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Synthesis of CeO_2 Microcrystals Fabricated on Biaxially Textured Ni-W Substrate by using an E-Beam Evaporation Technique

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Cerium-oxide (CeO_2) microcrystals have been synthesized on a biaxially textured Ni-5%W (200) substrate by using the Electron beam (e-beam) evaporation technique with CeO_2 powder as the source material. The substrate temperature and electron beam gun power at which the microcrystals were formed were 400 °C and 400 W, respectively. The X-ray diffraction (XRD) analysis confirmed the crystallinity and a (111) orientation of the CeO_2 crystals. Scanning electron microscope (SEM) image showed that the CeO_2 crystals had large lateral dimensions in the range from 0.5 to 2.0 μm. The Raman spectrum shows only one peak at 464 cm^{-1} corresponding to the of F_{2g} mode of the CeO_2 crystals. No reports are available on the preparation of CeO_2 crystals with such a large size on textured Ni-W substrate by using e-beam evaporation technique.

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I. INTRODUCTION

Cerium oxide (CeO_2), also known as ceria, is one of the most studied and useful functional rare-earth oxides. It has many potential applications in the field of superconducting, fluorescent, magnetic and catalytic materials, as well as other practical applications such as high oxygen storage, gas sensors, optical devices, and solid oxide fuel cells due to its ability to absorb and release oxygen easily, to exhibit higher ionic conductivity at lower temperatures, *etc.* [1–6]. The optical, electrical, mechanical, catalytic properties of materials are well known to change with changing grain size from nano size to bulk. The growth of rare-earth oxides with large grain sizes, high specific gravities, and high specific surface areas is one of the main directions towards their development and applications [7,8].

Efforts have been putforth by many workers to grow CeO_2 with different crystalline sizes by using several methods. However, most of the work as reported by different researchers is on the synthesis of nano size structures only [9–13], and only a few reports are available on the growth of large-size crystals. As per available literature, large-size CeO_2 crystals have mostly grown by using the flux method [14] and the hydrothermal method [15]. Compare to the hydrothermal method, the flux method requires high temperature and generally brings greater contamination of the flux. Recently, Songling *et al.* have prepared CeO_2 with crystal sizes larger than 20 μm by dipping cerium oxalic acid with the mixed solution of nitric acid and oxalic acid [16]. Ying *et al.* were also prepared CeO_2 crystals with sizes between $50 - 150$ μm by using oxalic acid precipitation, and they studied the effects of the reaction temperatures, the acidity of solution and the aging time [17].

The electron-beam (e-beam) evaporation technique enables deposition of films at temperatures from room temperature to high temperatures, and the films have many advantages like high purity, controlled thickness, and large area uniformity; the films can also be deposited on a wide variety of substrates. Many researchers have reported the deposition of CeO_2 thin films on various substrates such as amorphous glass, quartz, Si (111), Si (100), etc by using the e-beam evaporation technique. On the other hand, some researchers have also reported the deposition of CeO_2 on textured Ni-W substrate by using the same technique and by varying deposition parameters. They have observed the highly intense (111) and (200) orientations of CeO_2 under different optimum conditions. Recently, Lee *et al.* reported that CeO_2 layer had been deposited at a high deposition rate on biaxially-textured Ni-W substrate by using e-beam evaporation [18]. However, no reports are available on the synthesis of CeO_2 microcrystals by using e-beam evaporation technique. In this paper we report the formation of microcrystals of CeO_2 on biaxially textured nickel substrates

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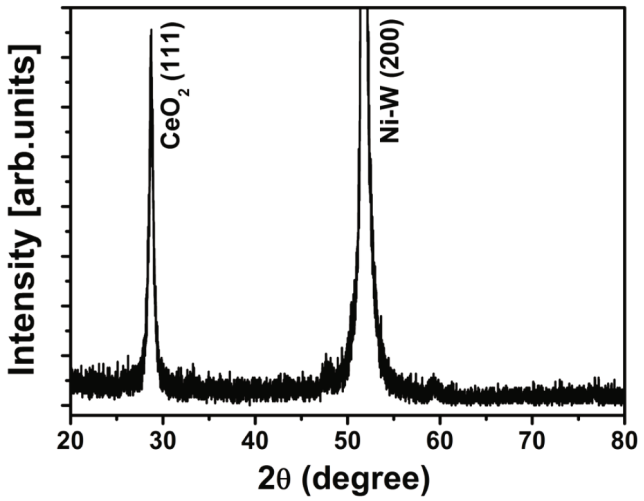

Fig. 1. XRD pattern of CeO_2 microcrystals deposited on biaxially textured Ni-W substrates at a 400 °C substrate temperature and an e-beam gun power of 400 W.

by using the e-beam evaporation technique.

II. EXPERIMENTS

The depositions of the CeO_2 crystals were carried out on biaxially textured Ni-5%W (200) substrate by using an in-house designed and fabricated electron beam evaporation system. We procured biaxially textured Ni-5 at% W (Ni-W) substrates from the manufacturer Evico GmbH, Germany. The substrates had thickness as of 80 μm, surface roughness as < 5 nm and texture $> 98\%$ cubic fraction; the majority of grains had lateral dimension in the range of $50 - 100$ μm. As a source material, CeO_2 powder of 99.99% purity was evaporated from a graphite boat. Prior to deposition, the evaporation chamber was evacuated to a pressure of 2×10^{-6} mbarr by using a diffusion pump backed by a rotary vacuum pump. The substrate temperature and the e-beam gun power were varied from RT to 500 °C and from 200 to 500 W, respectively.

The crystal structure and the phase characterization were carried out with an X-ray diffractometer (model no. D8-Avalance, Bruker, Germany) using Cu Kα radiation at 1.54 Å in the 2θ range from 20° to 80°. The surface morphology was examined by using a scanning electron microscope (SEM) (model no. LEO 400, Oxford Instruments, UK). The chemical composition of the deposited CeO_2 was determined by using an energy dispersive X-ray spectrometer (EDS) attached to the SEM. Raman spectra was measured by using Raman scattering spectroscopy (InVia Renishaw) at room temperature with a 514-nm Ar-ion laser as the excitation source.

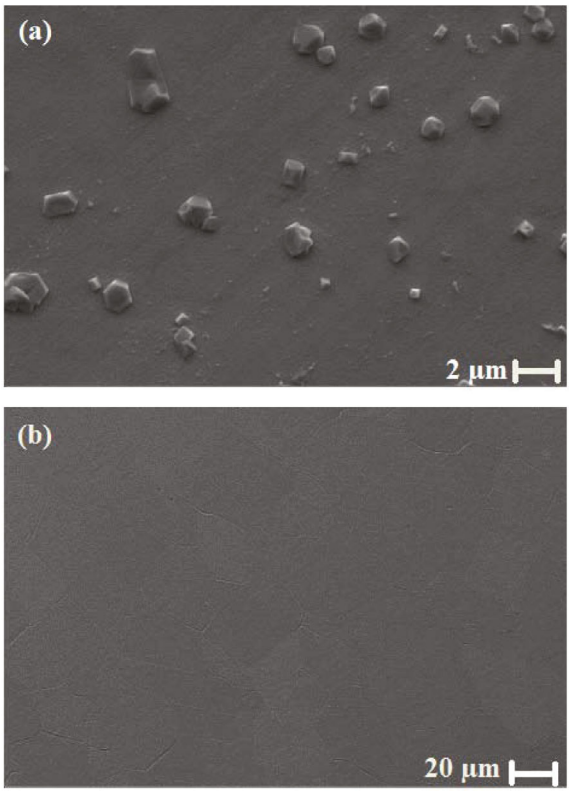

Fig. 2. (a) SEM image of CeO_2 microcrystals deposited on a biaxially textured substrate at a 400 °C substrate temperature and an e-beam gun power of 400 W. (b) SEM image of the textured Ni-W substrate.

III. RESULTS AND DISCUSSION

We prepared a range of samples by using e-beam evaporation at different substrate temperatures from room temperature to 500 °C and at different e-beam gun powers varied from 200 to 500 W. However, the formation of CeO_2 microcrystals was observed only for a substrate temperature on 400 °C and an e-beam gun power of 400 W, so the results are shown for these deposition parameters only. The XRD analysis (Fig. 1) of the as-deposited CeO_2 showed sharp, intense peaks at 2θ values of 28.59° and 51.69°, respectively. The observed peak at $2\theta = 28.59°$ matches the characteristic peak of cubic CeO_2, confirming the crystalline phase of the deposited CeO_2. Accordingly, the single XRD peak of CeO_2 corresponding to the (111) crystal lattice orientation was observed. The other peak matches the characteristic peak of the Ni-W substrate, corresponding to the (200) lattice orientation. The analysis of the peaks in the XRD pattern gave a clear indication that no traces of NiO, Ce metal or any other impurity were present. The formation of the pure CeO_2 is thereby confirmed.

The SEM image in Fig. 2(a) shows the surface morphology of the as-deposited CeO_2 crystals. Large-sized CeO_2 crystals with different sizes can be clearly seen in

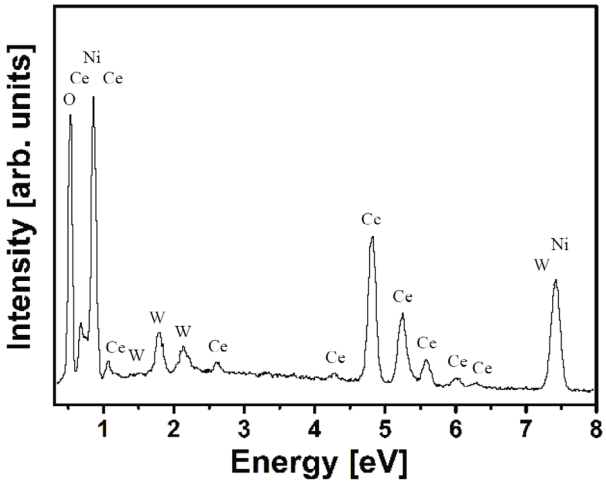

Fig. 3. EDS spectrum of CeO_2 microcrystals deposited on biaxially textured Ni-W substrate at a 400 °C substrate temperature and an e-beam gun power of 400 W.

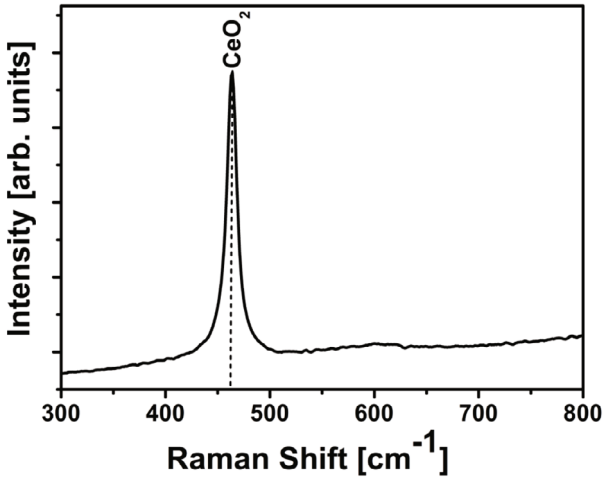

Fig. 4. Raman spectrum of CeO_2 microcrystals deposited on a biaxially textured Ni-W substrate at a 400 °C substrate temperature and an e-beam gun power of 400 W.

the micrograph. From the SEM micrograph the lateral dimensions of the crystals are estimated to be of micron size, lying in the range from 0.5 to 2.0 μm. No reports are available on the formation of CeO_2 crystals with micron sizes by using e-beam evaporation technique. The formation of well-defined CeO_2 crystal facets indicates that the crystals grew following a normal crystallization process rather than simple physical-vapor condensation. The observed very low density of microcrystals also confirms that their formation took following the normal growth mechanism through nucleation sites during the evaporation process. Figure 2(b) shows the surface micrograph of the biaxially textured Ni-W substrate used in this study, and low-angled grain boundaries can be clearly seen. Because the crystals were grown without any catalyst, the crystal formation and growth can be understood based on the vapor-solid (VS) mechanism [19, 20]. Crystal growth by the VS mechanism has two parts: nucleation and growth. In the present case, the grain boundaries on the Ni-W substrate may possible sources for nucleation centers. Thus, in the nucleation process, a seed base consisting of CeO_2 nano-islands is expected to be formed at the grain-boundary. The single oriented crystal formation suggests that only a particular crystalline plane in the grain boundaries favored the nucleation. In the second stage, the CeO_2 flux formed in the vapor phase was continuously deposited on the growth-initiated CeO_2 crystal to grow as big-sized crystal.

The EDS spectrum (Fig. 3) shows peaks corresponding to cerium (Ce), oxygen (O), nickel (Ni) and tungsten (W). The nickel and the tungsten peaks are due to the Ni substrate doped with W. The atomic Ce:O ratio in the deposited cerium microcrystals is found to be 33.33:66.67, confirming unambiguously that the crystals comprise pure CeO_2 only, which is in good agreement with the result obtained from XRD.

Further, we characterized the deposited CeO_2 microcrystals by using Raman spectroscopy performed at room temperature. The Raman spectrum (Fig. 4) shows an intense peak at a frequency of 464 cm^{-1}, which corresponds to the F_{2g} Raman mode of CeO_2. Generally, metal oxides with a fluorite structure, such as CeO_2, have only a single allowed Raman F2g mode. This mode represents a symmetric breathing mode of the oxygen atoms around each cation. The oxygen atom moves in this mode, and its frequency is nearly independent on the cations mass. McBride *et al.* reported that the Raman peak at 570 cm^{-1} was due to oxygen vacancies [20]. Anwar *et al.* observed a defect peak at 565 cm^{-1}, which corresponded to a disorder in the oxygen sublattice (oxygen vacancies) in the samples prepared by using the evaporation technique [22]. They reported that these defect peaks corresponded to disorder in oxygen sublattice more in the film deposited at room temperature and with nanocrystalline size. We have not observed any such peaks due to defects or oxygen vacancies, hence confirming again the formation of a pure CeO_2 phase.

IV. CONCLUSION

We have synthesized pure CeO_2 crystals with micron sizes on textured Ni-W substrate by using the electron-beam evaporation technique at temperature of 400 °C and E-beam gun power of 400 W. The XRD pattern confirms the crystallinity and identifies the phase of the deposited CeO_2 microcrystals. SEM micrographs show the lateral dimensions of the grown microcrystals to be in the range from 0.5 to 2.0 μm. EDS and Raman spectra confirm that the microcrystals comprise pure CeO_2 only.

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