Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 2634–2641

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microstructure development in novel titania–cobalt ferrite ceramic materials

Pietro Galizia, Carlo Baldisserri, Carmen Galassi*

CNR -ISTEC, Via Granarolo 64, I-48018 Faenza, Italy

Received 7 August 2015; received in revised form 13 October 2015; accepted 13 October 2015
Available online 20 October 2015

Abstract

The system cobalt ferrite (CFO)–titania (TO) has been studied in view to produce new in situ ceramic composites by conventional solid state reaction. To synthesize the CFO–TO composite, the processing parameters are optimized to yield a reliable and repeatable homogeneous distribution of the phases. Composition, crystalline structure and microstructure of the sintered bodies were investigated by XRD, SEM, microprobe analysis; the image analysis was performed to quantify the phase volume content and grain size. The final compositions after sintering differ significantly from the starting ones as a consequence of the reaction of titania with the ferrite and the formation of a new ternary compound $Fe_2CoTi_3O_{10}$ (FCTO). In this work we report for the first time the preparation of almost pure (about 95 vol%) single phase FCTO ceramics, its XRD patterns, and the microstructural characterization.

Highly densified and homogeneous composites were obtained with two to three phases combined. Four different phase distributions are shown, depending on the starting cobalt ferrite content.

Keywords: Solid state reaction; In situ ceramic composite; Ternary compound; Microstructure characterization

1. Introduction

Heterostructures based on ferrites and titanates have been developed in several different combinations of compositions and microstructures. Nowadays oxide heterostructures have received increasing attention as they often let to devise new applications by tuning or enhance certain properties [1]. In this view composite materials [2,3] have been thoroughly investigated and among them ferrites and their composites with dielectric, ferroelectric, piezoelectric materials are currently hot topic, in search of better properties. For example magnetodielectric composite materials have attracted increasing attention for their application as substrates for miniaturization and efficiency enhancement of antennas [4] while magnetoelectric composite materials are of interest in the smart manufacturing and mechatronics fields as actuators/transducers, sensors, non-volatile memories, etc. [5]. A growing number of papers have addressed the topic in search of compositions and microstructures matching the required combination of parameters for the different working conditions, including magnetodielectric, magnetoelectric or, in general, multifunctional materials with tailored macroscopic properties.

Composite materials combining ceramic phases let to modulate different magnetic/dielectric/ferroelectric properties by controlling the composition, microstructure and interface formation. The properties of the composite are affected by the number, type and volume ratio of the constituent phases, and may turn out to be an average, a superposition, or a more complex combination of the properties of the phases. It has been reported that the properties of these materials can be influenced by the degree of interconnectivity and by specific interfacial phenomena [6–8]. Microstructure characterization of the sintered ceramics in terms of number, type and volume ratio of the phases, grain size distribution, degree of interconnectivity, interfaces and porosity, is crucial to understand how they influence the functional properties and to achieving specific values of final properties [9–10].

*Corresponding author. Tel.: +0039 0546 699750.
E-mail addresses: pietro.galizia@istec.cnr.it (P. Galizia), carlo.baldisserri@istec.cnr.it (C. Baldisserri), carmen.galassi@istec.cnr.it (C. Galassi).

http://dx.doi.org/10.1016/j.ceramint.2015.10.069
0272-8842/

A fundamental role in the structure and properties of ceramics is played by starting composition mixture, shaping and densification processes. By varying the degrees of chemical affinity a composite with the same starting phases, or with entirely new phases can be obtained. The preparation routes must be carefully controlled in order to get two-phase or multi-phase composites with good phase distribution and high density, and with proper microstructure correlated with the functional properties.

We focused our attention on cobalt ferrite ($CoFe_2O_4$) and titanium oxide (TiO_2), that have been investigated intensively for decades owing to their excellent magnetic and dielectric properties: high coercivity and magnetostriction coefficient for the CFO [11,12], high static dielectric constants which increase with decreasing temperature obeying a modified Curie–Weiss law, high refractive index, incipient ferroelectricity and low-loss dielectric properties for TO respectively [13–16]. However, to the best of our knowledge, no one has investigated the reactivity of TiO_2 and $CoFe_2O_4$ mixtures heat treated at temperatures much higher than about 600 °C, at which the anatase-to-rutile conversion generally occurs, no does considerable literature exist documenting the properties of the compound $Fe_2CoTi_3O_{10}$ resulted from the reaction at high temperature of the two starting materials. The combination of such materials can be regarded as a useful, preliminary approach in the search of novel multifunctional materials for many applications. Moreover it is of most interest as a study of the cobalt ferrite titanium oxide reactivity, propaedeutic to the investigation of the interaction between titanates with ferrites as very often, at least limited reaction between the two phases significantly influence the final properties of the composite material.

In this work, we focus on the preparation and microstructural characterization of ceramic composites obtained starting from TiO_2 and $CoFe_2O_4$ powder mixtures. The samples were prepared by the conventional solid state reaction process, with TO/CFO molar ratios from 0.73 to 11.75. In this paper we report the study of the reactions and the resulting phases depending on the starting CFO/TO ratio. Microstructure and composition of the composites have been intensively studied and are discussed here.

2. Materials and methods

Cobalt ferrite (CFO) powders with $CoFe_2O_4$ composition were obtained by reacting Co_3O_4 (nanopowder Aldrich 637025), and Fe_2O_3 (Aldrich nanopowder 544884) powder mixtures at 800 °C for 4 h, and then performing planetary milling of the calcined products in ethanol medium for 2.5 h using zirconia jar with 250 cm^3 volume, zirconia balls of 5 mm of diameter and a fixed speed of 400 rpm. The milling media to powder mass ratio was 4:1. The pure crystalline CFO powders were mixed with commercial TiO_2 powder (Degussa P25) according to the compositional scheme $(100-x)TO-xCFO$, with $x=0$, 20.0, 30.0, 33.5, 40.0, 44.0, 49.5, 57.2, 80.0 and 100 wt%.

In Table 1 the starting compositions of the samples are reported as weight and molar percentages of the starting CFO content and the corresponding TO/CFO molar fraction. The correlation between samples' IDs and initial percent weight of CFO (x) is also shown.

Powder mixtures were wet ball-milled, dried and subjected to cold linear pressing at 70 MPa to produce 30 mm diameter, 2–3 mm thick disks. Isostatic pressing at 250 MPa was applied to the disks to obtain green homogeneous CFT bodies, which were then sintered in air at 1200 °C for 2 h. A constant heating rate of 150 °C/h was employed to reach the sintering temperature plateau, and the sintered samples were brought back to room temperature by natural cooling of the furnace. After sintering, the ceramic bodies were ground to remove the surface layers in order to ensure a reliable X-ray diffraction analysis.

The particle size measurements of the as calcined CFO powders and the postmilled ones-in terms of equivalent spherical diameters based on settling velocity ('velocity ESD')-were determined with a Micromeritics SediGraph 5100. Samples were prepared by diluting 1.50 g of CFO powder in 75 mL of 0.1 M Calgon dispersing solution, giving a sample concentration of 20 g l^{-1} ($\approx 0.4\%$ by volume) and then sonicated for 1 min immediately before analysis. The data collection was made with standard Micromeritics software (version 2.00) and the density distribution was calculated as the derivative of the measured cumulative mass percentage with respect to the velocity ESD (particles size) and was approximated using finite intervals [17]. The formation of the new phase FCTO from titania and cobalt ferrite was studied by differential scanning calorimetry (DSC), using a Netzsch STA 409 calorimeter, increasing the temperature of the TO–CFO stoichiometric powder mixture-held in an alumina crucible with the reference alumina powder-up to 1200 °C at the heating rate of 3 °C/min.

Phase compositions of the calcined and sintered samples and their relative phase volumes were determined by combining SEM, EDS and XRD data. XRD patterns were obtained at room temperature on a Bruker D8 X-ray diffractometer ($\theta-\theta$) using Cu Kα radiation in the range $15° \le 2\theta \le 70°$ and a 2.4°/min scanning rate. The average crystallite sizes were calculated using Debye Scherrer formula $D=(k\lambda/\beta\cos\vartheta)$, where D is the

Table 1
Starting compositions of the materials.

Sample identification	Starting CFO (wt%)	Starting CFO (mol%)	TO/CFO (mol/mol)
TO	0	0	-
CFT20	20	7.84	11.75
CFT30	30	12.73	6.85
CFT33	33.5	14.65	5.83
CFT40	40	18.50	4.41
CFT44	44	21.07	3.75
FCTO	49.5	25.00	3.00
CFT57	57.2	31.29	2.20
CFT80	80	57.66	0.73
CFO	100	100	0