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Original Article

Kinetic and thermodynamic effects of manganese as a densification aid in yttria-stabilized zirconia

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ABSTRACT

This work demonstrates the role of Mn as an effective sintering aid in Yttria-Stabilized-Zirconia (YSZ) is a result of the concomitant reduction of activation energies and change of interfacial energies caused by Mn segregation. Kissinger analyses of the heat of sintering showed a decrease in activation energy from 219.9 kJ/mol for YSZ to 103.4 kJ/mol for YSZ containing 3-mol% Mn. Direct microcalorimetry analyses showed that the average surface and grain boundary energies of YSZ decreased from 0.94 and 0.71 J/m^2, respectively, to 0.70 and 0.17 J/m^2 for 3-mol% Mn doped YSZ. The decrease in the ratio between surface and grain boundary energies indicates an increase in dihedral angle from 137.5° to 166.6°, meaning an increase in sintering stress. Segregation of manganese to grain boundaries was experimentally observed and is discussed to be responsible for both kinetic and thermodynamic changes in the system while suggesting interconnection by the thermodynamic extremal principle.

1. Introduction

Yttria-Stabilized-Zirconia finds commercial application as solid electrolytes for Solid Oxide Fuel Cells (SOFCs) [1,2]. YSZ powders typically require at least 1350 °C of sintering temperature in order to attain dense compacts (> 95% if theoretical density) [3]. Lowering this sintering temperature can allow better processing compatibility with the other components of the SOFCs and reduce production costs and device reliability. Transition metal oxides (TMOs), such as Mn, Fe, Co and Ni, have been found to be effective sintering aids for zirconium dioxide [4–8]. However, fundamental understanding on how these additives function is still lacking, while holding the key to allow improvement of composition and processing design and additive selection for other oxide systems.

Manganese has been shown to promote densification and lowering of sintering temperature for ceria [9–12], tin dioxide, and zirconia [1,13,14]. The explanation for the observed effects is mainly based on enhancement in diffusion by creation of excess of oxygen vacancies at high temperatures due to the reduction of manganese and consequent defect generation for charge balancing [15,16]. However, in zirconia the slowest diffusing elements are the cations [17], and an increase in oxygen vacancies is not obviously related to the cationic mobility. It has been then proposed that an increase in oxygen vacancies could distort the lattice and affect defect–defect interactions that could be responsible for an increase in total diffusion [6,18,19].

Even though diffusion can be enhanced by additives and dopants, it is generally not clear why specific densification mechanisms are activated in doped oxides. For instance, in doped SnO$_2$, manganese is proposed to change sintering mechanism from a non-densification mechanism, evaporation-condensation, to grain boundary diffusion [20]. There is no evidence for such claim other than the fact Mn is segregated to interfaces [16,21,22], and therefore a mass-transport change is potentially expected. In zirconia, it has been suggested that the densification of Mn-doped and pure YSZ are both dominated by volume diffusion, and Mn is mostly responsible for a reduction in sintering activation energy [13], as a result of incorporation of Mn ions into YSZ lattice. However, this conclusion was based on fitting of growth data rather than direct observation, and goes against evidences of segregation of Mn to the grain boundaries of YSZ, which would imply activation of a grain boundary diffusion mechanism.

Sintering mass transport mechanisms are dependent on mass sink, source and diffusion path in the system [23,24]. Curvature differences between the particle and the neck are typically described as the local driving forces for mass flow. However, it is acknowledged that the difference in chemical potential in between atoms from the grain boundaries and from the surface (or bulk) of the particle is a more accurate description as the gradient for mass flow [25]. This implies that the surface and the grain boundary energy also play a role in

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sintering, and could be directing specific mass transport mechanisms. Lange et al. have proposed the role of interfacial energies on the densification of materials in terms of sintering stress [26–29]. The dihedral angle, defined as the equilibrium angle formed at the plane where two surfaces and one grain boundary meet, was recognized as a key parameter during microstructural evolution in sintering [26–29]. In theory, large dihedral angles would be linked to high sintering stresses (potentially causing more densification) as compared to small dihedral angles; or in other words, the lower the ratio of grain boundary energy to surface energy is, the stronger the tendency to densification in both early and late stages of sintering [30]. By doing sintering simulations, Wakai et al. have also confirmed that densification is directly dependent, and may potentially be controlled by, interfacial energies [31].

Therefore, the role of dopants on the interface energetics shall also be regarded as relevant for sintering evolution in addition to kinetic parameters [16,23]. When dopants are added into an oxide particle, they may form solid solution, nucleate a second phase, or segregate to interfaces while keeping the crystalline structure of the host material. If the dopant shows spontaneous segregation, according to Gibbs formalism [16,32], there should be an effective lowering of the interfacial energies [33–35]. Therefore, since the driving forces for densification and grain growth are directly related to those excess energies [23], it is reasonable to assume that changes of interfacial energies with dopant segregation can directly affect sintering stress.

In the present study, the effects of Mn as a sintering aid in YSZ nanoparticles are systematically studied for dopant concentrations ranging from 1 to 3 mol% evaluating both kinetic and thermodynamic parameters. High surface area nano-powders were prepared by co-precipitation synthesis method to assure homogeneous samples. Powder compacts were sintered at different temperatures and times to perform a kinetic study, and nanopowders were subjected to microcalorimetric studies to determine interfacial energies. The results suggest manganese favors grain boundary diffusion mechanism while changing the ratios of interfacial energies, increasing the dihedral angle and hence the sintering stresses.

2. Experimental procedures

2.1. Powder synthesis

10YSZ and Mn-doped 10YSZ (1/2/3 mol% dopant + 99/98/97 mol % 10YSZ) were prepared by co-precipitation using nitrates as cationic precursors. Zirconium(IV) oxynitrate hydrate (Sigma-Aldrich, 99%), yttrium(III) nitrate hexahydrate (Alfa Aesar, 99.999%), and manganese (IV) nitrate tetrahydrate (Acros, 99.9%) were dissolved into deionized water (D.I. water) in the appropriate molar fraction to prepare the cation solution. This solution was slowly dripped into an ammonium hydroxide solution (3 times excess than stoichiometric amount for guaranteeing all cations react simultaneously). Nanocrystalline hydroxide precipitates were immediately formed as the cations reacted with the base. These hydroxide precipitates were washed once with water and three times with anhydrous ethanol. Precipitates were separated from solutions by centrifugation and dried in an oven at 90 °C for at least 48 h. The samples were then grinded before calcination in a box furnace (Lindberg blue M, Thermo scientific) at 450 °C for 2 h to obtain oxide nanoparticles.

2.2. Sintering studies

The sintering studies were carried out using fast firing [36]. Nanoparticles were pressed into pellets in 10 mm diameter tungsten carbide die by uniaxial pressing at 50 MPa, then were further pressed using Cold Isostatic Pressing (CIP) (CIP-20TZ, MTI Corporation) at 300 MPa. Green relative densities of pressed pellets were measured geometrically as 30.11% ± 0.11. During fast firing in a tube furnace, the pellets are pre-heated in marginal region of the tube for 1 min (measured to have temperature of 300 °C), and then rapidly inserted into central high temperature isothermal region with heating rate estimated at 500 °C/min (Lindberg blue. M, Thermo scientific). Samples were left at isothermal region at target temperature (1100 °C–1300 °C) for different times and air quenched by removing them from the tube furnace into air within 30 s.

2.3. Characterization of powders and sintered samples

The synthesized nanopowders were characterized by X-ray diffraction (XRD) using a Bruker-AXS D8 Advance X-ray diffractometer (Bruker AXS Inc. Madison, USA) with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) operated at an accelerating voltage of 40 kV and an emission current of 40 mA for initial crystallite size analysis and crystalline structure. The surface areas were measured by Brunauer–Emmett–Teller (BET) method using Micromeritics ASAP 2020 apparatus (Micromeritics, Norcross, GA). Density of pellets was measured by relative density (RD), defined as the ratio of experimental density, measure by Archimedes' method, to theoretical density (ρ_T), calculated with lattice parameter experimentally determined by XRD whole profile fitting.

Sintered samples were analyzed using scanning electron microscopy (SEM) on fracture surfaces. SEM was conducted using a FEI 430 Nano-SEM instrument, FEI Company, Hillsboro, Oregon. The grain size was measured by the line intercept method. Phase composition of the sintered samples was also analyzed by XRD.

The chemical surface analyses for the Mn-doped 10YSZ samples were performed by X-ray photoelectron spectroscopy (XPS) using a conventional XPS spectrometer (Omicron) with a high-performance hemispheric analyzer (EAC2000) with monochromatic Al Kα ($h\nu = 1486.6$ eV) radiation as the excitation source. The operating pressure in the ultra-high vacuum chamber (UHV) during the analysis was 10^{-9} Pa. The XPS high resolution spectra were recorded at 20 eV pass energy, 0.05 eV per step. The data analysis was performed using CasaXPS software (Casa Software Ltd., UK).

2.4. Differential scanning calorimetry – interfacial energies and activation energies

Differential scanning calorimetry (DSC 404 F1 Pegasus, Netzsch Instruments, Selb, Germany) was used to measure the "heat of sintering" and determine both grain boundary and surface energies. The method relies on the measurement of the heat evolved during densification and grain growth of a compacted powder. The integrated heat effect is associated with the quantified microstructural evolution to enable separation of contributions from grain boundaries and surfaces. In summary, although during sintering mass transport mechanisms are activated, from an energetic perspective, the process consists of surface area elimination and grain boundary area formation followed by elimination by grain growth. Therefore, if one can assure that during sintering of a compact inside a DSC the measured heat does not have other contributions other than sintering itself (avoiding heats of desorption of water or other molecules pre-adsorbed on the surface of the particles, heats of redox reaction of one or more of the elements, or heats of evaporation [37]) or it is corrected for any parallel reactions, the measured heat can be singularly attributed to the interface area change, and therefore interface energies calculated with good reliability [37–39].

In a typical procedure, a green compact was heated up to 900 °C in the DSC at a heating rate of 20 °C/min, and maintained under high purity argon atmosphere for 30 min to assure a stable manganese oxidation state [40] and elimination of any water (or other molecules such as CO_2) content from the sample. Thermogravimetry has demonstrated that for temperatures above 900 °C there is no mass change in the sample. The sample was then quenched and both grain size and surface area measured. This state is formally defined as "State 1". Another pellet of the same composition was similarly heated up to 900 °C in the