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On the spinel formation in $Co_{1-x}O/Co_2TiO_4$ composites via reactive sintering, exsolution and oxidation

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Abstract

The formation mechanism and microstructural development of the spinel phases in the $Co_{1-x}O/Co_2TiO_4$ composites upon reactive sintering the $Co_{1-x}O$ and TiO_2 powders (9:1 molar ratio) at 1450 °C and during subsequent cooling in air were studied by X-ray diffraction and analytical electron microscopy. The Co_2TiO_4 spinel occurred as inter- and intragranular particles in the matrix of Ti-doped $Co_{1-x}O$ grains with a rock salt-type structure during reactive sintering. The submicron sized Co_2TiO_4 particles were able to detach from grain boundaries in order to reach an energetically favorable parallel orientation with respect to the host $Co_{1-x}O$ grains via a Brownian-type rotation/coalescence process. Upon cooling in air, secondary Co_2TiO_4 nanoparticles were precipitated and the Ti-doped $Co_{1-x}O$ host was partially oxidized as $Co_{3-\delta}O_4$ spinel by rapid diffusion along the {1 1 1} and {1 0 0}-decorated interphase interface and the free surface of the composites.

Keywords: A. Firing; B. Defects; B. Impurities; Cobalt oxides

1. Introduction

The formation mechanism and microstructural development of spinel phases in oxide composites prepared by a sintering route are of concern to their engineering applications. In binary oxide systems with considerable solid solubility, the spinel can be formed by solid-state precipitation from a protoxide of rock salt-type structure or alternatively by reactive sintering of the end members. For example, in the $NiO/NiAl_2O_4$ composite prepared by reactive sintering NiO and Al_2O_3 powders with a negligible extent of nonstoichiometry, the $NiAl_2O_4$ spinel was found to precipitate as micron-sized plates having {1 0 0} habit plane and parallel epitaxial relationship with the rock-salt type host, i.e. Al^{3+}-doped NiO [1]. The $NiAl_2O_4$ spinel also occurred as equi-axed particles, which tended to detach from grain boundaries in order to reach parallel epitaxial relationship with respect to the host via a Brownian-type rotation/coalescence process of the confined particles at high temperature [2]. In binary transition metal oxide systems with rather limited solid solubility yet with varied charges of cations, it is of interest to know whether or not the spinel can be precipitation/oxidation tailored as nanoparticles from the protoxides, besides the formation of much larger sized inter- and intragranular particles via a reactive sintering route.

Here, the $Co_{1-x}O$–TiO_2 binary having the protoxide $Co_{1-x}O$ and the Co_2TiO_4 spinel with negligible mutual solid solubility [3] was chosen for the study. By careful scrutiny of phases and microstructures in the $Co_{1-x}O/Co_2TiO_4$ composites prepared by a reactive sintering route from the $Co_{1-x}O$ and TiO_2 powders, the combined effects of Ti^{4+} exsolution and cobalt oxidation to form spinel nanoparticles from the protoxide $Co_{1-x}O$ upon cooling in air were clarified. We focused also on the reorientation of the inter- and intragranular Co_2TiO_4 spinel particles via a Brownian-type rotation/coalescence process analogous to the cases in other ceramic composites prepared via a solid-state sintering route [2,4–8] or oxidation decomposition route [9].

2. Experimental

CoO (Cerac, 99.5%) and TiO_2 (Aldrich, 99.9%) powders 9:1 in molar ratio were mixed by a magnetic stirrer in ethanol at

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50 °C for 2 h followed by drying at 70 °C and grinding with an agate mortar and pestle. The powder mixture thus prepared was dry-pressed at 650 MPa into pellets ca. 5 mm in diameter and 2 mm in thickness. The pellets were then reactively sintered at 1450 °C for 0.5 h and 4 h followed by quenching in air.

The phases of the as-fired samples were studied by X-ray diffraction (XRD, CuKα, 40 kV, 30 mA, SIEMENS D5000) with a step scanning of 0.05° and fixed counts of 3 s per step in the 2θ range of 15–110°. Lattice parameters of the crystalline phases were determined by least squares fit using the computer software. The deviation of lattice parameters was determined as ±0.0002 nm.

The fired composites were polished and then thermally etched at 1300 °C for 5 min to reveal the grain boundaries using a scanning electron microscope (SEM, 20 kV, JSM-6400, JEOL) under back-scattered electron image (BEI) mode. Energy dispersive X-ray (EDX) analysis was used to analyze the composition of the co-existing phases.

The thin sections of the fired pellets were argon-ion milled to electron transparency and studied by analytical electron microscopy (AEM) using JEOL 3010 instrument at 300 kV for imaging and EDX analysis. The K-shell counts of Co and Ti without absorption correction [10] were used for the semi-quantitative determination of composition at the scale of individual grains. Bright field image (BFI), dark field image (DFI), lattice image and selected area electron diffraction (SAED) taken by transmission electron microscopy (TEM) were used to identify the phases.

3. Results

3.1. XRD

XRD traces (Fig. 1) indicated that the composite fired at 1450 °C for 0.5 h consists of Ti-doped $Co_{1-x}O$ protoxide, $Co_{3-\delta}O_4$ spinel and Co_2TiO_4 spinel with room temperature lattice parameters of 0.4259, 0.8073 and 0.8417 ± 0.0002 nm, respectively. The cell parameters are significantly smaller than the undoped cases, i.e., 0.4260 nm for $Co_{1-x}O$ (JCPDS#09-0402), 0.8084 nm for $Co_{3-\delta}O_4$ (JCPDS#42-1467) and 0.8435 nm for Co_2TiO_4 (JCPDS#39-1410), respectively, indicating a considerable extent of dissolution of smaller-size Ti^{4+} in the phases. The Ti-doped $Co_{1-x}O$, $Co_{3-\delta}O_4$ and Co_2TiO_4 showed little change of lattice parameters upon further aging at 1450 °C for a total of 4 h (Fig. 1).

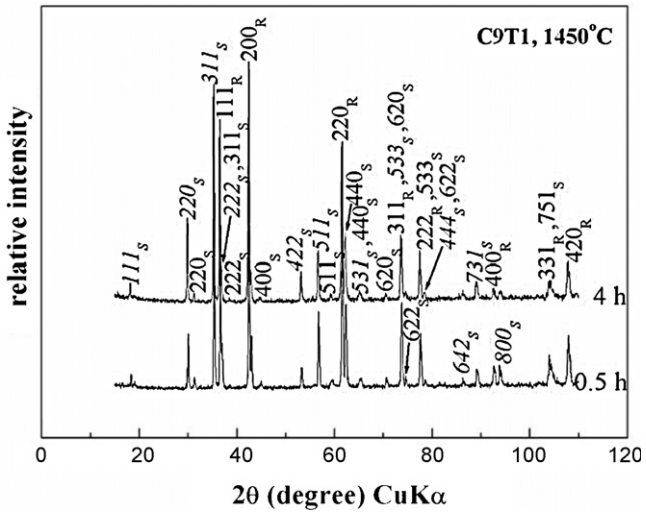

Fig. 1. XRD traces of the samples reaction sintered at 1450 °C for 0.5 h and 4 h followed by air-quenching to room temperature showing the rock-salt structure peaks of $Co_{1-x}O$ (denoted as $(h\,k\,l)_R$), $Co_{3-\delta}O_4$ (denoted as $(h\,k\,l)_S$) and Co_2TiO_4 (denoted as italic $(h\,k\,l)_S$).

3.2. SEM

The specimen reaction-sintered at 1450 °C for 0.5 h showed triple grain junctions characteristic to solid-state sintering despite the presence of intergranular pores (Fig. 2a). The composite actually consists of inter- and intragranular (smaller-sized) Co_2TiO_4 spinel, which gave darker contrast than the host $Co_{1-x}O$ grains in BEI mode. A longer firing time (4 h) at 1450 °C resulted in more intergranular pores and caused considerable coarsening and coalescence of the $Co_{1-x}O$ grains up to ca. 20 μm in diameter according to BEI in Fig. 2b. The size of the intergranular Co_2TiO_4,

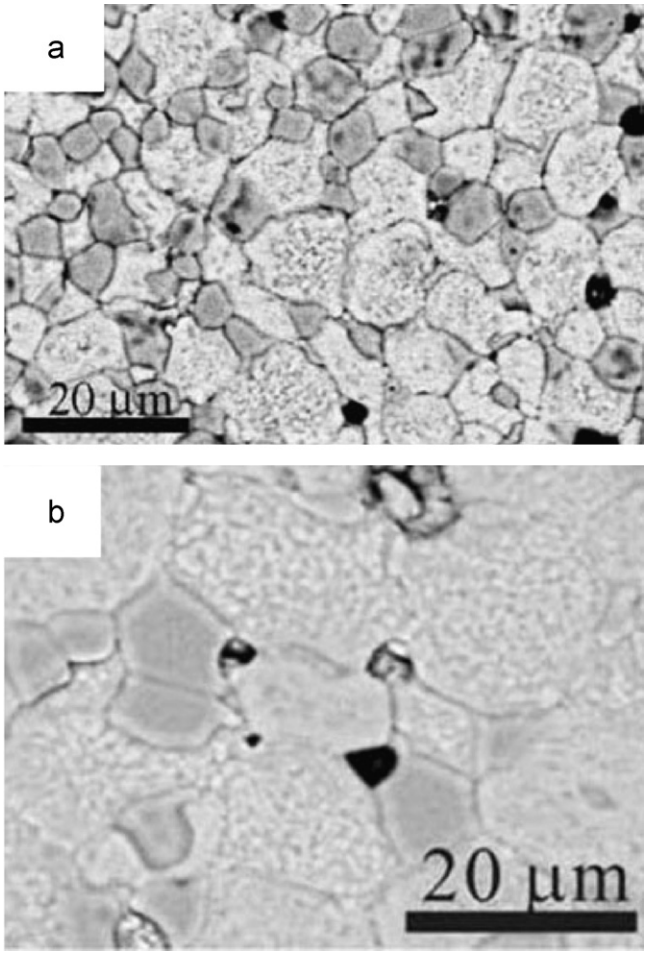

Fig. 2. SEM BEI of the composites fired at 1450 °C for (a) 0.5 h and (b) 4 h showing microstructures characteristic to solid-state sintering, intergranular pores and the Co_2TiO_4 (gray) and $Co_{1-x}O$ (bright) grains.