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Preparation of nanocrystalline nickel oxide from nickel hydroxide using spark plasma sintering and inverse Hall-Petch related densification

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ABSTRACT

Nanocrystalline nickel oxide (NiO) was prepared from nickel hydroxide by Spark plasma sintering (SPS) and the mechanisms involved in the densification of NiO were studied. Reverse precipitated nickel hydroxide powders were SPS processed at 400, 600 and 700 °C with 70 MPa pressure. Pure NiO with 12 nm crystallite size formed after 400 °C sintering process. However NiO grains had grown to 18 and 38 nm after 600 and 700 °C sintering respectively. NiO pellets prepared using 600 and 700 °C SPS sintering schedules had relative densities of 83% and 94% respectively. Two displacement rate regimes were observed during densification of NiO in both 600 and 700 °C sintering processes. Decomposition of nickel hydroxide and particle sliding of NiO led to first displacement rate maximum while inverse Hall-Petch based plastic deformation facilitated densification during the constant second displacement rate regime. No densification occurred during sintering holding times indicating the limited role that diffusion played during densification.

1. Introduction

Full densification of oxide materials using low temperatures and less applied pressures is needed to save energy and to realize better components. Nanocrystalline starting materials might help achieving this goal. A variety of sintering processes such as spark plasma sintering (SPS), flash sintering and cold sintering are available to densify oxides [1–3]. Out of these sintering methods, SPS is a versatile technique wherein full densification can be obtained by the simultaneous application of both heat and pressure in vacuum. It was also possible to retain nanocrystallinity after SPS [3]. Wide range of oxide materials with initial particle sizes of 20–200 nm were SPS processed. Consequently, the achieved density was also varying from as low as 50% to as high as 98%, depending upon the applied pressure, sintering temperature, sintering holding time and heating rate [3,4]. However, theoretical calculations had shown that for the same applied pressure and temperature, magnesium oxide with starting grain sizes of lesser than 20 nm would reach full densification in shorter sintering time than their coarser counterparts [5]. Hence it is an interesting proposition to prepare nanocrystalline oxides with less than 10 nm size and to densify those powders into pellet to full density in shorter sintering time. These less than 10 nm grains might also help to achieve full density at lower sintering temperatures and applied pressures while containing the final grain sizes of the sintered pellet at well below 20 nm. The underlying densification mechanisms of these fine nano particles also can be studied. These studies could help develop better microstructures which in turn would lead to improved mechanical and physical properties of various sintered oxide materials systems.

The initial particle size of oxides affects the final relative density and grain size after sintering. It was reported that nanocrystalline particles of yttria partially stabilized zirconia with less than 30 nm grain sizes was produced by chemical synthesis routes such as reverse precipitation [6]. This process involves precipitation of hydroxides and converting them into oxide by high temperature calcination. In general, new phase formation, agglomeration and grain growth occur during calcination. The calcined powders might contain both free particles and also agglomerated particles [6]. The bigger and agglomerated grains would affect the sinterability of oxides, leading to increased porosity levels. Therefore modifications in the calcination process are needed in order to retain very fine nanocrystals and also to attain full density with low temperatures and lesser applied pressures during sintering. In this regard, SPS may be considered for calcination wherein conversion of hydroxide into oxide can be carried out which in turn might produce fine nanocrystals. Later on, densification of the newly formed

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nanocrystalline oxide could be carried out to achieve full density. In this way, both synthesis and densification can be completed in one SPS sintering schedule.

Nickel oxide (NiO) was chosen as a model oxide system in order to show that calcination and full densification may be possible using SPS. NiO is a p-type semiconductor with a wide band gap of 3.2–4 eV and has cubic Rock-salt crystal structure. This material has recently received widespread attention due to its potential application areas such as gas sensors, lithium ion batteries, catalysts, supercapacitors and also inverted perovskite solar cells [7–10]. Yield strength of NiO single crystal increases by $\sim$65% at its Neel temperature due to change in the ferromagnetic ordering [11]. Magnetic anomaly was observed in NiO when the particle size was lesser than 26 nm. As the electrical properties are concerned, NiO is an insulator at room temperature. However, the DC electrical conductivity of 7 nm NiO was two orders higher than their 60 nm counterparts at room temperature [12–14]. Given the magnetic, electronic and functional properties of NiO and its particle size dependence, it is important to prepare nanocrystalline NiO and also to study its densification behaviour in order to fine tune its properties. To the best of our knowledge, this is the first report on preparation of NiO directly from Ni(OH)$_2$ powders using SPS and concurrent densification.

2. Experimental procedures

Ni(OH)$_2$ powders were synthesized by reverse precipitation method. Nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) and NaOH pellets (E-Merck, India) were used as nickel precursor and precipitating agent respectively. A 0.5 M nickel nitrate precursor solution was added drop by drop into 1 M NaOH solution at room temperature. The solution was stirred vigorously throughout the precipitation process and also for an another 2 h after the completion of precipitation process. The resulting precipitates were filtered and washed several times with deionized water and ethanol, followed by drying at 110 °C for 12 h. The dried Ni(OH)$_2$ precipitates were then ground for 15 min with mortar and pestle.

SPS was carried out using graphite dies and punches (SPS, Dr. Sinter). Required quantity of Ni(OH)$_2$ starting powders were poured into a graphite die having 10 mm inner diameter. Graphite foils were used in order to separate the Ni(OH)$_2$ powders from graphite punch surfaces. However, no graphite foil was used between the inner die walls and the powders. Three sintering studies were carried out at the temperatures of 400, 600 and 700 °C using 70 MPa applied pressure. Holding time was 5 min and the heating rate was 50 °C min^{-1}. The temperature was measured using a thermocouple at a hole drilled in the die which was 4 mm away from the sample. A 15 or 25 MPa pressure was applied initially on the Ni(OH)$_2$ powders. Then the applied pressure was gradually increased to a maximum of 70 MPa pressure. This pressure was reached at the sintering temperature and held at that maximum applied pressure during the sintering holding time. Power was switched off immediately after the sintering holding time. However, applied pressure was maintained at 70 MPa until just before the removal of the pellet from SPS chamber. Temperature, applied pressure, ram displacement and vacuum pressure of the SPS chamber were recorded and plotted against time. Displacement rate was derived from ram displacement and time. Density of the NiO pellets was measured using Archimedes technique. Phase analysis was carried out with X-ray diffraction (XRD) using Cu K$_\alpha$ radiation (X′pertPRO, PANalytical diffractometer). A step size of 0.01° and a time per step of 10 s was used. A Si standard was used to determine the instrumental broadening.

3. Results and discussions

XRD pattern of the reverse-strike precipitated Ni(OH)$_2$ powder matched with hexagonal phase, Fig. 1a [15]. Ni(OH)$_2$ powders when sintered at 400 °C, fractured into pieces during the removal of the sample from the die. This was due to the porous nature of the sintered pellet which had low sintered density at the time of removal. Fracture of NiO pellet was also observed when nanocrystalline NiO powders were consolidated with 400 °C and 100 MPa pressure using SPS [16]. The fragmented pieces were ground into powder using mortar and pestle and then XRD was carried out. The powder XRD pattern matched with that of face centered cubic NiO [17]. Ni(OH)$_2$ had fully transformed to NiO after 400 °C sintering, Fig. 1b. There was no change in the crystal structure of NiO after sintering at 600 or 700 °C, except change in the X-ray peak intensity. The first highest intense XRD peak of NiO occurs at a diffraction angle of 43.4°, corresponding to (200) plane. The second highest peak is at 37.2° which corresponds to (111) plane [17]. This closely matched with the XRD pattern of 400 °C sample, Fig. 1b. As the sintering temperature increased, intensity reversal occurred among planes. In 600 °C pellet, (111) was the first highest intense peak while (200) was the second highest. The trend continued also in 700 °C sintered pellet. This indicated the occurrence of preferred orientation in < 111 > direction. It was reported that substrate temperature dependent preferred orientation occurred during electron beam physical vapour deposition (EBPVD) of NiO [18]. It was also shown that preferential orientation occurred in < 200 > direction at a substrate temperature of 100 °C whereas < 111 > and < 220 > directions had shown preferential orientation at 450 °C [18]. Thermal energy available for nucleation and growth of NiO films was less at lower temperatures, leading to preferential growth in < 200 >. However, the higher thermal input energy altered the grain

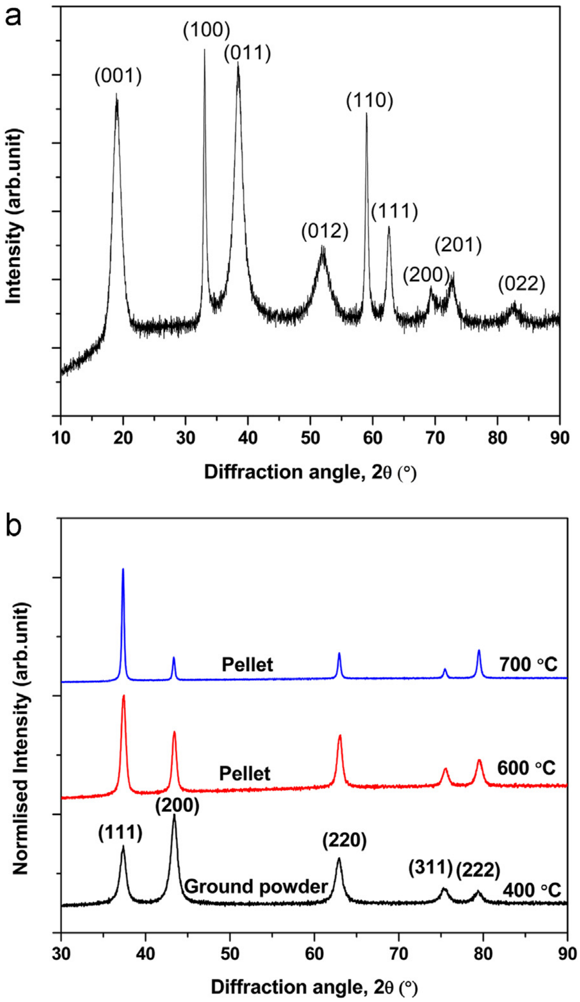

Fig. 1. (a) XRD pattern of nickel hydroxide powder, (b) XRD patterns of NiO which was SPS processed from 400° to 700 °C, showing preferred orientation in (111) plane.