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Protective Alumina Coatings Prepared by Aerosol Deposition on Magnetocaloric Gadolinium Elements

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Abstract: In this work the preparation of a protective insulating alumina coating on magnetocaloric gadolinium elements was investigated. In order to prepare a dense ceramic coating at room temperature the aerosol deposition technique was used. The study reveals that the powder morphology and particle size are important parameters that influence the deposition efficiency, powder packing and consequently also the density and functional properties of the alumina coating. The optimal powder pre-deposition treatment includes heating the powder to 1150 °C, followed by milling. The deposition of this powder resulted in the preparation of dense alumina coatings with a low specific electrical conductivity of $6.4 \cdot 10^{-14}$ $\Omega^{-1}m^{-1}$.

Keywords: protective alumina coating, aerosol deposition, magnetocaloric gadolinium

Korundna zaščita magnetokaloričnih hladilnih elementov pripravljena z metodo nanašanja delcev v curku aerosola

Izvleček: V članku smo preučevali pripravo zaščitnih korundnih prevlek za magnetokalorične hladilne elemente iz gadolinija. Prevleke smo pripravili z metodo za nanašanje delcev v curku aerosola, ki omogoča pripravo gostih prevlek že pri sobni temperaturi. Ugotovili smo, da morfologija prahu in velikost delcev pomembno vplivata na učinkovitost nanosa in pakiranje prahu ter posledično tudi na gostoto in funkcionalne lastnosti prevlek. Optimalni postopek obdelave prahu pred nanašanjem vključuje termično obdelavo prahu pri 1150 °C ter mletje v planetarnem mlinu. Iz predhodno obdelanega prahu je mogoče pripraviti goste korundne prevleke z nizko specifično električno prevodnostjo, ki znaša $6.4 \cdot 10^{-14}$ $\Omega^{-1}m^{-1}$.

Ključne besede: korundne zaščitne prevleke, nanašanje delcev v curku aerosola, magnetokalorični gadolinij

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1 Introduction

Magnetocaloric (MC) refrigeration technology is gaining importance as it represents an alternative to conventional vapor-compression technology for specific applications [1,2]. One of the best candidates for a MC material operating at around room temperature is gadolinium, with an adiabatic temperature change of ΔT_{ad} ~ 12 K for a magnetic field change of 5 T at a temperature of 294 K [3].

Many of the MC refrigeration prototypes are based on the principle of active magnetic regeneration. This principle is suitable for implementing in large refrigeration devices, where also an efficient heat-exchange system is needed [2]. The heat-exchange media are typically water or water-based fluids, which can cause the gadolinium working elements to corrode [4].

Caloric research is also developing towards the use of MC cooling technology in electronics. In this case, for the efficient transfer of heat, more sophisticated heat-management systems are needed, such as thermal switches or thermal diodes [5,6]. One way to activate these thermal switches is by using an electric field, which can be detrimental for the working elements. In addition to problems with the oxidation of gadolinium, new challenges appear regarding the protection of the gadolinium elements against possible electrical breakdown. These problems can be solved by the deposition of a protective layer on the top of the gadolinium element.

Polycrystalline aluminum oxide (Al_2O_3), more often referred as alumina, is an abundant and one of the most widely used ceramic materials. Alumina is used in versatile applications due to its excellent properties, e.g., high electrical insulation, heat resistance, chemical inertness and high mechanical hardness. Those properties make alumina one of the best materials for protecting materials against harsh environments [7–10]. In order to deposit a protective alumina layer on gadolinium metal an aerosol deposition (AD) method can be used.

AD is a spray-coating process for producing dense thick films, where the deposition mechanism is based on the collision of fine particles with the substrate's surface. A powder is mixed with a carrier gas to form an aerosol, which is then ejected through a nozzle and deposited onto the substrate under vacuum [11,12]. The AD process occurs at room temperature; thus this method makes it possible to combine materials that are normally not stable or compatible at high temperatures. Aerosol-deposited alumina thick films exhibit excellent corrosion resistance [13] and electrical insulation [14]. For example, they have a high electrical breakdown strength, exceeding 600 $kV{\cdot}cm^{-1}$ [14,15]. These films can also be used as anti-scratch and anti-smudge coatings due to their promising mechanical properties [12]. The high hardness of AD alumina films (between 1100 HV and 1800 HV [13,16–18]), which is comparable with the hardness of bulk alumina, and a good adhesive strength of 64 MPa [19] were reported.

In this work the AD of a protective alumina coating on gadolinium cooling elements was investigated. The properties of the alumina powder are of high importance for efficient deposition and good particle packing. Therefore, special attention was given to the predeposition treatment of the starting powder in order to prepare a dense insulating protection layer.

2 Materials and Methods

For AD a raw Al_2O_3 commercial powder AL-160SG3, Showa Denko, Japan (further denoted as the R powder) and its two modifications; heated (H) powder as well as heated and milled (HM) powder were used. The H and HM powders were thermally treated in a chamber furnace (Custom-made, Terna, Slovenia) at 1150 °C for 1 h (with 5 $K{\cdot}min^{-1}$ heating and cooling rates). These annealing conditions were chosen based on the sintering curve of pressed Al_2O_3 pellets at the point where the densification starts (1150 °C). The HM powder was after annealing milled in a planetary mill (PM400, Retsch, Germany) at 200 min^{-1} for 1 h using yttria-stabilized-zirconia milling balls in iso-propanol as a liquid medium. The particle size distribution of the powders was determined by using a light-scattering granulometer (S3500, Microtrac, USA).

The aerosol deposition equipment was provided by Invertech, Germany. The commercial gadolinium substrates (Metall Rare Earth Limited, Hong Kong) were used. A scheme of the AD apparatus is shown in Figure 1. The process parameters during the AD were kept the same for the deposition of all three powders (shown in Table 1).

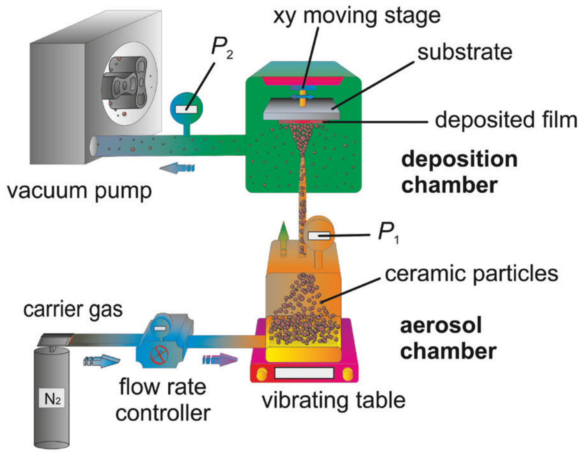

Figure 1: Scheme of the AD apparatus.

Table 1: Process parameters used during the AD.

Process parameters	
P_1	150–250 mbar
P_2	0.2–0.5 mbar
Nozzle geometry (slit size)	$(0.5 \cdot 10)\ mm^2$
Carrier gas species	N_2
Gas flow rate	$4\ L{\cdot}min^{-1}$
Distance between nozzle and substrate	5 mm
Sweep speed	$5\ mm{\cdot}s^{-1}$

The thickness and root-mean-square roughness (R_q) of the prepared layers were evaluated from line profiles measured with a contact profilometer (DektakXT, Bruker, USA) by using the software Vision64 (Bruker, USA). The thickness was evaluated from the step height of the film after curvature removal using a quartic polynomial. R_q was evaluated from the roughness profile obtained after filtering the total profile using Gaussian regression (cut off 0.08 mm).

The alumina powders and thick films were microstructurally analyzed using a field-emission scanning electron microscope (FE-SEM, JSM 7600F, Jeol, Japan). The microstructural analyses of the thick films were made on polished cross-sections.

Prior to the electrical characterization, gold electrodes with a diameter of 1.5 mm were deposited on the top of the film's surface by magneton sputtering (Cinquepascal SRL, Italy). The current density–electric field (*J*–*E*) measurements were made using a Keithley 237 high-voltage-source measurement unit (Keithley Instruments, USA). Each sample was exposed to step-like voltages from negative to positive polarity in the range up to 150 kV·cm^{-1}. The whole measurement consisted of seven equal field steps. The specific direct current (DC) conductivity (σ_{DC}) was obtained at 150 kV·cm^{-1}, assuming Ohm's law.

3 Results

In order to evaluate the characteristics of all three powders used for the deposition experiment we first examined the particle size distribution. Figure 2 shows the particle size distributions (solid line) and the corresponding cumulative curves (dashed line). In the inset the d_{10}, d_{50} and d_{90} values for each powder are collected. According to the literature, the optimal particle size for the aerosol deposition of ceramic powders ranges between 0.2 µm and 2 µm [11,12]. In the R and HM

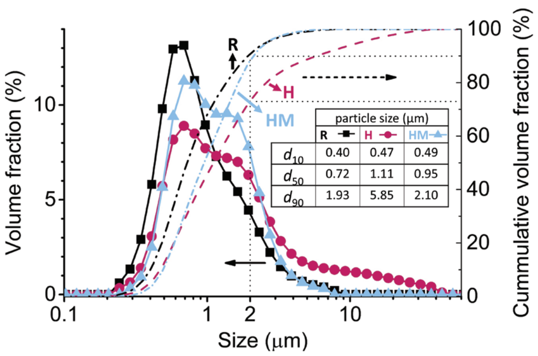

Figure 2: Particle size distributions (solid line) and the corresponding cumulative curves (dashed line) of R, H and HM powders. The d_{10}, d_{50} and d_{90} values of all three powders are presented in the inset table.

powders, 90 vol% of the particles fit well in this range, while in the H powder the percentage of such particles is smaller (i.e., ~75 vol%). This indicates that the R and HM powders could exhibit better deposition characteristics in comparison to the H powder.

The FE-SEM micrographs of the powders are shown in Figure 3. By comparing the R and H powders, it is clear that in the R powder the particles are sharper and more irregularly shaped. The heat treatment causes particle coarsening in terms of merging the small agglomerated particles together and creating necks between them. After heating the particle surface appears smoother.

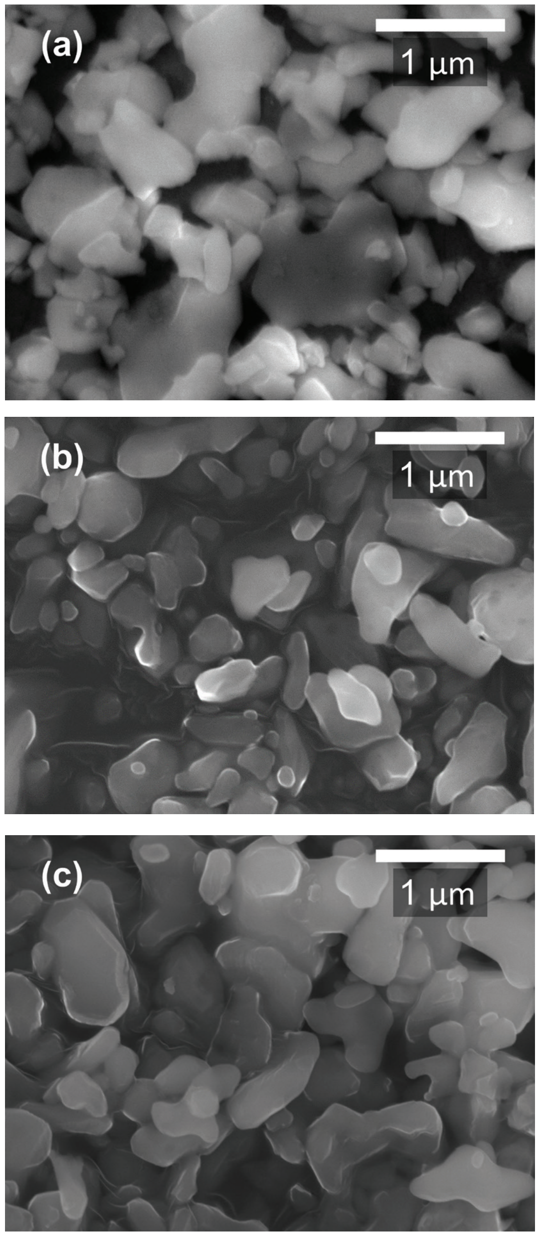

Figure 3: Secondary-electron FE-SEM images of (a) R, (b) H and (c) HM powders.

The additional milling treatment reduces the average particle size (HM powder). However, compared to the particles of R powder, the surface of the HM powder remains smooth and more uniform in size.

After the examination of the powder, all three types of powders were deposited on polished gadolinium elements. The line profiles of the films deposited on the substrates are shown in Figure 4. The H powder has the lowest deposition rate, which is reflected in the very small film thickness (~0.9 µm) and the high surface roughness (R_q ~0.2 µm). On the other hand, the R and HM powders were much more effectively deposited on the gadolinium element, resulting in films with thicknesses of 10.9 µm and 6.4 µm, respectively. Also, the roughness of both films was smaller (R_q ~0.1 µm) compared to the roughness of the film prepared from the H powder.

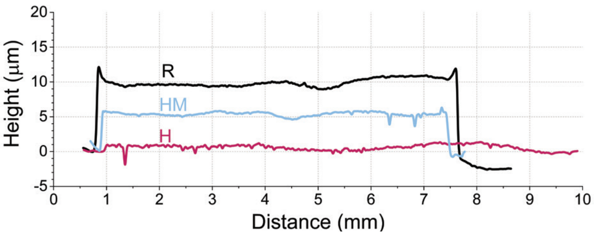

Figure 4: Line profiles of deposited alumina layers on gadolinium elements.

To investigate the electrical conductivity of alumina coatings, *J–E* measurements were performed at room temperature (Figure 5). The films prepared from the H powder (thickness <1 µm) were electrically conductive, and the leakage current was too high to perform the measurements. This enhanced conductivity is most probably the consequence of the non-uniform deposition of the H powder onto the gadolinium substrate

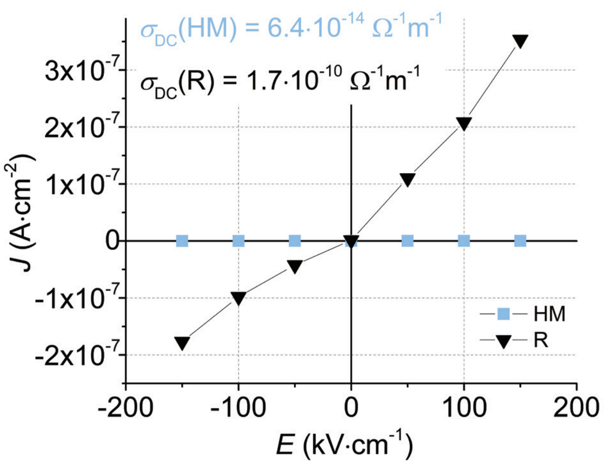

Figure 5: *J-E* curves and calculated σ_{DC} values of thick films prepared from R and HM powders.

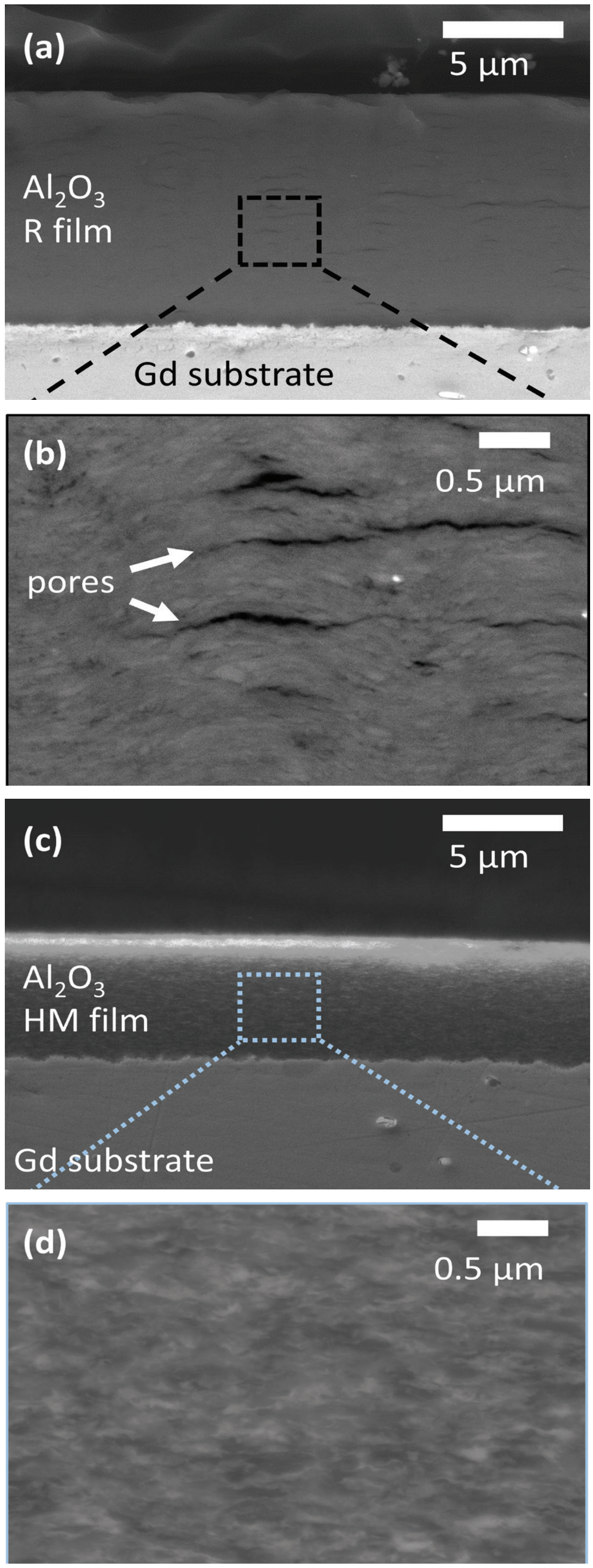

Figure 6: FE-SEM cross-sectional images of thick films prepared from (a,b) R and (c,d) HM powders. The micrographs in Figures (a,c) and (b,d) were taken with a secondary-electron and backscattered-electron detector, respectively.

(Figure 4). The lowest σ_{DC} was obtained in the films prepared from the HM powder, i.e., $6.4 \cdot 10^{-14}\ \Omega^{-1}m^{-1}$, which is comparable to the conductivity of the sintered bulk alumina [20]. The films prepared from the R powder possess a significantly (4 orders of magnitude) higher σ_{DC}, i.e., $1.7 \cdot 10^{-10}\ \Omega^{-1}m^{-1}$.

In order to understand why alumina coatings prepared from R powder are more conductive than those prepared from HM powder, the FE-SEM microstructural analyses of those films in cross-section were performed. The images of the R and HM films are shown in Figures 6 (a,b) and (c,d), respectively. Both the R and HM films exhibit good adhesion to the gadolinium substrate. In Figure 6 (a, c) a larger thickness of the R film in comparison to the HM film (in agreement with line profiles in Figure 4) is revealed, indicating better deposition rate of the R powder. Larger thickness of the layer can also lead to higher probability for defects in microstructures, which could lead to higher conductivity of the sample. Furthermore, a closer look of R film (Figure 6 (b)) reveals micro-sized pores elongated in the horizontal direction. Similar elongated pores were already reported in aerosol deposited alumina films [13]. Such microstructure is most probably the main reason for the high electrical conductivity of these films. On the other hand, the films prepared from the HM powder (Figure 6 (d)) are very dense and pore-free. This indicates better packing of the HM powder during the deposition, in comparison to the R powder, which could be related to the more smooth and uniform size of HM powder. The films prepared from the HM powder possess the lowest electrical conductivity and are therefore the most promising for the protection and electrical insulation of the magnetocaloric elements.

4 Summary and Conclusions

To summarize, the processing of alumina protective layers on magnetocaloric gadolinium elements was studied. The protective coating was prepared by the aerosol deposition technique, which enables the preparation of dense films at room temperature. In order to study the influence of powder size and morphology on the deposition rate, different pre-deposition treatments of the powders were used. The optimal powder treatment includes heating the powder to 1150 °C for 1 h and subsequent milling in a planetary mill. The deposition of such thermally treated and milled powder yielded a dense, few-micrometers-thick alumina protective layer with promising electrical insulation properties (a specific DC conductivity below $10^{-13}\ \Omega^{-1}m^{-1}$).

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6 Conflicts of Interest

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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