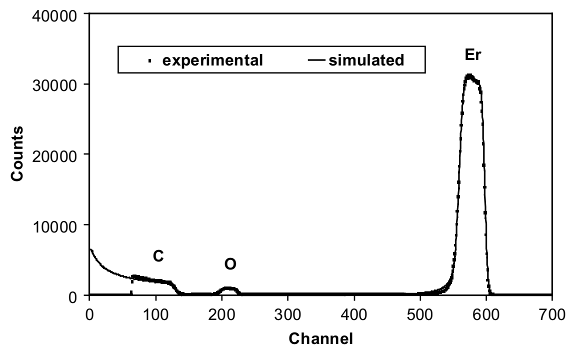

Fig. 2. 1.5 MeV ^{4}He Rutherford Backscattering spectrum of a 50 nm Er_2O_3 layer on graphite. The analysis performed using the program SIMNRA [12] yields a stoichiometric composition without any traces of impurities for both, erbia as well as alumina.

ing will prevail and no film deposition will occur. Metastable crystal polymorphs form at temperatures as low as 450 °C. Below this value, the films are amorphous. An approximate crystal phase diagram for vacuum arc-deposited alumina with respect to temperature and bias voltage can be found in [14].

In the case of erbia, no assessment of a complete phase diagram was performed yet. However, a temperature of 570 °C together with a bias voltage of −100 V resulted in a cubic crystal structure, which is in agreement with results reported in literature [8]. An X-ray diffraction spectrum from such a film is shown in Fig. 3. The solid vertical lines denote diffraction peaks taken from a calculated ICDD powder diffraction file [15]. From the fact that our measured spectrum displays all of the peaks calculated for a powder diffraction spectrum with mostly corresponding intensities, it can be concluded that these film are polycrystalline without any specific texture. This is in agreement with other reports [16].

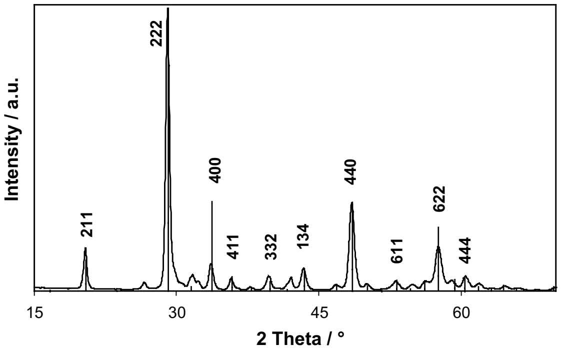

Fig. 3. XRD spectrum of an erbia film deposited at 570 °C with a bias voltage of −150 V. The vertical lines denote the amplitudes and angles of a calculated database powder diffraction file [15].

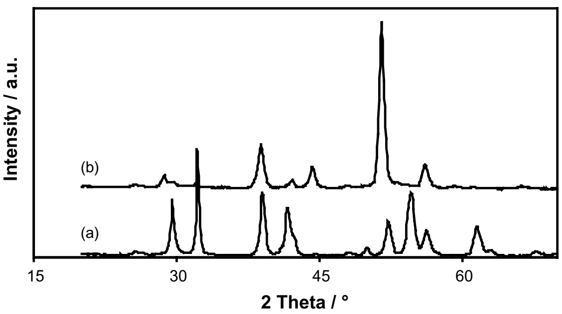

Fig. 4. XRD spectra of erbia deposited at room temperature with a bias of −100 V: (a) grazing incidence; (b) full θ–2θ scan.

In contrast to films produced by CVD, which were amorphous at a substrate temperature of 500 °C [17], our coatings showed crystallization already at room temperature, when deposited with a moderate bias voltage of −100 V. The crystal phase we obtained from our X-ray diffraction analysis could not be clearly matched with the data available from [8]. Fig. 4(a) shows an X-ray diffraction pattern obtained from such a coating under grazing incidence. If we compare this spectrum with the full θ–2θ scan shown in Fig. 4(b), the diffraction peaks are distinctly different. From this we conclude that these films grow in a strongly textured fashion. To obtain more information about the crystal structure these films are currently investigated by transmission electron microscopy.

To investigate the diffusion barrier performance of our thin films, we use coatings deposited onto PdAg30 (Pd doped with 30 at.% silver) substrates. This material combines the high hydrogen permeation rate of Pd with dimensional stability. Pure Pd shows swelling upon hydrogen loading at elevated temperatures, which may lead to crack formation.

The samples were installed with the coated surface facing the detector side of the setup. Fig. 5 shows permeation data as a function of applied deuterium pressure. The solid line corresponds to an uncoated PdAg30 substrate, while the symbols denote permeation data through the two different types of coatings deposited on PdAg30. As can be seen, a 0.25 μm alumina coating reduces the permeation by a factor of 40, while a 1 μm erbia film yields a reduction factor of 200. This shows that both types of ceramics are suitable as hydrogen isotope diffusion barriers. The influence of the degree of crystallization and the crystal phase on the permeation reduction is currently under investigation. The pressure dependence yields a permeation flux **J** proportional to $\mathbf{p}^{0.65}$ for both samples, which is close to the 'diffusion limited case', whereas an exponent of one would show the 'surface limiting case', an increasing of the coating

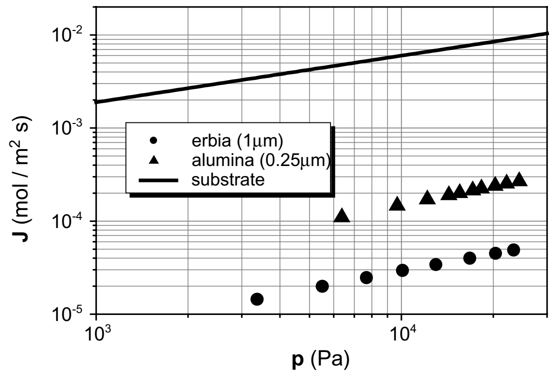

Fig. 5. Results from deuterium permeation experiments. The solid line corresponds to D permeation through an uncoated PdAg30 substrate. The triangles correspond to an Al_2O_3 coating deposited at 873 K without bias voltage. The circles correspond to Er_2O_3 deposited at 520 °C without bias voltage.

thickness would have no effect to the permeability. In our case a reciprocal variation of **J** with film thickness is expected. With this in mind, we expect both types of materials to have a similar diffusion barrier performance.

4. Summary

We coated various substrates with Al_2O_3 and Er_2O_3 thin films by reactive filtered vacuum arc deposition using high purity metallic cathodes and investigated their composition by Rutherford Backscattering and their crystal phase by X-ray diffraction.

In the case of alumina, the corundum crystal phase appeared at temperatures above 800 °C. By applying −200 V of RF bias voltage, we were able to reduce this temperature to 650 °C. Meta-stable crystal phases appeared at temperatures as low as 450 °C.

In the case of erbia, we deposited a cubic crystal phase at a substrate temperature of 570 °C with a bias voltage of −150 V. At room temperature, however, we obtained a crystal phase, which could not be identified using the ICDD powder diffraction file data base.

Investigating the diffusion barrier performance of these materials by measuring deuterium permeation through coated PdAg30 substrates, we obtained a permeation reduction factor of 40 for a 0.25 µm alumina film and a factor of 200 for a 1 µm erbia coating.

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