Experimental observations of the co-sintering of porous triple-layer SOFCs including curvature evolution

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Abstract

Triple-layer co-sintering of SOFCs results in an improved production process via reduced time and effort. Understanding the sintering shrinkage behaviour of each porous layer during the co-sintering process leads to the minimisation of mismatched stresses along with avoidance of severe warping and cracking. In multilayer structure, sintering behaviour is mainly characterised by the in-plane properties rather than the thickness properties. The induced in-plane stresses contribute to curvature evolution in the structure, which can be utilised in the design of a SOFC.

In this paper, sintering mismatch stresses have been analysed in bi- and triple-layer structure. Materials used are Ni-CGO for anode; CGO for electrolyte; and LSCF for cathode. These materials are tape-casted with 20μm thickness and assembled for multilayer structure by hot pressing. Bilayers, consisting of Ni-CGO/CGO and CGO/LSCF, were co-sintered up to 1200°C. The largest sintering mismatch stress was calculated at interface of bi-layer structure in the upper layer. In-situ observation, to monitor the shrinkage of each material and the curvature evolution of the bi-layer, is performed using a long focus microscope, Infinity K-2. With these values, the main factors such as viscosity; shrinkage rate of each material; and curvature rate are investigated to determine the sintering mismatch stresses. That enables the prediction of curvature for triple-layer structure and the prediction is validated by in-situ monitoring of the triple-layer structure co-sintering.

The monitored results enabled the suppression of curvature development in the triple-layer structure during co-sintering. In addition, the study investigates how stress evolution affects microstructure (i.e. grain size, porosity) using SEM images. The sintered structure with porosity is utilised in the development of single-chamber SOFC.

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1. Introduction

Triple-layer co-sintering of SOFCs results in an improved production process via reduced time and effort. Understanding the sintering shrinkage behaviour of each porous layer during the co-sintering process leads to the minimisation of mismatched stresses along with avoidance of severe warping and cracking. In multilayer structure, sintering behaviour is mainly characterised by the in-plane properties rather than the thickness properties. The induced in-plane stresses contribute to curvature evolution in the structure.

In this study, sintering behaviour has been analysed in bi- and triple-layer structures. With these values, the main factors such as viscosity, shrinkage rate of each material, and curvature rate are investigated to determine how these factors affect the curvature evolution of the structures during co-sintering. That enables the prediction of curvature for triple-layer structure and the prediction is validated by in-situ monitoring of the triple-layer structure co-sintering. The sintered structure with porosity is utilised in the development of single-chamber SOFC.

2. Experimental procedure

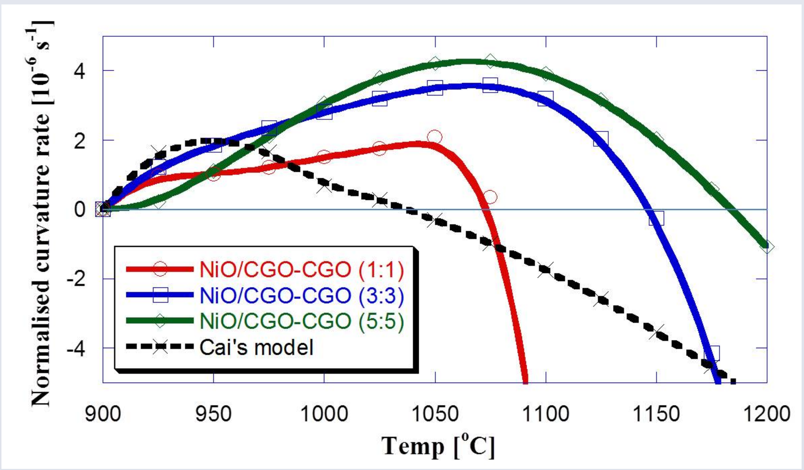
- NiO/CGO (0.3µm) for anode, CGO (0.3µm) for electrolyte, LSCF (1µm) for cathode
- Single layer: Tape-casted with 20µm thickness
- Multi-layer assembly by hot pressing under 5MPa, 50C, 5min
- Bi-layers (NiO/CGO-CGO and CGO-LSCF) and triple-layer (NiO/CGO-CGO-LSCF)
- Sintering process: 1°C/min to 750°C, and then 3°C/min to 1200°C, holding 15mins
- Curvature monitoring by a long focus microscope, Infinity K-2

Why experimental observation?

❖Typical models including Cai's for curvature of bi-layer structure

(m: thickness ratio, n: viscosity ratio, $\Delta\dot{\varepsilon}$: strain rate difference between layers)

$$\dot{k} = \left[\frac{6(m+1)^2 mn}{m^4n^2 + 2mn(2m^2+3m+2)+1}\right]\Delta\dot{\varepsilon}$$



In the bi-layer structures with same thickness ratio of 1, the curvature evolutions were different during the co-sintering process

Necessary to monitor the curvature evolution of the multi-layer structure during the co-sintering process as well as their final shapes

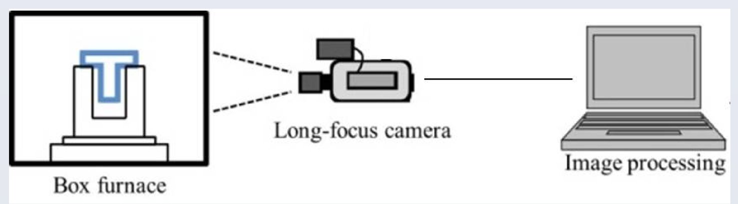


Fig. 1 In-situ monitoring for shrinkage measurement and curvature evolution

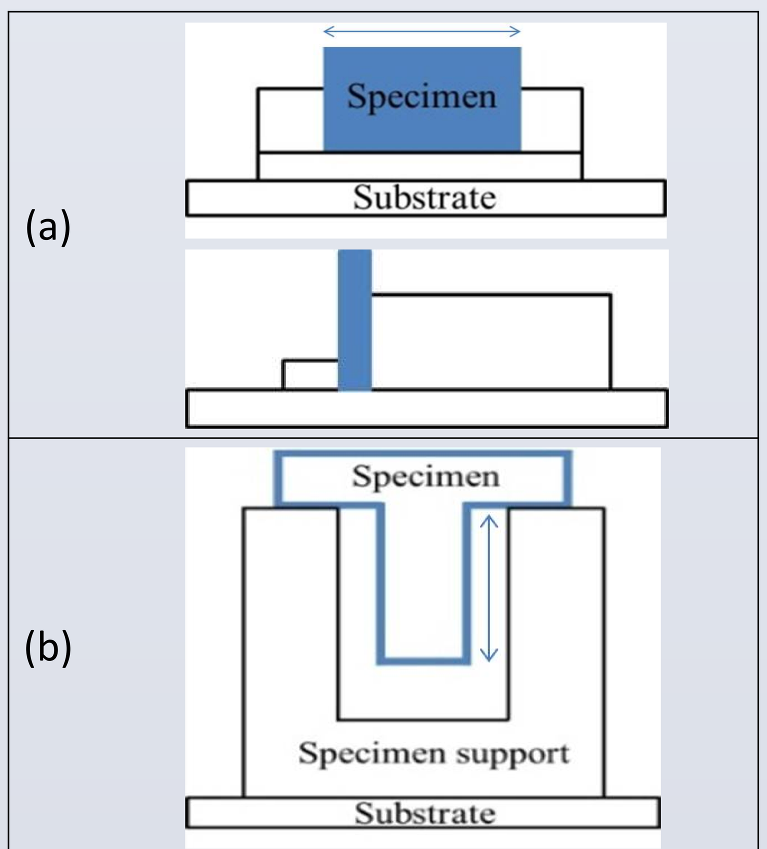


Fig. 2 Shrinkage measurement; (a) free sintering, and (b) vertical sintering

3. Results

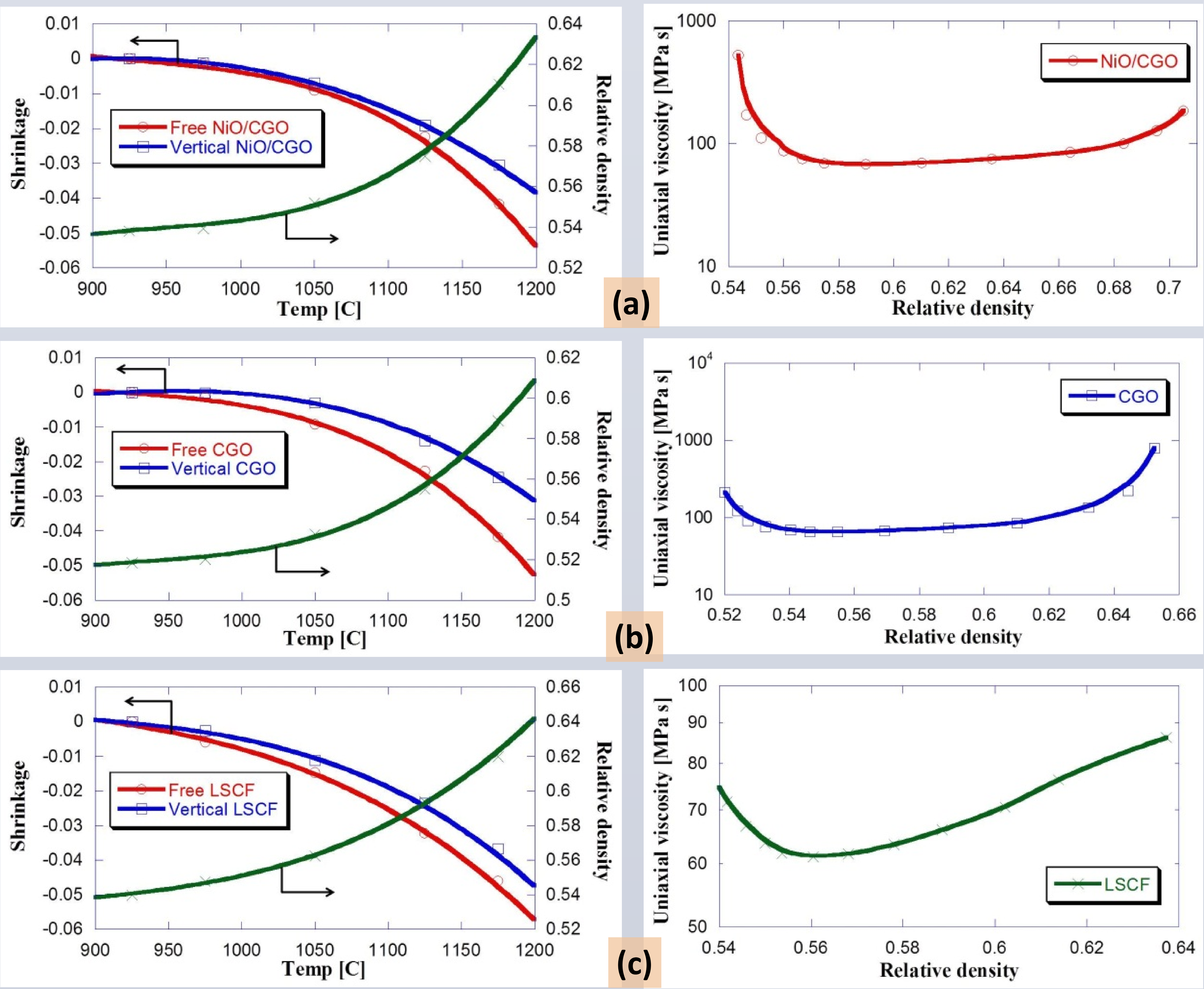


Fig. 3 Plots showing shrinkage and relative density vs. temp. and viscosity vs. relative density of each material; (a) NiO/CGO-CGO, (b) CGO, and (c) LSCF

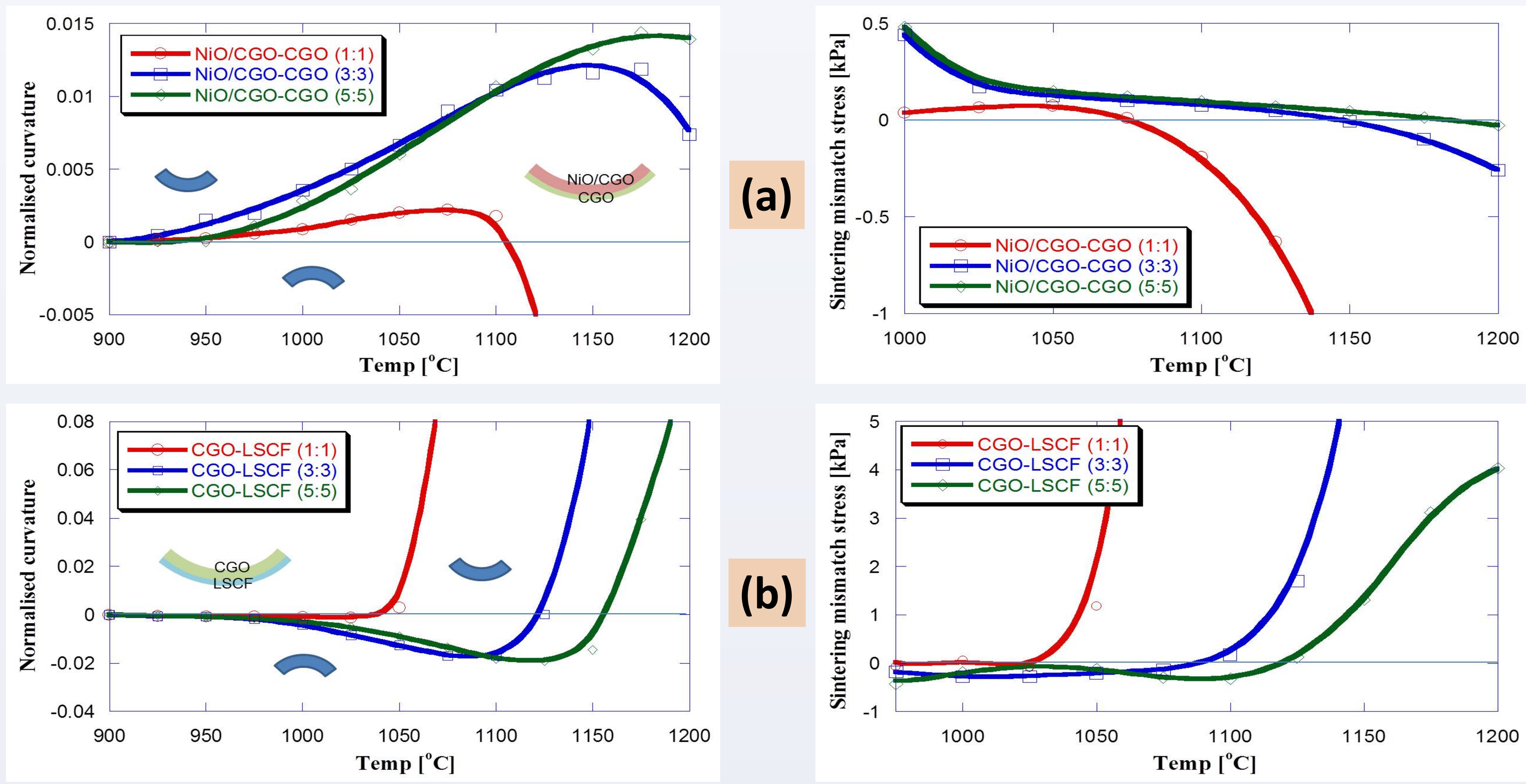


Fig. 4 Curvature evolution and mismatch stress of bi-layer structures; (a) NiO/CGO-CGO and (b) CGO-LSCF

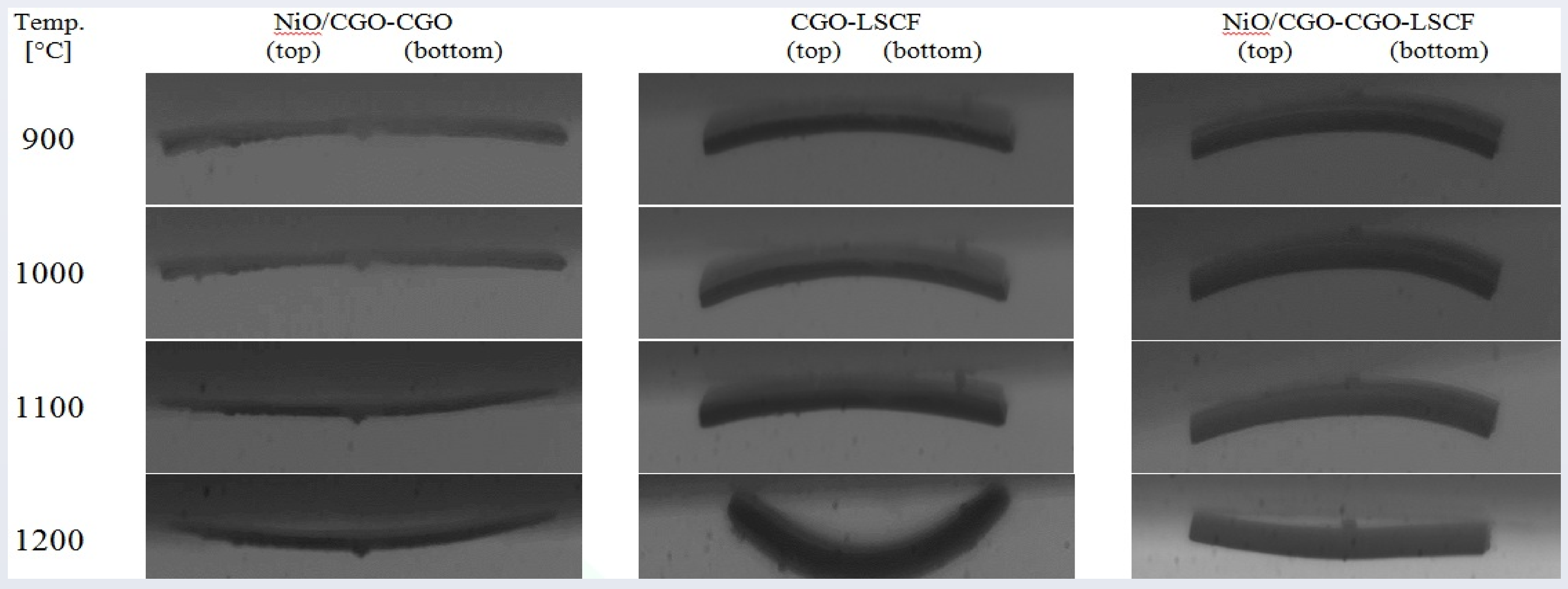


Fig. 5 Curvature evolution of bi-layer structures; (a) NiO/CGO-CGO, (b)CGO-LSCF, and (c) NiO/CGO-CGO-LSCF

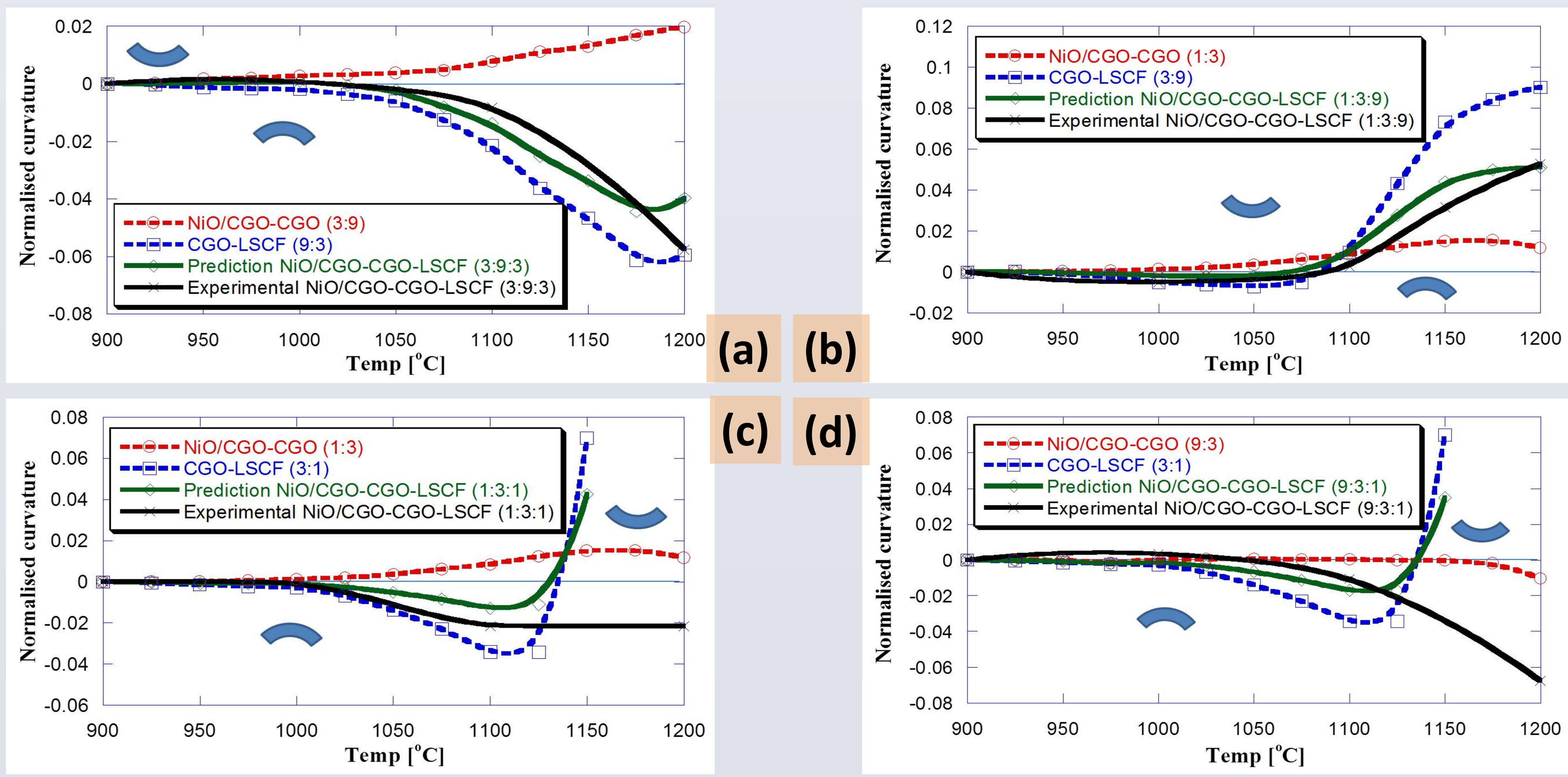


Fig. 6 Curvature evolution of triple-layer structures (NiO/CGO-CGO-LSCF) consisting of (a) 3:9:3, (b) 1:3:9, (c) 1:3:1, and (d) 9:3:1

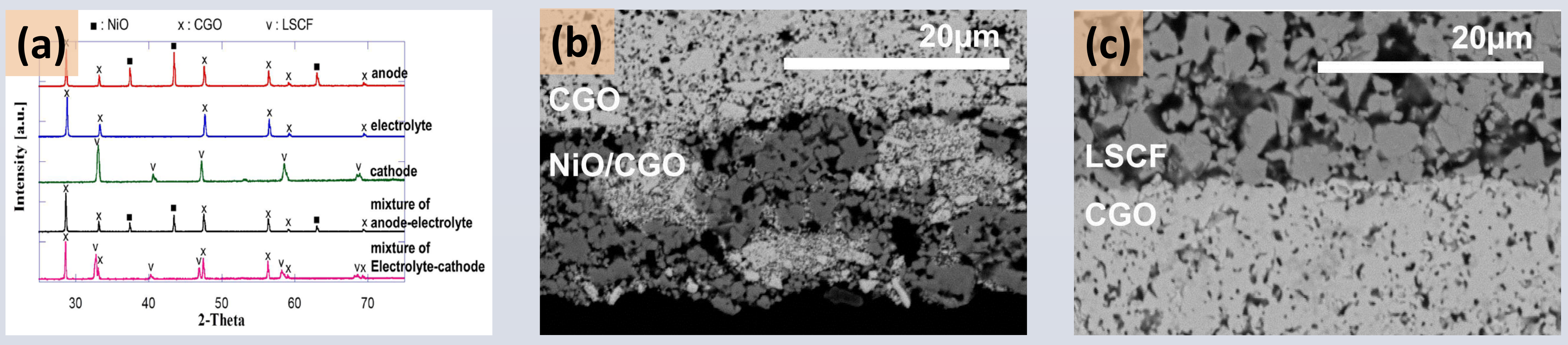


Fig. 7 (a) XRD result of triple-layer structure, (b) and (c) cross sectional image at interfaces

4. Discussions and Conclusions

- In order to measure uniaxial viscosity of each material, shrinkage measurements were carried out by in-situ monitoring in free and vertical sintering
- Curvature evolution of bi- and triple-layer structure during co-sintering was influenced by not only mechanical stiffness from total thickness but also sintering behaviour related with initial density, shrinkage rate and viscosity
- Successfully demonstrated curvature prediction of a triple-layer structure, based on bi-layer curvature observations
- During the co-sintering of porous triple-layer structure, no defects were observed and the whole layer had similar final density due to different initial conditions
- In XRD results, it was confirmed that third phase formation was not occurred during co-sintering
- SEM images showed that layers were well adhered to the adjacent layer, and no delamination was detected
- These results will be utilised for fabrication of wavy SC-SOFCs using the co-sintering of the triple-layer structure

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