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Compositionally graded YSZ–NiO composites by surface laser melting☆

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Abstract

Laser surface melting has been applied to near eutectic NiO–YSZ sintered ceramics. The objective is to generate a functional gradient composite material with graded microstructure and composition. At low solidification rates the resultant material has a graded composition, with a severe NiO segregation towards the surface. A thick NiO layer whose thickness depends on the travelling speed is formed. Below this layer the microstructure is eutectic like with composition varying with depth. In contact with the ceramic, excess YSZ coming from the hypereutectic composition forms an almost continuous YSZ layer. The thickness of both segregated layers, NiO and YSZ can be controlled by traverse speed. Thickness decreases as travelling speed increases until a limiting travelling rate of 110 mm/h, at which no more segregation is found. Possible causes to explain the relevant NiO segregation towards the surface are discussed.

Keywords: NiO; YSZ; Eutectics; Laser surface melting; Functional gradient material

1. Introduction

The fabrication of in situ composites by solidification of oxide eutectics (DSEO) has been the subject of strong attention in the last decade due to the excellent mechanical properties they presented. This is particularly true for the eutectics with Al_2O_3 as a component and with fine and homogeneous microstructure.[1–4] Directional solidification allows size control over the final microstructure, and being that an advantage, other applications different than the structural ones have been proposed: single crystalline porous matrix,[5] photonic materials[6] or metal–ceramic composites with particularly stable interphases.[7]

Laser melt processing of materials is also a well-known subject among technologist and material scientist working with metals.[8] Its application to ceramics is scarcer[9–11] as ceramics tend to be fragile, and special attention has to be paid to handle the processing thermal stresses. The procedure we are interested in generates a surface dense crystallised eutectic composite on top of a dense[11] or porous[12] eutectic ceramic, with the same or different compositions.[13] Applications of the procedure exist in all areas where dense and smooth thick ceramic covering layers are required: erosion and abrasion resistance, wear resistance, etc. Other modifications as in surface tube remelting, can be used to generate different geometries, useful for example to produce filter tubes with enhanced surface catalytic activity (due to its nanometer size porous microstructure[14]).

Surface remelting of eutectic oxides results normally in a graded microstruture[10,12] with average homogeneous composition. Sometimes, however, we have observed macroscopic segregation. For example, in laser surface remelting of $CaZrO_3$–CaSZ eutectic at 100 mm/h,[15] a $CaZrO_3$ single phase surface layer is observed, accompanied by a graded composition below it. It goes from 100 vol% $CaZrO_3$ at the surface to an eutectic like microstructure 62 vol% $CaZrO_3$–38 vol% CaO stabilized ZrO_2 at 200 μm below the surface and down to the ceramic. A similar behaviour was observed by Yoshikawa et al.[16] on Al_2O_3–YAG thin fibers produced by the micropulling down method. They report a self-cladding of YAG on the Al_2O_3–YAG core eutectic. When solidifying slightly YSZ rich YSZ–Al_2O_3 hypereutectics, we have observed that the first solid phase to

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deposit at the interface with the ceramic is YSZ. Size and compositionally graded materials have also been found in the realization of laser cladding and laser alloying of metals.[17,18]

In the following we present the results of the surface laser melt processing of YSZ–NiO near eutectic ceramics at different solidification rates. The starting composition was slightly enriched in YSZ to generate a continuous dense YSZ electrolyte layer separating the porous ceramic substrate from the composite resolidified layer. The objective of this work is primarily to establish the conditions upon which a graded composition is attained for this mixture and explore its physical origin. The second objective is to evaluate its applicability as a single-step procedure to create eutectic – thin YSZ – eutectic three-layer structure for possible uses, particularly in the field of solid oxide fuel cells.

2. Experimental details

Porous ceramic plates were prepared by colloidal processing. Starting powders of NiO (99.99% from Aldrich) were attrition milled for 5 h in isopropanol with zirconia milling balls. 58.28 wt% of this NiO powder and 41.72 wt% YSZ (yttria-stabilized zirconia) from Tosoh (TZ-8YS, grain size 0.25 μm) were mixed and an extra 1.8 wt% graphite powder (Alpha Aesar 99%, particle size <45 μm) added to create porosity, and dry mixed. The powder mixture was added to a solution prepared with H_2O and ethanol as solvents and PVA (15000 molecular weight, 81381 Fluka). The suspension was stirred and ultrasonicated several times. Finally, the slurry was slip cast on to plaster moulds, allowed to dry overnight, and then sintered. The ceramic plate thickness was from 2 to 3.6 mm, and cut to stripes around 7 mm width. Final density was 80%. The microstructure of the ceramic consists of fine and dispersed grains of NiO and YSZ, as well as dual porosity.

Laser surface melting was performed with a high power diode laser from Rofin-Sinar (940 nm wavelength) as described elsewhere.[11] The sample was preheated by placing it on a metallic support that was kept at 1080 °C during processing. An almost homogeneous intensity laser line with size $w_x = 10$ mm (along X direction) and $w_y = 1$ mm (along Y direction) is focussed on the surface of the sample that travelled along the Y direction at a fixed traverse speed. Laser powers of 60–70 W were used (that is, fluences of 600–700 W/cm^2), and traverse speeds from 10 to 500 mm/h.

Scanning electron microscopy was used to observe the samples microstructure, using a JEOL 6400 Scanning Electron Microscope (SEM) equipped with a Link Analytical X-ray detector for microanalysis by energy dispersive spectroscopy (EDS).

3. Results

3.1. Microstructure

In Fig. 1 we give SEM micrographs of transverse (XZ) polished cross-sections of samples processed at increasing laser scanning rates from 20 to 500 mm/h. At rates below 100 mm/h, primary YSZ (bright phase) has nucleated and deposited near to the interface with the unmelted, underlaying ceramic; and a layer of NiO (dark phase) has been formed on the free upper surface. The thickness of these single phase layers increases as processing rate decreases. A closer view of the upper layer is presented in Fig. 2 for two slow processing rates. One can observe

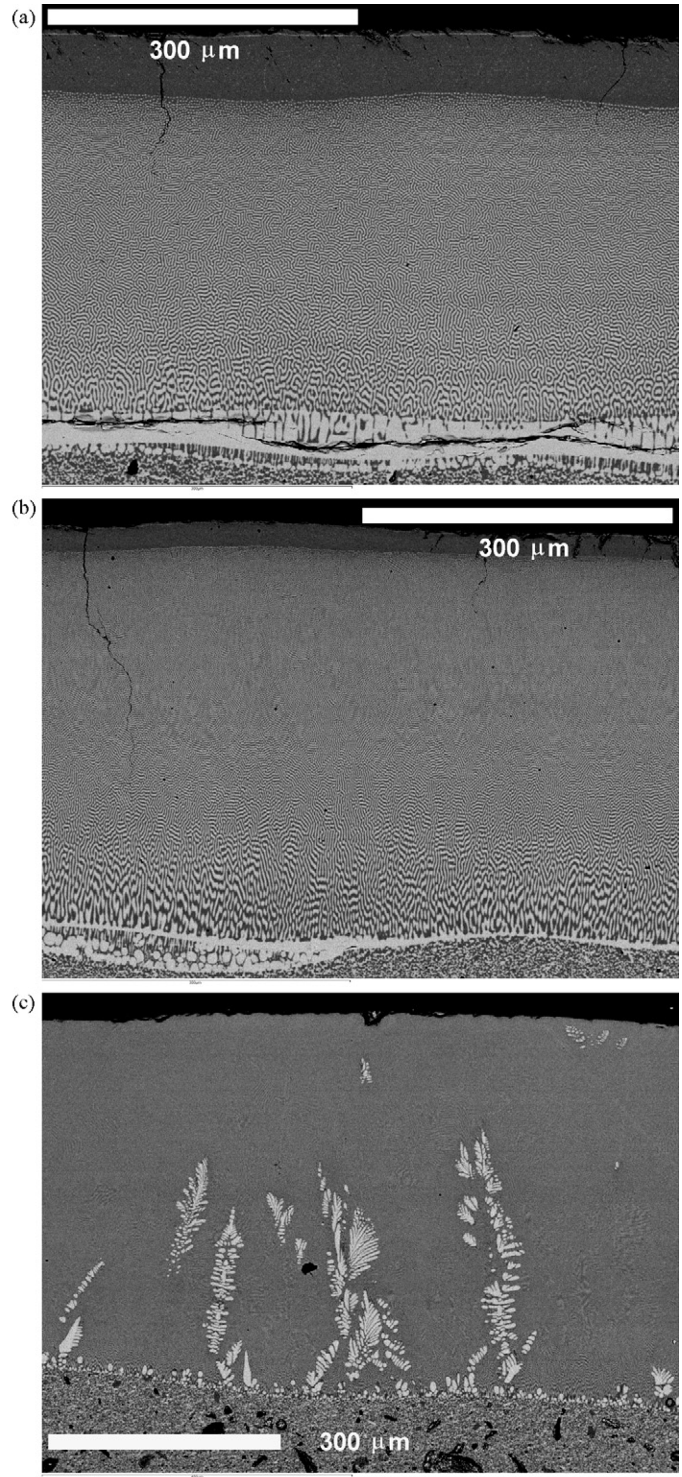

Fig. 1. SEM micrographs of polished transverse cross-sections of laser melt samples processed at increasing traverse speeds: (a) 20 mm/h; (b) 60 mm/h, and (c) 500 mm/h. Bright phase: YSZ; dark: NiO.