**On the Thermodynamic Stability and Microstructure
of Variably Cooled and Co-doped $\text{Y}_2\text{O}_3\text{-ZrO}_2$ for
Application to Thermal Barrier Coatings**

by

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ABSTRACT

For application to thermal barrier coatings (TBCs), ytterbia (Yb_2O_3), ceria (CeO_2) and niobia (Nb_2O_5) are investigated for their effect as co-dopants on the stability of 7 wt% yttria (Y_2O_3) stabilized zirconia (ZrO_2), known as 7YSZ. Zirconia TBCs must be stabilized to prevent transformations between cubic fluorite (f), tetragonal (t) and monoclinic (m) phases during operation, since the latter causes cracking and failure. However, with an increasing use of co-dopants, very little data exists on the cooling rate sensitivities of the stabilizing mechanisms involved. Together with microstructural effects, this is the focus of the current study. It is found that slower cooling rates consistently result in more m phase formation, and are therefore not desirable in general. Further, lattice distortions are the most sensitive mechanism to cooling rate, and oxygen vacancies are the least sensitive. The addition of Yb_2O_3 stabilizes f phase by dilative lattice distortions and the production of oxygen vacancies. CeO_2 stabilizes t phase with similar distortions and also produces metastable oxygen vacancies which are retained depending on cooling rate. Nb_2O_5 results in more m phase by annihilating oxygen vacancies produced by Y_2O_3 . Microstructural analyses additionally reveal that m, t and f phases can be identified qualitatively according to whether a crack produces intergranular, textured transgranular, or smooth transgranular fracture through grains, respectively. A mostly connected network of porosity of up to 16 vol% is also revealed in the manufactured ceramics, and improvements are suggested based on sintering theory.

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TABLE OF CONTENTS

List of Tables.....	viii
List of Figures.....	ix
Nomenclature.....	xvii
1 Introduction	1
1.1 Development of Zirconia Coatings	2
1.2 Yttria as a Stabilizing Dopant	4
1.3 Design Philosophy for New Coatings	5
1.4 Thesis Objectives	6
2 Literature Review and Relevant Theory	8
2.1 Zirconia	8
2.1.1 Atomic Bonding Characteristics and Polymorphism Overview	8
2.1.2 Crystal Structures	11
2.1.2.1 Monoclinic (m)	12
2.1.2.2 Tetragonal (t)	15
2.1.2.3 Non-transformable Tetragonal (t')	16
2.1.2.4 Cubic Fluorite (f)	18
2.2 Zirconia Stabilization	19
2.2.1 Mechanisms of Phase Stabilization	19
2.2.1.1 Trivalent Dopants	22
2.2.1.2 Tetravalent Dopants	24

2.2.1.3	Pentavalent Dopants	26
2.2.2	Predicted Effect on Tetragonality	27
2.3	Yttria Stabilized Zirconia (YSZ)	28
2.3.1	The Yttria-Zirconia Phase Diagram.....	28
2.3.2	Identification of 7YSZ.....	30
2.3.3	Phase Transformations.....	31
2.3.3.1	Diffusion-controlled Cubic to Tetragonal ($f \rightarrow t$)..	32
2.3.3.2	Displacive Cubic to Tetragonal ($f \rightarrow t'$)	37
2.3.3.3	Martensitic Tetragonal to Monoclinic ($t \rightarrow m$)	41
2.3.4	Phase Morphologies	49
2.3.4.1	Monoclinic (m)	49
2.3.4.2	Tetragonal (t)	52
2.3.4.3	Non-transformable Tetragonal (t').....	55
2.4	Strength and Toughness of Zirconia Ceramics	60
2.4.1	Transformation Toughening.....	60
2.4.2	Ferroelasticity.....	65
2.5	Bond Coat Interlayer and Thermally Grown Oxide	69
2.6	Coating Deposition Technologies.....	72
2.6.1	Plasma Spraying (PS).....	73
2.6.1.1	Optimal Process Parameters.....	75
2.6.1.2	Microstructure Development.....	75
2.6.1.3	Stress State	77
2.6.1.4	Coating Stiffness	78
2.6.1.5	Performance Evolution	79

2.6.2	Electron Beam Physical Vapour Deposition (EB-PVD)	82
2.6.2.1	Microstructure Development.....	84
2.6.2.2	Stress and Stiffness.....	90
2.6.2.3	Performance Evolution	92
2.7	Pressing and Sintering of Ceramic Powders	94
2.7.1	Cold Powder Pressing	95
2.7.1.1	Definition of Packing Density	95
2.7.1.2	Effect of Particle Shape	95
2.7.1.3	Effect of Particle Size.....	97
2.7.1.4	Additives	98
2.7.1.5	Pressing Pressure	99
2.7.2	Solid State Sintering	100
2.7.2.1	Driving Forces and Sintering Mechanisms	101
2.7.2.2	Stages of Sintering	104
2.7.2.3	Initial Stage (Neck Formation)	104
2.7.2.4	Intermediate Stage	106
2.7.2.5	Effect of Agglomerates and Green Density.....	110
2.7.3	Diffusion.....	111
2.7.3.1	Fick's Laws	112
2.7.3.2	Diffusion in a Sphere	114
2.7.3.3	Grain Boundary Diffusion.....	114

3 Experiments 116

3.1	Overview	116
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3.2	Co-dopant Selection.....	119
3.2.1	Ytterbia	119
3.2.2	Ceria	120
3.2.3	Niobia.....	120
3.3	Co-doped Compositions.....	121
3.3.1	Yb:7YSZ	122
3.3.2	Ce:7YSZ	123
3.3.3	Nb:7YSZ	124
3.3.4	Summary of Accumulative Stabilizing Mechanisms	125
3.4	Powder Preparation.....	126
3.5	Uniaxial Cold Pressing	129
3.5.1	Additive Selection	130
3.5.2	Pressing Pressure and Green Integrity	131
3.5.3	Twelve Step Pressing Process	133
3.6	Sintering and Variable Cooling.....	135
3.7	Bulk Density Measurements.....	137
3.8	Grinding and Polishing	138
3.9	Scanning Electron Microscopy (SEM).....	139
3.10	Porosity Measurements.....	140
3.11	Grain Size Measurement.....	141
3.12	X-ray Diffraction (XRD).....	143
3.13	Energy Dispersive X-ray Spectrometry (EDS).....	144
3.14	Hardness and Modulus Testing.....	145

4	Results and Discussion	147
4.1	Condition of Sintered Disks	147
4.2	Phase Retention of Sintered Samples.....	149
4.2.1	XRD Results	149
4.2.2	Analysis of 7YSZ.....	155
4.2.3	Stability of Co-doped Compositions	159
4.2.3.1	Yb:7YSZ	159
4.2.3.2	Ce:7YSZ.....	161
4.2.3.3	Nb:7YSZ.....	163
4.2.4	Stabilizing Mechanisms	164
4.2.4.1	Cooling Rate Sensitivity.....	164
4.2.4.2	Relative Effectiveness	166
4.3	Elemental Distributions.....	167
4.3.1	Origin of Segregation	168
4.3.2	Effect of Segregation	169
4.4	Sintered Microstructures	169
4.4.1	As-pressed Surfaces.....	169
4.4.2	Fracture Surfaces	171
4.4.3	Polished Surfaces	174
4.5	Porosity, Grain Size and Bulk Density.....	175
4.6	Mechanical Properties.....	178
4.6.1	Expected Effect of Co-dopant Properties.....	180
4.6.2	Expected Effect of Retained Phases.....	180
4.6.3	Observed Effect of Porosity	180

4.6.4	Net Properties of Compositions	181
4.6.4.1	7YSZ.....	181
4.6.4.2	Yb:7YSZ	182
4.6.4.3	Ce:7YSZ.....	182
4.6.4.4	Nb:7YSZ.....	183
5	Conclusions	184
6	Recommended Future Work	186
	List of References	188
	Appendix A: Mixture Calculations.....	200
	Appendix B: Detailed Compositions.....	202
	Appendix C: Die Set Drawings	204

LIST OF TABLES

Table 1 – General crystallographic information	11
Table 2 – Dense random packing density for various particle shapes [99]	96
Table 3 – Summary of samples produced.....	117
Table 4 – Analysis techniques and prepared samples investigated.....	118
Table 5 – Ionic properties for relevant elements	119
Table 6 – Co-doped sample compositions	121
Table 7 – Summary of (co-)dopant stabilizing effects	125
Table 8 – Basic information of commercially obtained powders.....	127
Table 9 – Phase contents, lattice parameters and densities	154
Table 10 – Bulk density, porosity and grain size	176
Table 11 – Maximum values for hardness and Young's modulus	179

LIST OF FIGURES

Figure 1 – Cutaway drawing of an example gas turbine engine, the Pratt & Whitney F100 (engine image from [1])	1
Figure 2 – Cutaway drawing of the X-15 with a zirconia-lined XLR99 engine [5]	3
Figure 3 – A complete thermal protection system (layer thicknesses not to scale).....	4
Figure 4 – Simplified unit cells showing the crystal structures of a) monoclinic (m) phase, b) tetragonal (t) phase and c) cubic fluorite (f) phase for pure ZrO_2 (solid dots are Zr^{4+} , open circles are O^{2-}) [23]	10
Figure 5 – Measured atomic locations (and accompanying thermal ellipsoids) in a unit cell of m- ZrO_2 , projected onto the (100) plane [28]	13
Figure 6 – An alternative perspective of three monoclinic unit cells, showing each Zr^{4+} cation surrounded by seven O^{2-} anions [29]	14
Figure 7 – The bct interpretation of a t- ZrO_2 unit cell, inside the more common face centred ‘pseudofluorite’ interpretation, which is illustrated here as also appearing body centred [29]	15
Figure 8 – The planes in a tetragonal unit cell for which maps of neutron scattering density are shown in Figure 9 (modified from [23])	17
Figure 9 – Maps of neutron scattering density at (a) $y = 0$, (b) $y = 1/4$, (c) $y = 1/2$, and (d) $y = 3/4$, revealing the tetragonal structure of t’ phase [31]	18
Figure 10 – A face centred unit cell of cubic fluorite [29]	18
Figure 11 – The relaxation a) of a f- ZrO_2 crystal near an O^{2-} vacancy and b) the local lattice (solid black is Zr^{4+} , grey is O^{2-} and small grey is vacancy) [10]	20
Figure 12 – Free energy vs. composition curves and the related phase diagram for a typical stabilized zirconia system with dopant ‘B’ [33]	22
Figure 13 – Cation-oxygen vacancy associations when dopants (M^{3+}) are undersized and oversized (assembled from [34])	23

Figure 14 – The effect of over and under sized tetravalent dopant cations (both which increase tetragonal stability) on the tetragonality (c/a) of zirconia ($Zr-O_I$ is strong, $Zr-O_{II}$ is weak) [22]	25
Figure 15 – The zirconia rich side of the ZrO_2 – $YO_{1.5}$ phase diagram including non-equilibrium transformation regions (T_0) and retained metastable phases (above horizontal axis) upon quenching from the cubic region [38]	29
Figure 16 – Cycles to failure vs. yttria concentration in zirconia [7].....	31
Figure 17 – a) A unit cell of high temperature cubic fluorite with arrows indicating the direction of O^{2-} anions with the $f \rightarrow t$ transition, and b) the resultant tetragonal structure (O^{2-} sub-lattice shown as dark dots, Zr^{4+} lattice with white dots) [40]	33
Figure 18 – Schematic time-temperature-transformation diagram for Y_2O_3 - ZrO_2 alloys ('c' refers to cubic fluorite) [26].....	34
Figure 19 – Sample data showing the trend of O-O distance with increased temperature in pure t- ZrO_2 with stoichiometry overlay (constructed with data from [25])	36
Figure 20 – Gibbs free energy versus Y_2O_3 content curves for t and f phases at the indicated temperatures ('ss' indicates solid solution and 'c' is the cubic phase, f) [26]	37
Figure 21 – Change of tetragonal lattice parameters with additions of yttria [37]	40
Figure 22 – Schematic of the strain imposed on a cylinder by the $t \rightarrow m$ transformation [38]	42
Figure 23 – The temperature-dependant strain energy required to initiate the $t \rightarrow m$ transformation in constrained and unconstrained t- ZrO_2 (S is entropy) [44]	44
Figure 24 – Grain size and yttria concentration dependency of the $t \rightarrow m$ transformation temperature [45]	45
Figure 25 – Schematic of a TEM foil edge of t- ZrO_2 before and after annealing in humid air which infused the lattice with water causing large internal strain (non-hatched represents t phase, hatched m phase) [51].....	47
Figure 26 – TTT diagrams for 2 mol% Y_2O_3 + ZrO_2 ceramics sintered at a) 1600°C and b) 1450°C [53]	48

Figure 27 – Predicted morphologies of m-ZrO ₂ particles (arrows show direction of reference and twin lattice parameters) [54].....	50
Figure 28 – Twinned monoclinic particles in a cubic matrix of PSZ [54].....	50
Figure 29 – Regions indicating the transformed phase and accompanying morphologies as a function of normalized grain size ($D = d$ in the text, and $D_{uc} = d_{critical}$ for unconstrained particles) and temperature or alloy composition [32]	52
Figure 30 – Tetragonal colonies in a cubic matrix (in PYSZ), where two t-ZrO ₂ twins appear as light or dark contrasts [56].....	53
Figure 31 – Schematic of four tetragonal colony variants in the (001) plane consisting of the (t_1, t_2) pair (redrawn from [58])	54
Figure 32 – Model of precipitate colonies changing direction by angle α due to thickness changes of lamellae [56].....	55
Figure 33 – t'-ZrO ₂ domains forming colonies (C) in a herringbone pattern [59]	56
Figure 34 – Three-dimensional shape of the colonies created of tetragonal domains, differently arranged with respect to the $\langle 111 \rangle$ longitudinal colony axis (modified from [59])	58
Figure 35 – Small anti-phase domain boundaries inside the domains of t'-PYSZ [59].....	59
Figure 36 – A schematic of APBs showing the different displacements of oxygen anions in a) adjacent sub-domains and b) as viewed from the (001) direction (O ²⁻ is black, Zr ⁴⁺ is white, and image is modified from [42])	59
Figure 37 – Bulk strength vs. grain size for TZP [61]	62
Figure 38 – TEM image of t phase (background) transformed to m phase (foreground lamellae) at a crack tip in PYSZ [55].....	63
Figure 39 – Toughness of PYSZ, YSZ and other ceramics [62].....	64
Figure 40 – Schematic showing a hysteresis loop for ferroelastic materials, where the shaded region is energy absorbed in reorientation of domains during fracture (redrawn from [63])	65
Figure 41 – A compressive stress/strain response at 500°C for a 3 mol% YSZ single crystal [62].....	66

Figure 42 – The ferroelastic process zone ($h_f \approx 3 \mu\text{m}$) near a crack in YSZ containing three t' variants, with a darker contrast due to twin planes which are not present in the virgin single-variant material [62]	68
Figure 43 – A modified TGO microstructure by addition of hafnia [66].....	71
Figure 44 – Schematic cross section of a plasma spraying torch [3].....	73
Figure 45 – Plasma spray a) powder feedstock [75], b) splat structure [76] and c) fracture surface cross section of a deposited microstructure [77].....	74
Figure 46 – Cross section of a typical plasma sprayed microstructure [3]	74
Figure 47 – Schematic cross section of a typical YSZ microstructure produced by plasma spraying [8]	74
Figure 48 – A transverse fracture surface of plasma sprayed 8YSZ showing lamellae, columnar grains, and very little inter-lamellar contact [80].....	76
Figure 49 – Plasma sprayed zirconia exhibiting globular voids (spherical porosity), microcracking and inter-lamellar pores in a) a SEM image of a fracture surface [81] and b) a schematic illustration [80]	76
Figure 50 – Schematic representation of the variation of coating stiffness with imposed strain, and the associated behaviour of microcracks [80]	79
Figure 51 – A transverse fracture surface showing sintered lamellar interfaces bridged by trans-lamellar grain growth [76].....	80
Figure 52 – A thermally sprayed YSZ top coat and underlying bond coat a) before and b) after 1374 thermal cycles to 1121°C, and c) the effect on Young's modulus [86]	81
Figure 53 – The effect of isothermal sintering at 1400°C on thermal conductivity for yttria (Y-), dysprosia (Dy-) and ytterbia (Yb-) stabilized zirconia (SZ) [81]	82
Figure 54 – Schematic of a typical EB-PVD process [3]	83
Figure 55 – Schematics showing a) conventional rotation, b) related geometric variables and c) the associated flux pattern at square pyramidal grain tips [92]	85

Figure 56 – a) The columnar microstructure of EB-PVD coatings [3] and b) an accompanying schematic [8]	86
Figure 57 – Columnar tips as viewed at the coating surface, produced at a) 0 rpm, clearly displaying {111} facets, and b) 5 rpm, with rounded tips due to shadowing of the incident vapour stream [91].....	87
Figure 58 – a) A cross section and b) a fracture surface, revealing inter-columnar gaps (1), globular and elongated spheroid nano-pores arranged in layers (2), and ‘feather arms’ (3) in a columnar grain of a EB-PVD zirconia coating [93]	89
Figure 59 – Residual stress vs. in-plane elastic modulus (stiffness) for EB-PVD coatings, where open symbols designate properties measured perpendicular to the plane of incidence and closed symbols designate properties parallel to it [94]	92
Figure 60 – Sintered columnar grains for 1 hour at a) 1100°C and b) 1400°C [96]	93
Figure 61 – Effect of relative roundness on random packing density [99].....	96
Figure 62 – Particle size ratio versus packing density for bimodal, spheroid powders [99].....	97
Figure 63 – Logarithmic compaction curves for two YSZ powders, one averaging 102 μm particle diameter (solid dots) and the other 256 μm (open dots) [102]	100
Figure 64 – Effect of sintering temperature on sintered density of 8YSZ [102]	101
Figure 65 – A plot illustrating the competitive nature between coarsening and densification (redrawn from [104])	102
Figure 66 – The six methods of material transport which support coarsening and densification during sintering [99].....	103
Figure 67 – Contact angle, ϕ , and neck radius, ρ_n , a) before, b) during and c) after active necking (neck material omitted for clarity) (redrawn from [103]).....	105
Figure 68 – Dihedral angle (ϕ_e) in three pore configurations (based on [103]) ..	106
Figure 69 – The effect of a) pore size distribution (and therefore particle size distribution) on b) grain growth and densification [108]	109

Figure 70 – Microstructure of pore-impregnated and sintered MgO-doped Al_2O_3 for 5 minutes at 1620°C [107]	110
Figure 71 – Diffusion coefficient (D) plotted against temperature for a number of $\text{YO}_{1.5}$ concentrations (mol%, as labelled) [110]	113
Figure 72 – The zirconia-rich portion of a ternary $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Yb}_2\text{O}_3$ phase diagram at 1400°C (F_{ss} is f- ZrO_2 , T_{ss} is t- ZrO_2 , and C_{ss} is a rare-earth type) [14]	122
Figure 73 – A ternary $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-CeO}_2$ phase diagram at 1600°C [15]	123
Figure 74 – The ternary $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram at 1500°C (C_{ss} is f- ZrO_2 , T_{ss} is t- ZrO_2 and NT_{ss} is t'- ZrO_2 [16])	124
Figure 75 – 7YSZ and equivalent co-doped compositions located on the binary $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram	126
Figure 76 – SEM micrographs of commercially obtained a) 7YSZ, b) Yb_2O_3 , c) CeO_2 and d) Nb_2O_5 powders	127
Figure 77 – SEM micrographs of 70 hours ball milled a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ powders	129
Figure 78 – Three-part die sets with a common radius of 2.54 cm, not including tolerances (see Appendix C)	130
Figure 79 – Pressed green disks	132
Figure 80 – A damaged die set (insert not shown)	133
Figure 81 – A collection of 12 green disks (two layers of 6) in a rigid box	134
Figure 82 – Green disks (7YSZ) loaded in the furnace on crafted alumina holders	135
Figure 83 – Fan, air and furnace cooling schemes	136
Figure 84 – The measurement of bulk density, showing a) the scale and configurations for b) zeroing the balance, c) reading w_{dry} and d) reading $w_{immersed}$	137
Figure 85 – Example resin mounted specimens of (from the left) 7YSZ, Yb:7YSZ, Ce:7YSZ, and Nb:7YSZ	139
Figure 86 – Mounted specimens for observing fracture surfaces in the SEM ...	140
Figure 87 – a) An SEM image of a polished microstructure (Nb_2O_5 co-doped specimen at 1000X) and b) digitally isolated pores	141

Figure 88 – Example measurement of average grain size in ImageTool (line shown is drawn on a Nb:7YSZ microstructure at 2000X)	142
Figure 89 – A display of ideal and worst case conditions of ceramic disks after sintering	147
Figure 90 – Typical underside cracking displayed on nearly all sintered disks, as viewed with a stereomicroscope (shown here is a 7YSZ, furnace cooled sample)	148
Figure 91 – 7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples	150
Figure 92 – Yb:7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples	151
Figure 93 – Ce:7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples	152
Figure 94 – Nb:7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples	153
Figure 95 – Measured phase content versus cooling scheme for 7SYZ	155
Figure 96 – Measured phase content versus cooling scheme for Yb:7SYZ	160
Figure 97 – Measured phase content versus cooling scheme for Ce:7SYZ	161
Figure 98 – Measured phase content versus cooling scheme for Nb:7SYZ	163
Figure 99 – Elemental maps of a) a polished region showing concentrations of b) Zr^{4+} , c) Y^{3+} and d) the co-dopant, Yb^{3+} (dashed white lines border porosity)	167
Figure 100 – As-pressed and sintered surfaces of a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ ceramic disks	170
Figure 101 – Fracture surfaces of a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ specimens	172
Figure 102 – Tetragonal grains (arrows) surrounded by monoclinic and cubic grains in a 7YSZ specimen	174
Figure 103 – Polished and etched surfaces of a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ specimens	175
Figure 104 – Magnified views of a) open porosity (in Yb:7YSZ) and b) a region of enhanced local sintering (in Nb:7YSZ)	177

Figure 105 – Force-penetration curves for variably cooled 7YSZ samples (the curves shown correspond to maximum hardness values measured)	179
Figure 106 – Sample force-penetration curves (both Yb:7YSZ, furnace cooled) showing moderate (sample 1) and extensive (sample 2) cracking and collapse (indicated by arrows) of indented material	181

NOMENCLATURE

ABBREVIATIONS

APB	Anti-phase domain boundary
APS	Atmospheric plasma spraying
BC	Bond coat
bct	Body centred tetragonal
EB-PVD	Electron-beam physical vapour deposition
f	Cubic fluorite phase of zirconia, f-ZrO ₂
fcc	Face centred cubic
LPPS	Low pressure plasma spraying
m	Monoclinic phase of zirconia, m-ZrO ₂
PS	Plasma spraying
PYSZ	Partially yttria stabilized zirconia
t	Tetragonal phase of zirconia, t-ZrO ₂
t'	Non-transformable tetragonal phase of zirconia, t'-ZrO ₂
TBC	Thermal barrier coating
TGO	Thermally grown oxide
TIT	Turbine inlet temperature
TTT	Time-temperature-transformation
TZP	Tetragonal zirconia polycrystal
VPS	Vacuum plasma spraying
YSZ	Yttria stabilized zirconia
7YSZ	7 wt% YSZ

VARIABLES

a, b, c	Crystallographic lattice parameters
A_C	Normalized area of microcrack fracture surface
A_i	Particulate interfacial area
A_s	Particle surface area
A_T	Normalized area of twin planes
C_{defect}	Concentration of lattice defect
C_i	Concentration of diffusing species
d	Grain or particulate diameter
$d_{critical}$	Critical grain diameter below which cooling does not induce $t \rightarrow m$ transformation
d_p	Pore diameter
D	Diffusion coefficient
E	Young's modulus
f	$(1 - f)$ is loss of constraint
G	Gibb's free energy
h	Size of process zone
H	Enthalpy
η	Tetragonal twin domain thickness ratio
j	Correlation factor between diffusivity and concentration
J	Flux
K_0	Fracture toughness without strengthening phenomena
K_c	Fracture toughness
l	Distance from EB-PVD flux source to target point
L	Distance from EB-PVD flux source to target's axis of rotation directly above

m	Empirical value for fitting particulate size distribution data
m_k	Cation mol% of element k
M_s	Constrained martensitic start temperature ($t \rightarrow m$)
$\Delta\mu_n$	Chemical potential for neck formation
n	Pore coordination in two dimensions
n_c	Critical pore coordination above which pores are stable
n_s	Pore coordination in three dimensions
P	Applied pressure
r	Particulate radius
r_k	Ionic radius of element k
r_p	Pore radius
R	Ratio of pore and grain diameters
R_c	Critical ratio of pore and grain diameters, above which pores do not shrink during sintering
S	Entropy
t_1, t_2, t_3	Tetragonal twins
t	Time
T_0	Non-equilibrium displacive transformation temperature
T_m	Melting temperature
T	Temperature
U_s	Surface energy
U_{SE}	Strain energy
U_{ESE}	External strain energy
U_{ISE}	Internal strain energy
v	Empirical value representing the spread of an EB-PVD plume
V	Volume

V_A	Atomic volume
V_m	Molar volume
V_t	Volume fraction of tetragonal phase
w	Weight
W	Mass fraction of particles less than a given size
x	Position
z_k	Valency of element k

GREEK SYMBOLS

α	Coefficient of thermal expansion
β	Angular (shear) lattice parameter for m phase
γ_c	Microcrack fracture energy per unit area
γ_i	Interface tension
γ_s	Surface tension
γ_T	Twin plane energy per unit area
δ	Grain boundary thickness
ε	Strain
ν	Poisson's ratio
ξ	Angle between EB-PVD plume axis and line of sight
ρ	Density
ρ_n	Neck radius between sintering particles
σ	Stress
ϕ	Sintering sphere contact angle
ϕ_e	Dihedral angle
Ω_a	Diffusion volume

1 INTRODUCTION

It has always been a prime directive to improve the performance of aircraft, and the powerplant is one major source for advancement. The powerplants in most of today's aircraft are gas turbine (jet) engines (Figure 1), and a design parameter of great importance is the turbine inlet temperature (TIT) of the working fluid (air). Higher TITs boost the efficiency of combustion so that fuel consumption is reduced and thrust-to-weight ratios are increased. However, the inherent melting temperatures of the composing metal parts set a strict upper limit on the TIT. Near or above this limit structural integrity is compromised, risking catastrophic failure of the aircraft.

Figure 1 – Cutaway drawing of an example gas turbine engine, the Pratt & Whitney F100 (engine image from [1])

1.1 DEVELOPMENT OF ZIRCONIA COATINGS

Over the period of 1940 to 1970, spanning much of World War II and the Cold War, the inherent temperature limit of the metallic gas turbine components was addressed by the production of many generations of new cobalt- and nickel-base superalloys for components in contact with the hot working gas. These new alloys with their higher melting temperatures allowed the thermal capability of turbines to rise significantly from 760°C to 1040°C [2]. But as incipient melting limited further improvements in this way, attention was diverted to air cooling, wherein air is pumped through internal passageways cast into turbine blade and vane airfoils. This increased operating temperatures another 150°C, and specialized manufacturing such as the production of single crystal components improved them further [2]. Today, single crystal superalloys have reached an upper temperature limit of around 1325°C (those that are polycrystalline have a lower limit, near 1200°C), but at the same time, typical TITs are 1425°C [3]. This large difference is possible without component failure because of the incorporation of ceramic thermal barrier coatings (TBCs), a third method of reducing heat exposure to metallic components.

Far earlier, before the time of aeroplanes, the metallic element zirconium was first identified in 1789 and a crude impure powder was made by 1824 [4]. In 1950 with the development of nuclear power, the first high purity (98%) sample was produced. Zirconium dioxide (ZrO_2), or zirconia, was quickly recognized in the late 1950's as an important ceramic for many applications, not the least of which was thermal insulation [2]. In the United States, NASA was the first to

research and apply zirconia TBCs inside the X-15 aircraft (Figure 2), designed in 1955 for hypersonic and space research. In 1963, the X-15's zirconia-lined XLR99 aircraft engine carried pilot Joe Walker to a record altitude of 108 km, officially making him an astronaut [5].

Figure 2 – Cutaway drawing of the X-15 with a zirconia-lined XLR99 engine [5]

Aerospace research into zirconia coatings progressed greatly after the X-15. Indeed, a typical thermal protection system today includes far more than just a layer of ZrO_2 . The four primary constituents, as illustrated in Figure 3, are the TBC itself, the metallic substrate component, an aluminum-containing bond coat (BC) located between the substrate and the TBC, and a thermally grown oxide (TGO) that forms on the bond coat at the interface with the TBC. The TBC, again, is the thermal insulator, while the bond coat provides oxidation protection since oxygen is highly diffusive through zirconia at high temperatures. The substrate is usually a nickel-base superalloy and sustains the structural loads. Finally, the TGO is a product of bond coat oxidation which forms during coating application and grows in service with further exposure to oxygen. It also plays an

important role in metal/coating adhesion and provides limited relief of thermal expansion mismatches between those two layers [6].

Figure 3 – A complete thermal protection system (layer thicknesses not to scale)

With a shifted focus in thermal design from superalloy development, to air cooling, and now to TBCs, today even zirconia is approaching an upper limit to its capabilities. Although thermal insulation remains their primary purpose, most motivation for new and improved TBCs now comes from issues with the phase stability of zirconia in thermally cyclic operating conditions, and ultimately, its overall resistance to failure.

1.2 YTTRIA AS A STABILIZING DOPANT

At high temperatures, the atomic structure (i.e. the phase) of ZrO_2 is such that zirconium cations (Zr^{4+}) form a face centred cubic crystal structure in which oxygen anions (O^{2-}) reside. On cooling to intermediate temperatures, the crystal is distorted and becomes tetragonal. At even lower temperatures, including room temperature, further distortion leads to a phase called monoclinic.

Associated with the formation of the low temperature monoclinic phase is a large volume change which, especially in cyclic thermal environments, causes TBCs to crack and eventually fail. To avoid this, partial or full retention of high temperature phases is routinely achieved by adding a stabilizing dopant oxide to ZrO_2 , usually yttria (Y_2O_3). There remains an issue, however, because time at high temperatures allows the stabilized phases to decompose and eventually transform into monoclinic. Full stabilization is possible, but it is not mechanically favourable, as will be discussed in the literature review.

Yttria was originally selected as a stabilizing dopant in zirconia because other primary options, such as MgO and CaO , produced zirconia alloys with vital flaws such as volatility and a lack of corrosion resistance [7, 8]. The primary stabilizing mechanism of the trivalent Y^{3+} cation is to substitute Zr^{4+} and produce oxygen (O^{2-}) vacancies to maintain charge balance. This effectively reduces or eliminates the thermodynamic driving force for transformation on cooling [9, 10]. Further, the composition of 7 wt% $\text{Y}_2\text{O}_3 + \text{ZrO}_2$ maximizes the number of thermal cycles to failure [7], and so has become an industrial standard known as 7YSZ.

1.3 DESIGN PHILOSOPHY FOR NEW COATINGS

The continued improvement of TBCs is driven by the need for more reliable and longer-lasting thermal protection systems. There are two methods to do this. One is to develop new alternative TBC materials, and this is always an open subject. Many materials have been proposed, including zirconates such as ZrSiO_4 , ZrTiO_4 , and perhaps the most promising, $\text{NaZr}_2(\text{PO}_4)_3$, but none of these rival ZrO_2 in all areas and none are nearly as developed [2].

The second method for further improving TBCs is to enhance the performance of current zirconia technology, which can be accomplished by addition of co-dopants to augment the stabilizing effects of the primary dopant, Y_2O_3 . Exactly which elements are ideal co-dopant candidates is the subject of much international research, but from an understanding of Y^{3+} stabilization mechanisms, it follows that co-dopants be selected based on cationic properties. Specifically, valence affects stability via oxygen vacancies, ionic radius affects it by lattice distortions, and atomic mass alters thermo-mechanical properties. It is of great interest to establish ideal combinations of these mechanisms, such that the best options for co-dopant cations are identified. The current thesis is in direct support of those efforts.

1.4 THESIS OBJECTIVES

Investigations into the effect of co-dopants have been performed by a number of researchers [11 – 19]. However, many studies are performed isothermally, and when thermal cycles are imposed on co-doped zirconia, little to no attention is given to the effect of cooling rate. It is known that the proportion of phases retained will change with varying cooling schemes (this is a widely understood thermodynamic principle), but a lack of knowledge exists on the cooling rate sensitivity of different stabilizing mechanisms. Since the application is to industrial coatings deposited by techniques with variable cooling schemes, and since coating performance will ultimately be judged by its behaviour in the cyclic thermal conditions of gas turbine engines, the effect of cooling rate on the stabilizing mechanisms of co-doped ZrO_2 is paramount.

This thesis investigates the stabilizing mechanisms of co-dopants, their sensitivities to cooling rate, and also their effects on the mechanical properties of standard 7YSZ. Appropriately, there are three primary objectives:

1. Co-dope 7YSZ ceramic samples with several oxides (separately) that affect stability via different mechanisms. Then, expose samples to different cooling schemes and examine the resultant phase contents to establish the cooling rate sensitivity of each mechanism.
2. Conduct microstructural analyses of the samples produced to analyze the effect of different phase contents as well as the processing techniques applied.
3. Provide insight into the effect of co-dopants and cooling rate on mechanical properties, namely hardness and Young's modulus.

To accomplish these objectives, three co-dopants were selected based on their cationic properties such that a variety of mechanisms could be studied. The co-dopant oxides were Yb_2O_3 , CeO_2 , and Nb_2O_5 . When added to 7YSZ, Yb^{3+} would provide additional oxygen vacancies plus compressive lattice deformations. Ce^{4+} would not affect oxygen vacancies but would deform the ZrO_2 lattice in compression. Lastly, Nb^{5+} would remove oxygen vacancies (called 'annihilation' in literature) and introduce tensile lattice deformations.

This thesis provides a prerequisite literature review that precedes the presentation of experimental work. Results are interpreted and discussed in the context of thermodynamics, kinetics and other relevant theory, and conclusions are drawn relevant to the current state of TBC technology.

2 LITERATURE REVIEW AND RELEVANT THEORY

The following is a detailed review in preparation for the experimental portion of this thesis. Zirconia and its phases are first covered in section 2.1, followed by its stabilization in section 2.2. Section 2.3 then details yttria stabilized zirconia, its phase transformations, and its morphologies. Building off of this, section 2.4 accounts for the high strength and toughness of zirconia alloys. Expanding the review to full thermal protection systems, the bond coat interlayer is briefly covered in section 2.5, and industrial deposition technologies are discussed in section 2.6. Lastly, in section 2.7, theory is given for the material processing techniques applied in the current thesis research.

2.1 ZIRCONIA

Zirconia is a ceramic with low thermal conductivity, which is ideal for TBCs since they act as thermal insulators. An introduction to ZrO_2 and zirconium metal now follows. The interactions between Zr^{4+} and O^{2-} are discussed until reaching ZrO_2 stoichiometry, at which point the crystallographic phases of zirconia are introduced and then detailed.

2.1.1 ATOMIC BONDING CHARACTERISTICS AND POLYMORPHISM OVERVIEW

Zirconium exhibits chemical behaviour and bonding characteristics that are dramatically different from other transition metals on the periodic table, perhaps only comparable to hafnium [20]. It is a metal with a very high electron affinity,

and produces an oxide (ZrO_2) that is uncommonly covalent in nature. The reason for this is that, in general, ionic compounds rise in covalent character with increasing cationic charge and decreasing cationic size, because both things enhance the electron cloud polarization around bonded anions [20]. Zr^{4+} cations are relatively small (0.84 Å when coordinated eightfold [21]) and have a high charge (4+), so bonding in ZrO_2 is largely covalent.

Even so, the distribution of oxygen in a zirconium lattice is primarily determined by the geometry of the metal matrix and not by the balancing of valence [20]. At low concentrations, oxygen simply dissolves interstitially into the Zr lattice without causing structural changes. Only upon surpassing a critical composition ($\text{ZrO}_{0.3}$, or 23 mol% O^{2-} [20]) does an ordered oxygen sublattice begin to appear, as covalent Zr-O bonds start to be balanced.

The ideal crystal structure for ZrO_2 is cubic fluorite (f) phase (that of calcium fluoride, CaF_2), illustrated in Figure 4c, but the small size of Zr^{4+} is unfavourable for the eightfold coordination with oxygen that is required by this symmetry [9]. As such, the fluoritic structure can only be sustained at very high temperatures (> 2370°C) where, for thermal reasons, interatomic spacing is large. Upon cooling from high temperatures, interatomic spacing reduces, and the cubic cation lattice is strained as the oxygen sublattice becomes overcrowded [22]. The result is the tetragonal (t) phase of ZrO_2 , illustrated in Figure 4b, which is more stable than cubic fluorite at lower temperatures because oxygen overcrowding is reduced. With further cooling, the system is strained even more, producing the monoclinic

(m) phase (Figure 4a). Lattice parameters (dimensions) are inflated, symmetry is severely distorted and the oxygen coordination of Zr^{4+} is reduced from 8 to 7.

Figure 4 – Simplified unit cells showing the crystal structures of a) monoclinic (m) phase, b) tetragonal (t) phase and c) cubic fluorite (f) phase for pure ZrO_2 (solid dots are Zr^{4+} , open circles are O^{2-}) [23]

Each crystal structure of ZrO_2 can be visualized as containing a Zr-Zr cation lattice and a O-O sublattice. Zr-Zr bond lengths tend not to vary much from an ordered symmetry, so the Zr-Zr lattice is said to be rigidly bound. Meanwhile, Zr-O bond lengths are more disordered, so the O-O sublattice is said to be loosely bound.

The efficiency of the balancing act between Zr-O bonding and the geometry of the Zr-Zr lattice is measured in terms of Gibb's free energy (G) for each crystal structure, given by

$$G = H - TS \quad (1)$$

where T is temperature, H is enthalpy and S is entropy. Precisely which phase is stable at a given set of conditions depends on which has the lowest free energy.

Assuming atmospheric pressure, m phase is stable up to 1170°C , at which point t phase allows lower free energy so becomes the stable structure. This

changes again at 2370°C with the transition to f phase. Melting occurs at 2680°C, so the transformations are $m \xleftrightarrow{1170^{\circ}\text{C}} t \xleftrightarrow{2370^{\circ}\text{C}} f \xleftrightarrow{2680^{\circ}\text{C}} \text{liquid}$ in pure ZrO_2 .

Crystallographic information is tabulated in Table 1, and each ZrO_2 phase is detailed further in the following subsection. The ionic positions listed in the table are described in detail within the International Tables for Crystallography [24]. However, in the current context, Figure 4 provides a sufficient understanding.

Table 1 – General crystallographic information

Phase name (range of stability) [†]	Monoclinic (m) (< 1170°C)	Tetragonal (t) (1170 – 2370°C)	Cubic Fluorite (f) (> 2370°C)
Space group	$P2_1/c$	$P4_2/nmc^{\ddagger}$	$Fm\bar{3}m$
Zr^{4+} coordination with O^{2-}	7	8	8
Lattice parameters	$a_m \neq b_m \approx a_f$ $c_m > a_f$	$a_t = a_f \approx \sqrt{2} \cdot a_{t bct}$ $c_t \approx a_t$	$a_f = 5.269 \text{ \AA}^{\S}$
Unit cell volume	$V_m \approx 2V_f$	$V_t \approx V_f$	$V_f = a_f^3$
Ionic positions	Zr^{4+} : 4e O^{2-} : 4e	Zr^{4+} : 2b O^{2-} : 4d	Zr^{4+} : 4a O^{2-} : 8c

Subscript m = monoclinic, t = tetragonal and f = cubic fluorite ($a_{t|bct}$ is a_t for t phase interpreted as bct, see Figure 7)

[†] As given by Reed [3].

[‡] For the bct interpretation of t phase (Figure 7)

[§] For pure ZrO_2 at 2410°C [25] (a_f will reduce with temperature)

2.1.2 CRYSTAL STRUCTURES

The crystallography of m, t and f ZrO_2 phases is now expanded. In addition, the non-transformable t' phase is also included for later reference. Not discussed is the artifactual orthorhombic (o) crystal structure that sometimes occurs in thin foil ZrO_2 specimens. The o phase is a low pressure and metastable phase relative to t- ZrO_2 and forms by a displacive (diffusionless) $t \rightarrow o$ transformation [26]. It is rarely documented to exist naturally in bulk

material at standard pressures and, when it does, it is reported as unexpected (in [27], for example). Discussion of relevant phases will proceed according to rising temperature, beginning with m-ZrO₂.

2.1.2.1 Monoclinic (m)

The monoclinic crystal structure (Figure 4a) is the most distorted modification to that of ideal cubic fluorite. It is represented by the naturally occurring mineral 'baddeleyite' and provides each Zr⁴⁺ cation with seven O²⁻ neighbours. When the cation lattice is considered independently, each Zr⁴⁺ is coordinated with 12 other cations.

Sevenfold coordination with oxygen differentiates m-ZrO₂ from the higher temperature t and f phases that have coordination numbers of 8 (Table 1). Each O²⁻ anion that neighbours a Zr⁴⁺ cation has a characteristic distance ranging from 1.85 to 2.511 Å [28]. This yields very low local symmetry, and it is for this reason that m phase is said to be locally disordered. Order is found, however, both in Zr-O and Zr-Zr bonding shells when multiple unit cells are considered. Zr-O bonding has been reported to occur in layers of stronger and weaker bonds, separated within a Zr-Zr lattice that is itself ordered via three subshells [9, 28]. Indeed, the simplified crystal structure in Figure 4a is misleading because it is not indicated that the exact positions of atoms change slightly. Although this causes small changes in the values for lattice parameters a_m , b_m and c_m , it does so predictably with minor deviances. Figure 5 illustrates this very well. By noting the difference in average deviations, the figure also reveals the rigidly bound Zr-Zr lattice relative to the loosely bound O-O sublattice.

Figure 5 – Measured atomic locations (and accompanying thermal ellipsoids) in a unit cell of m-ZrO₂, projected onto the (100) plane [28]

X-ray absorption studies [9] show that while each Zr⁴⁺ cation has twelve Zr⁴⁺ neighbours, they are located at one of three distinct distances. This gives rise to what are referred to as subshells (three of them), which are imaginary cationic lattices made up of nearest neighbours (NN), or next nearest neighbours (NNN), et cetera. When considered separately, each subshell has a characteristic cation co-ordination number. As refined by Winterer [28] in 2000, the first subshell has a Zr-Zr bond length of 3.46 Å and a co-ordination of 7. The second has a length of 3.96 Å with a coordination of 4. The third has a bond length of 4.54 Å and a coordination of only 1, for a total cation coordination of 12 since all subshells exist in the same real Zr-Zr lattice. Bond length is an indication of bond strength, with smaller lengths corresponding to higher strengths.

Similarly, Zr-O bonds in m-ZrO₂ also occur in subshells. Figure 6 is an alternative perspective that emphasizes the ordering of O²⁻ around Zr⁴⁺. The

sevenfold coordination of zirconium is illustrated by the numbered oxygen ions 1 to 7. A Zr-Zr sublattice is also shown for reference and it can be seen that the central Zr^{4+} (to the numbered O^{2-} ions) is equivalent to the face centred Zr^{4+} at the position $\frac{1}{2}, 0, \frac{1}{2}$ in Figure 4a.

Figure 6 – An alternative perspective of three monoclinic unit cells, showing each Zr^{4+} cation surrounded by seven O^{2-} anions [29]

Zr-O bonds with oxygen ions 2, 4, 5 and 6 (Figure 6) are strong, and consequently yield small bond lengths of 1.885 – 2.360 Å. Conversely, bonds with 1, 3 and 7 are weak and have Zr-O distances of 1.914 – 2.511 Å. In this perspective, zirconium ions can be thought of as forming layers parallel to (100) planes with strong Zr-O bonds on one side and weak bonds on the other [29], with an average Zr-O bond length of 2.16 Å and an average Zr-Zr length of 3.720 Å [9]. The tetragonal phase exhibits a similar layered structure.

2.1.2.2 Tetragonal (t)

The tetragonal (t) phase provides zirconium with eightfold oxygen coordination, and the Zr-O bond lengths are less various than for m phase. It is therefore considered to be more ordered. As indicated in Figure 4, the cationic lattice of t phase is very close to that of the face centred cubic (fcc) lattice of f phase, but it exhibits a small degree of tetragonality, with c_t/a_t being about 1.015 or 1.02 [30]. In addition to this 'pseudofluorite' interpretation, t phase can also be described as body centred tetragonal (bct). Figure 7 shows both interpretations. The tetragonal and pseudofluorite cells share a common c_t axis, about which the a_t parameter for the bct interpretation ($a_{t|bct}$) is rotated 45° [29].

Figure 7 – The bct interpretation of a t- ZrO_2 unit cell, inside the more common face centred 'pseudofluorite' interpretation, which is illustrated here as also appearing body centred [29]

Like m phase, the near fcc cation lattice provides Zr^{4+} with 12 cation neighbours, although with a nearly regular Zr-Zr length of 3.61 – 3.63 Å [9].

There are no Zr-Zr subshells as in m-ZrO₂. The c_t parameter in pure ZrO₂ at high temperature ranges from 5.2689 to 5.3175 Å between 1160°C and 2165°C [25].

Between layers of the Zr-Zr cation lattice, the O²⁻ sublattice is arranged into two Zr-O subshells each with four O²⁻ anions. One subshell occurs with Zr-O bond lengths of 2.09 – 2.10 Å and the other occurs with lengths of 2.33 – 2.35 Å. Respectively, the Zr-O subshells are strong and weak, and it is their displacement and different bond lengths that give rise to the tetragonality of t-ZrO₂.

2.1.2.3 Non-transformable Tetragonal (t')

Being very similar to t phase, t' is not a unique phase of ZrO₂ but is important because once produced it does not undergo the t → m transformation, and thereby avoids the issues associated with m phase. It is differentiated primarily by morphology (section 2.3.4), not crystal structure, and is discussed here for reference later.

The t' phase is metastable in all conditions, and requires a stabilizing dopant (such as Y₂O₃) for production (section 2.3). Further, it can only be produced by quenching (rapid cooling), because this disallows the formation of equilibrium phases and retains high amounts of stabilizer in a tetragonal form.

The tetragonality of t' is much smaller relative to equilibrium t phase, with c_t/a_t ratios ranging between 1.0025 and 1.0075 depending on the exact stabilizer content [26]. In addition, oxygen anions in t' are offset from the normal t phase locations by 0.046 (normalized units) in the (100) direction (along the elongated tetragonal axis, c_t) [31].

This value of offset was identified by investigating the neutron scattering density of four unit cell (t') planes which are illustrated in Figure 8. The corresponding maps of neutron scattering density appear in Figure 9. Each plane is defined by its location along the y -axis, which is perpendicular (and positive, pointing right) to the c_t and a_t dimensions in Figure 7. Figure 9a at $y = 0$ thus correlates to a plane in the middle of the pseudofluorite structure in Figure 7, or the (101) plane in Figure 4b.

Figure 8 – The planes in a tetragonal unit cell for which maps of neutron scattering density are shown in Figure 9 (modified from [23])

Figure 9 – Maps of neutron scattering density at (a) $y = 0$, (b) $y = 1/4$, (c) $y = 1/2$, and (d) $y = 3/4$, revealing the tetragonal structure of t' phase [31]

2.1.2.4 Cubic Fluorite (f)

The highest temperature phase and ideal crystal structure of pure zirconia is cubic fluorite, $f\text{-ZrO}_2$ (Figure 10). Like both m and t phase, the fcc cation lattice is 12 coordinated and, according to the $Fm3m$ space group [24], the oxygen anions are located inside of it at $1/4, 1/4, 1/4$ in perfect eightfold symmetry. The single shell of Zr-O bonds is thus eightfold coordinated as well.

Figure 10 – A face centred unit cell of cubic fluorite [29]

Cubic fluorite is a difficult phase to investigate experimentally because it only exists above 2370°C unless a stabilizer is added. There is an abundance of data available for stabilized cubic materials such as with yttria, but such dopants manipulate the structure and disallow the extraction of true lattice parameters. High temperature measurements are difficult, but one experimental value is $a_f = 5.269 \text{ \AA}$, as measured in pure zirconia at 2410°C [25].

2.2 ZIRCONIA STABILIZATION

ZrO₂ is an excellent thermal insulator, but if not stabilized, the cyclic thermal conditions within gas turbines will lead to transformation-induced cracking very quickly. This happens because there is a large 4% volume change and an 8% shear strain [32] associated with the $t \rightarrow m$ formation of the monoclinic phase. It is therefore of prime interest to stabilize high temperature phases and avoid the $t \rightarrow m$ reaction. The atomic mechanisms that accomplish this, and dopant properties which introduce them, are the topic of the following subsections.

2.2.1 MECHANISMS OF PHASE STABILIZATION

As was described previously (section 2.1.1), the root of zirconia's polymorphism is its ideal cubic fluorite phase for which the small radius of Zr⁴⁺ is unfavourable. Pure f-ZrO₂ is stable at high temperatures, but upon cooling, the cation network is strained by oxygen overcrowding into the tetragonal phase. With further cooling, the system is strained even more into the monoclinic phase. Fundamentally, high temperature phase stabilization is attained by relieving this

lattice strain and thereby reducing the driving force for phase transformations upon cooling [22].

A literature review has revealed three primary mechanisms for lattice strain reduction and therefore phase stabilization. The first mechanism and perhaps most intuitive is the removal of O^{2-} from the oxygen sublattice to reduce oxygen overcrowding. This can be done by the addition of bivalent or trivalent dopant cations which substitutionally replace Zr^{4+} in the ZrO_2 lattice and necessitate the removal one O^{2-} anion to maintain balance. The result is an oxygen vacancy. For a neighbouring cation in a high temperature phase, the vacancy reduces oxygen coordination from eight to sevenfold, and the cationic network can relax [10, 18]. On this basis, models have shown [10] that high concentrations of O^{2-} vacancies are theoretically enough to fully stabilize f and t phases. From one such model, an illustration of the relaxation effect on the cation network is shown in Figure 11.

Figure 11 – The relaxation a) of a f- ZrO_2 crystal near an O^{2-} vacancy and b) the local lattice (solid black is Zr^{4+} , grey is O^{2-} and small grey is vacancy) [10]

Experimental results [9], however, show that adopting sevenfold oxygen coordination is only sufficient for partial stabilization. Full stabilization requires introduction of the second primary mechanism of phase stabilization.

Tetragonality reduction via doping with oversized cations relieves oxygen overcrowding, reduces lattice strains, and causes the phase to approach a cubic state [22]. This lowers the driving force for transformation to monoclinic symmetry. Since the dopant is oversized, it dilates the local lattice as it imposes compressive strain.

Finally, the third mechanism for high temperature phase stabilization is the production of an ordered cation lattice which increases tetragonality while decreasing the driving force for monoclinic transformation. This is accomplished with undersized dopants as described in sections 2.2.1.2 and 2.2.1.3, which induce tensile strains on the local ZrO_2 lattice.

Cationic size and valence properties determine the stabilizing ability of potential dopants. The net effect of dopants is to reduce the free energy of tetragonal and cubic phases at low temperatures, and thereby prevent transformation to the monoclinic phase. The impact on the free energy of zirconia and the related production of a phase diagram is shown in Figure 12.

With there being so many potential dopants on the periodic table, the range of ionic property combinations to choose from is vast. Appropriately, a generalized discussion follows on trivalent, tetravalent and pentavalent dopant options. Atomic mass is an ionic property that is omitted since it does not affect stability.

Figure 12 – Free energy vs. composition curves and the related phase diagram for a typical stabilized zirconia system with dopant 'B' [33]

2.2.1.1 Trivalent Dopants

Oversized trivalent dopants (such as Y^{3+}) form oxygen vacancies, and due to their larger cationic radii, they adopt eightfold coordination with oxygen, leaving O^{2-} vacancies to pair with Zr^{4+} cations (as lattice neighbours). When trivalent dopants are undersized instead, their radii are smaller than the parent

Zr^{4+} cations and they substitute Zr^{4+} randomly. In that case, according to Li *et al.* [34], they are sixfold coordinated with oxygen and are in competition with Zr ions for oxygen vacancies. It is in fact more energetically favourable for undersized dopants to associate with vacancies. For this reason, for the same dopant concentration, undersized trivalent dopants will only produce half as much seven-coordinated Zr^{4+} as those that are oversized, and therefore the resultant stabilization of high temperature phases is only half as effective [34]. Hence, the minimum concentration of oversized trivalent dopants for f- ZrO_2 stabilization is 11 mol% M_2O_3 (where M is the dopant cation), whereas the minimum concentration for those that are undersized is 20 mol%. In each case, these are the concentrations where Zr^{4+} is equally likely to be in sevenfold coordination as it is to be in eightfold [20]. This behaviour for oversized trivalent dopants (Y^{3+}) is seen in section 2.3.3.2 (Figure 21), with the tetragonality of t- ZrO_2 decreasing until lattice parameter convergence, at which point f- ZrO_2 forms instead. An illustrated summary of the effect of trivalent dopants as they relate to the association of cations and oxygen vacancies is provided in Figure 13.

Figure 13 – Cation-oxygen vacancy associations when dopants (M^{3+}) are undersized and oversized (assembled from [34])

Further, since the eight-coordinated oversized dopants are in compression, much stiffer interatomic potentials result in a relatively small matrix distortion. In contrast, the six-coordinated undersized dopants are in tension (dilatation) and can cause larger distortions in the neighbouring cation network, contributing more disorder to the parent ZrO_2 lattice.

2.2.1.2 Tetravalent Dopants

Tetravalent cations have the same valence as Zr^{4+} , and in the absence of O^{2-} vacancy production, their methods of stabilization are of interest. They are relatively inefficient at tetragonality reduction (and therefore stabilizing ability), ranking third after oversized and undersized trivalent cations [22]. Li *et al.* [22] investigated the subject with use of the two most commonly used oversized and undersized tetravalent stabilizers (Ce^{4+} and Ge^{4+} , respectively), and their results revealed very different mechanisms at work.

Oversized tetravalent dopants substitute Zr^{4+} to produce compressive lattice deformations which dilate the cation network. In section 2.1.2.2, tetragonal crystallography was described as composed of weaker and stronger Zr-O bonds, arranged in layers of tetrahedra. Since larger tetravalent cations than Zr^{4+} adhere to a more symmetric arrangement of eightfold oxygen coordination, they reduce the disparity of the Zr-O layers in t- ZrO_2 [22]. This reduces tetragonality and relieves oxygen overcrowding as illustrated in Figure 14. Strain energy thus decreases, which indicates increased stability (as discussed).

Figure 14 – The effect of over and under sized tetravalent dopant cations (both which increase tetragonal stability) on the tetragonality (c/a) of zirconia (Zr-O_I is strong, Zr-O_{II} is weak) [22]

When the undersized case is investigated, however, it exhibits the exact opposite trend, with tetragonality being increased while stability is enhanced. This occurs by production of an ordered cationic lattice. More specifically, it occurs by the production of a bifurcated (two-component) tetrahedron with layers of Zr-O and M-O (M is the undersized dopant). Conversely to oversized tetravalent cations, undersized ones adhere to a less symmetric coordination with oxygen, and when they are used as dopants in ZrO_2 they strengthen the disparity of the tetragonal Zr-O layers causing increased tetragonality. The new, ordered tetragonal structure appears in Figure 14 and is more thermodynamically stable than that of Zr-Zr, and so with growing tetragonality, stability follows.

2.2.1.3 Pentavalent Dopants

When doped in zirconia together with a trivalent cation such as Y^{3+} , pentavalent cations compensate for trivalent charge on a one-to-one (trivalent-to-pentavalent) basis, and prevent or annihilate oxygen vacancies. At low concentrations in 7YSZ, the outcome is tetragonal and cubic destabilization via the reduced concentration of seven-coordinated Zr^{4+} . Since the layered tetragonal structure (by variations of Zr-O bond lengths, section 2.1.2.2) becomes stronger in the absence of Zr-associated oxygen vacancies, tetragonality also increases [35].

Two commonly used pentavalent dopants are Nb^{5+} and Ta^{5+} , both of which are undersized (compared to Zr^{4+}) and occupy substitutional sites. Dopant-oxygen bond lengths are different from Zr-O though, for example the length of Nb-O is much shorter at 1.90 Å [35]. This further increases t- ZrO_2 tetragonality by contributing to its layered structure.

At low temperature and concentration, equal additions of Y^{3+} and Nb^{5+} ($YNbO_4$) to ZrO_2 produce disordered solid solutions, with the larger Y^{3+} cations inflicting small compressive distortions and the smaller Nb^{5+} causing dilatation and larger tensile distortions. This follows the discussion of trivalent dopants.

However, similar to undersized tetravalent dopants (Ge^{4+} in the previous subsection), $YNbO_4$ doping at higher temperature or concentration begins ordering the tetragonal cation lattice, increasing tetragonality such that oxygen overcrowding is reduced and stability is improved (without any oxygen vacancies) [35]. When this happens at low concentration (< 20 mol% $YNbO_4$)

but high temperature, the smaller Nb cations migrate to the preferred sites near Y, which is less mobile with its larger ionic radius. When ordering occurs at high concentrations (20 mol% YNbO₄ or more), the smaller Nb adopts fourfold oxygen coordination while the larger Y cations are eight-coordinated [35].

In each case, ordering does not involve Zr, however eight-coordinated Zr⁴⁺ becomes thermodynamically stable. The root of this again relates to the small ionic radius of Zr⁴⁺, which strains the ZrO₂ lattice at lower temperatures and overcrowds O²⁻, causing instability. With addition of an even smaller cation species which adopts fourfold coordination, a more favourable packing in the form of an ordered layerlike structure becomes possible, and oxygen overcrowding is alleviated [35].

2.2.2 PREDICTED EFFECT ON TETRAGONALITY

In addition to the compressive and dilative lattice distortions discussed above for over- and under-sized dopants, empirical equations exist for the changes in tetragonal ZrO₂ lattice parameters with the concentration of dopants. For a_t and c_t at room temperature, they are expressed as follows [11]:

$$a_t = 0.5086 + \sum_k (0.0255\Delta r_k + 0.00015\Delta z_k) \cdot m_k \quad (2)$$

$$c_t = 0.5189 + \sum_k (0.0213\Delta r_k + 0.00064\Delta z_k) \cdot m_k \quad (3)$$

where a_t and c_t are in nanometres, Δr_k (in nm) is the difference in ionic radius ($r_k - r_{Zr}$) of the k th dopant cation (r_k) and Zr⁴⁺ (r_{Zr}) in eightfold coordination (with values from Shannon [21]), Δz_k is the cation valency difference ($z_k - z_{Zr}$) and m_k is the mole percent of the k th dopant cation in the t phase. For any number of

dopants then, the Δr_k term with its coefficient accounts for distortions caused by over or undersized cations, and the Δz_k term with its coefficient accounts for distortions resulting from valency differences and therefore O^{2-} vacancies.

The accuracy of Equations 2 and 3 has shown to be very good [11]. For example, in $2.6 \cdot \text{MgO} + 4.5 \cdot \text{Y}_2\text{O}_3 + 92.9 \cdot \text{ZrO}_2$ (mol%), calculated values for a_t and c_t were 5.114 and 5.136 Å, respectively, and measured values were 5.108 and 5.138 Å. Similarly, calculated values for $1.5 \cdot \text{Nb}_2\text{O}_5 + 3 \cdot \text{Y}_2\text{O}_3 + 95.5 \cdot \text{ZrO}_2$ (mol%) were 5.1007 and 5.1861 Å, compared to measured ones of 5.0967 and 5.1950 Å.

2.3 YTTRIA STABILIZED ZIRCONIA (YSZ)

Early stabilization of zirconia (beginning in the 1960's) was done with small amounts of bivalent calcia (CaO) or magnesia (MgO), producing one oxygen vacancy per dopant cation. However, magnesia showed to be volatile at high temperatures [7] and is insoluble in tetragonal zirconia above 1 mol% [36]. Also, both magnesia and calcia were unstable and lacked corrosion resistance [8], so yttria (Y_2O_3) became the preferred stabilizer. Yttrium's similar size and mass to that of zirconium allowed it to substitutionally dissolve into the Zr-Zr lattice over a wider range of concentrations. This broadened the potential compositions for stabilized zirconia ceramics, and continues to enable more flexibility in their fabrication today [7].

2.3.1 THE YTTRIA-ZIRCONIA PHASE DIAGRAM

Y^{3+} is a successful stabilizer because it is an oversized trivalent cation (section 2.2.1.1). With its smaller valence, Y^{3+} substitutes Zr^{4+} in the Zr-Zr cation

lattice with a net charge of -1 (Y_{Zr}^- , in Kröger-Vink notation). Since O^{2-} vacancies have a net charge of +2 (V_O^{++}), it is clear that two Y^{3+} cations are required for the formation of one O^{2-} vacancy. This reaction is summarized as [17]

In 1975, Scott [37] produced the currently most referenced Y_2O_3 - ZrO_2 phase diagram. Plotted in terms of $YO_{1.5}$ to emphasize the cationic Y^{3+} concentration, the ZrO_2 -rich side is shown in Figure 15.

Figure 15 – The zirconia rich side of the ZrO_2 - $YO_{1.5}$ phase diagram including non-equilibrium transformation regions (T_0) and retained metastable phases (above horizontal axis) upon quenching from the cubic region [38]

From the phase diagram, concentrations of $\text{YO}_{1.5}$ greater than 18 mol% will stabilize the cubic crystal structure such that is retained on cooling to room temperature. If cooling is rapid (if the material is quenched), then concentrations as low as 14 mol% will do the same. These concentrations that stabilize the cubic phase are called yttria stabilized zirconia (YSZ). Below these concentrations, transformations will occur upon cooling from the cubic region.

In the range of 4 to 14 mol% $\text{YO}_{1.5}$, quenching produces the metastable non-transformable t' phase (section 2.1.2.3) which does not undergo transformation to m phase like equilibrium t - ZrO_2 does, making it highly desirable. This concentration range is referred to as partially yttria stabilized zirconia (PYSZ). However, with time at high temperatures such as during TBC operation, the t' phase will decompose into equilibrium phases which transform normally (hence the need for stability investigations such as the focus of this thesis).

2.3.2 IDENTIFICATION OF 7YSZ

The most common yttria-zirconia composition is 7 wt% partially yttria stabilized zirconia, referred to in industry as 7YSZ. The equivalent molar mixture is $3.95 \cdot \text{Y}_2\text{O}_3 + 96.05 \cdot \text{ZrO}_2$ (or, with unit cations, $7.59 \cdot \text{YO}_{1.5} + 92.41 \cdot \text{ZrO}_2$). This is roughly the limiting concentration at which the t' phase is formed and thermal cycle life is best in plasma sprayed coatings (plasma spraying is detailed in section 2.6.1). 7YSZ was first identified as the ideal yttria-zirconia alloy by Stecura in 1985 [7], when the graph in Figure 16 was produced. At compositions below 7YSZ, $t \rightarrow m$ transformations occur, and above it, the less tough cubic phase is stabilized.

Figure 16 – Cycles to failure vs. yttria concentration in zirconia [7]

2.3.3 PHASE TRANSFORMATIONS

Now having reviewed the primary phases of zirconia and the effect of stabilizers (especially Y₂O₃), the transformations between phases can be detailed. In their simplest ideal case, phase transformations can be thought of in terms of a spherical product particle in a parent matrix. Lange [39] was one of the first to approach zirconia transformations in this way (more specifically that of $t \rightarrow m$). The change of total free energy (ΔG) due to a transformation is given by

$$\Delta G = \Delta G_C + \Delta U_{SE} + \Delta U_S \quad (5)$$

Here, ΔG_C (< 0 when $T < T_0$) is the chemical free energy (dependent on temperature and composition), ΔU_{SE} (> 0) is the strain energy associated with the transformed particles (dependent on the surrounding matrix, the size and shape of the particle, and the presence of stresses), and ΔU_S (> 0) is the change in

energy associated with the surface of the particle (creation of new interfaces and microcracking) [38].

The following subsections will describe phase transformations in PYSZ ceramics in the context of Equation 5. Unless otherwise specified in the discussion, the composition can be assumed to be 7YSZ or very near that, so long as it is possible to form t' on quenching from the cubic phase (see the phase diagram in Figure 15).

An appropriate transformation to begin with is that which occurs at the highest temperature on cooling, i.e. the homogenous precipitation of the tetragonal phase from a cubic matrix. It is a good introduction to this topic since it exhibits a familiar diffusion-controlled nature.

2.3.3.1 Diffusion-controlled Cubic to Tetragonal ($f \rightarrow t$)

This reaction occurs upon slowly cooling from the cubic (f) region into the two phase ($t + f$) region of the Y_2O_3 - ZrO_2 phase diagram. The change of crystal structure occurs by the displacement of oxygen anions parallel to what becomes the tetragonal c axis. Two oxygen sublattices displace from their equilibrium cubic fluorite positions (Figure 17a) in opposite directions and into their stable tetragonal locations (Figure 17b), very slightly elongating the axis of motion.

Figure 17 – a) A unit cell of high temperature cubic fluorite with arrows indicating the direction of O^{2-} anions with the $f \rightarrow t$ transition, and b) the resultant tetragonal structure (O^{2-} sub-lattice shown as dark dots, Zr^{4+} lattice with white dots) [40]

Following the t and f solvus lines of the phase diagram (Figure 15), the two phases dissolve different concentrations of Y_2O_3 at equilibrium (tetragonal dissolves less, cubic dissolves more). The nucleation and growth of t- ZrO_2 by $f \rightarrow t$ thus involves extensive diffusion as the tetragonal precipitates displace Y^{3+} and enrich the surrounding cubic matrix. Cation diffusivity is very slow through the rigid Zr-Zr lattice, so the transformation necessitates very long annealing times in the two phase region to reach equilibrium [26].

Where equilibrium is not sought, cooling rate remains an important factor. Cooling rates that provide insufficient time at high temperatures will form less tetragonal precipitates. Less yttrium will have been displaced and the cubic matrix will be insufficiently enriched to maintain stability at room temperature. Upon further cooling, the system will then undergo the only mechanism by which its overall free energy can be reduced, and that is the displacive transformation $f \rightarrow t'$ discussed in section 2.3.3.2.

In the time-temperature-transformation (TTT) diagram shown in Figure 18, curve R_1 represents a fast cooling rate that avoids the $f + t$ nose and thus disallows the diffusional $f \rightarrow t$ reaction. It follows that only yttria-rich t' is formed, which occurs by the displacive $f \rightarrow t'$ reaction that begins at T_0 . In contrast, curves R_2 and R_3 allow sufficient diffusion and yield different amounts of equilibrium t phase, depending on the time spent in the $t + f$ region. R_2 represents a more rapid cooling rate and will initially precipitate low-yttria t - ZrO_2 , but T_0 will be reached before equilibrium is achieved. Remaining cubic structures will be insufficiently enriched and will transform to t' with the same composition. On reaching T_0 , the phase content will consist of low-yttria t phase and high-yttria t' [26, 37]. Only R_3 is slow enough to approximate equilibrium conditions and sufficiently enrich the cubic matrix so that it is stabilized to room temperature. The overall phase content in the case of R_3 (on reaching T_0) would be a combination of equilibrium t and f phases.

Figure 18 – Schematic time-temperature-transformation diagram for Y_2O_3 - ZrO_2 alloys ('c' refers to cubic fluorite) [26]

There is in fact disagreement about the nature of the $f \rightarrow t$ transition and whether tetragonal separation occurs by spinodal decomposition (a thermodynamically second order transformation) or by a homogenous nucleation process (first order). However, computer models [40] and experimental observations [26] provide evidence that seems to point to a first order transformation.

On the topic of initiation, Aldebert and Traverse [25] emphasize the role of stoichiometry as it relates to temperature and phase stability. Their experiments show that, on heating, the $t \rightarrow f$ transformation (opposite to $f \rightarrow t$) is lead by a dramatic loss of ZrO_2 stoichiometry. From this it follows that the $f \rightarrow t$ transformation (on cooling) is affected in the opposite way. On heating $t\text{-ZrO}_2$, the O^{2-} network expands with the Zr-Zr cation lattice as thermal energy causes an increase in average interatomic distances. While this happens, both ionic and covalent bonding is maintained. The O-O bond lengths continue to increase linearly until 1925°C , but then become strained by the tetragonal symmetry which hinders their continued expansion. ZrO_2 stoichiometry is simultaneously observed to suffer, as shown in Figure 19. This trend presumably continues until the transformation to cubic fluorite occurs which restores stoichiometry to ZrO_2 . It follows that, on cooling, increased stoichiometry would act as a hindrance to the $f \rightarrow t$ transformation. These experimental accounts agree nicely with the model that the oxygen sublattice in the cubic phase becomes overcrowded on temperature reduction, requiring an elongation of the Zr-Zr cation lattice into the tetragonal phase [35].

Figure 19 – Sample data showing the trend of O-O distance with increased temperature in pure t-ZrO₂ with stoichiometry overlay (constructed with data from [25])

The orientation relationship between the parent f and product t phase is well established. Any a axis of the f phase can become the c axis of the t phase as yttria is displaced out the transformation zone, giving rise to three variant orientations of t precipitates, designated appropriately as t_1 , t_2 and t_3 [26]. All orientations are believed to nucleate in a coherent manner, but the large compositional difference between tetragonal precipitates and the yttria-rich cubic matrix cause high coherency strains. The associated high strain energy is detrimental to precipitate growth because it adds to the free energy of the tetragonal phase, which increases $\Delta G^{t \rightarrow m}$ (Equation 5) and reduces the driving force. Growth can therefore only continue if strain energy is reduced. This is accomplished by morphological characteristics that form out of necessity, which are covered in detail in section 2.3.4.2.

2.3.3.2 Displacive Cubic to Tetragonal ($f \rightarrow t'$)

Rapid cooling from the cubic region places zirconia systems in a highly unstable state. Without sufficient time at high temperatures to permit the diffusion-controlled transformation to t -ZrO₂, and without the simultaneous yttria enrichment of f -ZrO₂, the unstable cubic zirconia can only decrease its free energy by a diffusionless transformation to the metastable t' phase. This tetragonal structure retains the original composition of the parent f -ZrO₂ and its crystal structure minimally differs from equilibrium t phase as has already been discussed (section 2.1.2.3).

Free energy versus composition curves for t and f phases are shown in Figure 20 and schematically illustrate when and why t' occurs instead of the diffusionally driven production of equilibrium t phase. For a given alloy of composition C_0 , Figure 20 gives three cases.

Figure 20 – Gibbs free energy versus Y₂O₃ content curves for t and f phases at the indicated temperatures ('ss' indicates solid solution and 'c' is the cubic phase, t) [26]

During cooling, while $T > T_0$ as in Figure 20a, diffusion is rapid enough to control the regular $f \rightarrow t$ transformation. The resultant phase content includes

both t and f phases as discussed the previous subsection 2.3.3.1, and the usual construction of a tangent line (in Figure 20a) to both free energy curves gives t and f equilibrium compositions C_1 and C_2 , respectively. In other words, on cooling, the homogenous cubic alloy of composition C_0 lowers its overall free energy by $\Delta G_{prec.}^{c \rightarrow t}$ by separating into two differently-structured (t + f) solid solutions with compositions C_1 and C_2 .

Figure 20b shows an alloy of composition C_0 at $T = T_0$, which is the defining case for T_0 where the free energies of t and f are the same. This marks the temperature at which diffusion can no longer occur quickly enough to provide the free energy change necessary via regular $f \rightarrow t$. When cooling reduces temperature to $T < T_0$ (Figure 20c), the cubic alloy of composition C_0 can most easily lower its overall free energy by $\Delta G_{disp.}^{c \rightarrow t}$ if it displacively transforms to a single tetragonal phase with the same uniform (C_0) yttria content. When this happens, the result is the t' phase.

Figure 20c further highlights the metastability of t'-ZrO₂ since an additional drop in free energy can be obtained with the transition of t' into a two-phase alloy including both t and f crystal structures with compositions C_1'' and C_2'' , respectively [26]. Low temperatures generally prohibit the diffusion required for this (t' $\rightarrow$ t + f) reaction to occur, but Jones [2] points that it happens in plasma sprayed YSZ when aged at 1200°C or annealed at 1288 – 1482°C. He also points out that in other similar heat treatments, the monoclinic phase is not affected by the decomposition process.

Because this transformation is displacive and is not controlled by the nucleation and growth of a new phase, any grain of the parent f phase can transform independently to a single grain of t' phase at some critical temperature below T_0 . Any a_f axis of f-ZrO₂ can become the c_t axis of t'-ZrO₂, therefore the c axis of a t' grain is effectively oriented at random within a polycrystalline material [26]. The tetragonality of t' creates internal stresses that must be relieved for precipitates to grow. This is done by mechanical twinning which is described along with other morphological t' properties in section 2.3.4.3.

Scott [37] was first to notice the t' phase while developing the Y₂O₃-ZrO₂ phase diagram that is now generally accepted (Figure 15). Complementary to the preceding work of Lefevre [41], Scott also documented the smooth transition into and out of the t' region that is loosely defined in the phase diagram by dotted lines. Figure 21 is Scott's plot that shows the effect of composition on the lattice parameters of tetragonal and cubic phases. The data points were obtained by rapidly cooling ZrO₂ from the cubic region and taking measurements from the room temperature specimens. It reveals a smooth change of measured lattice parameters and shows that they are simply a function of composition.

More recently, it has been shown [42] that the decreasing tetragonality with increasing yttria in Figure 21 is due to smaller displacements of O²⁻ along the c axis. This further supports the oxygen overcrowding model [35], since more Y³⁺ leads to more O²⁻ vacancies which allow O-O relaxations and that negate the need for larger O²⁻ displacements.

Figure 21 – Change of tetragonal lattice parameters with additions of yttria [37]

Some researchers (for example [43] in 2001) have interpreted Figure 21 as indicating that lattice parameters cannot be used to clearly distinguish t and t' phases. However, Scott [37] collected data using X-ray diffraction techniques that would have captured average values for cubic, tetragonal and monoclinic phases, and did not specifically take measurements from t or t' regions. Therefore, the converging values of c_t and a_t in the figure should be interpreted as an increasing presence of t' precipitates, since the higher yttria content acts to reduce the tetragonality toward unity (as described already). This better agrees with most literature. Among others, Harmsworth and Stevens [30] have documented smaller c_t/a_t ratios for t'-ZrO₂ (1.007 for 10 mol% yttria) and much larger c_t/a_t ratios for pure (non-stabilized) t-ZrO₂ (1.015 – 1.02).

Figure 21 reveals a hidden competitive process between f → t and f → t' transformations. In the figure, tetragonal phases do not appear past about 13 mol% YO_{1.5} and the cubic phase appears as early as 12 mol% YO_{1.5}. Yet, in the

$\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram (Figure 15), the cubic phase is not stable until near 18 mol% $\text{YO}_{1.5}$ and, as has been explained, unstable yttria-rich f- ZrO_2 transforms to t'- ZrO_2 upon cooling. This discrepancy is due to strain effects of the t precipitates on the surrounding f matrix. As the f $\rightarrow$ t transformation produces coherent t precipitates, there is an accompanying high internal strain within the cubic matrix due to their tetragonality, albeit small. This hinders the f $\rightarrow$ t' transformation by action of the associated stresses, even far below T_0 , and evidently to room temperature [26]. The cubic symmetry of the matrix is therefore retained, albeit it metastable below T_0 .

t and t' phases are very closely related, but the most important difference is that t' is non-transformable to the monoclinic phase. The reason that the t $\rightarrow$ m transformation is preferably avoided becomes more apparent in the following subsection.

2.3.3.3 Martensitic Tetragonal to Monoclinic (t $\rightarrow$ m)

Arguably the most important phase transformation in zirconia ceramics is the martensitic t $\rightarrow$ m transformation. This is because of the substantial 4% volume expansion that is associated, and the large shear strain (near 8% [32], illustrated in Figure 22). Being martensitic, this reversible process is very fast and involves the simultaneous and cooperative movement of atoms over distances less than an atomic diameter [38]. It can occur during cooling (athermally) or by being stress induced (most commonly near a crack tip) [26] but it is always diffusionless because the transformation occurs at low temperatures where the monoclinic phase is stable and Y^{3+} cations are effectively immobile. In

non-equilibrium conditions, like those of cooling, the athermal $t \rightarrow m$ transformation in pure ZrO_2 starts, peaks and ends at 1053°C , 1049°C and 1021°C , respectively [29]. When stress induced, $t \rightarrow m$ can occur at any lower temperature.

Figure 22 – Schematic of the strain imposed on a cylinder by the $t \rightarrow m$ transformation [38]

The orientation relationships between the t and m phases is such that the c_t and a_t axes become the a_m , b_m or c_m axes of the m lattice (statistically randomly) with an angular distortion, β (see Figure 4) [26]. However, for reasons that are still being researched, this simple morphological relationship does not translate to simple habit planes that separate the two phases.

Before transforming to monoclinic, tetragonal particles inside of bulk zirconia are constrained by neighbours and by surrounding matrix material. Considering the alternative case of unconstrained t phase that is in the process of cooling, Equation 5 (describing the free energy change between two phases)

reduces to $\Delta G^{t \rightarrow m} = \Delta G_c$ because $\Delta U_{SE} = \Delta U_S = 0$. This complete dependence of total free energy ($\Delta G^{t \rightarrow m}$) on chemical free energy (ΔG_c) means that the transformation starts as soon as $\Delta G_c < 0$, which occurs at the non-equilibrium transition temperature T_0 (for $t \rightarrow m$) in Figure 15. However, in the constrained case of t particles in a bulk material, surface and strain energy changes (ΔU_S and ΔU_{SE}) are no longer zero. They are instead both positive, making $\Delta G^{t \rightarrow m}$ more positive, and inhibiting the transformation from taking place until some lower temperature M_s [44]. Thus, in dense zirconia ceramics where $T_0 > M_s$, external strain energy must be supplied to relieve internal strain energy and initiate transformation.

This concept is simplified by realizing that strain energy change ($\Delta U_{SE} = U_{SE}^m - U_{SE}^t$) can be thought of as the sum of internal strain energy, ΔU_{ISE} (> 0), and external strain energy, ΔU_{ESE} (< 0). ΔU_{ISE} is positive due to resisted volume expansion by surrounding matrix material, while ΔU_{ESE} is negative since it strains the matrix and allows transformed particles to relax. With that in mind,

$$\Delta U_{SE} = \Delta U_{ISE} + \Delta U_{ESE} \quad (6)$$

This is the basis of transformation toughening (discussed shortly in section 2.4) and can be visualized following Figure 23. In the figure, total free energy ΔG (from Equation 5) is plotted against temperature as two lines that represent constrained and unconstrained cases. During cooling, free energy follows these lines downward. At any temperature $T > M_s$ for constrained particles it can be seen that external strain energy is required to induce the $t \rightarrow m$ transformation.

content during cooling to room temperature, it must contain grains below a critical size, the value of which increases with stabilizer additions. As higher concentrations of stabilizer are added, the critical grain size increases and allows larger grains to retain the t phase to lower temperatures. In the figure, dotted lines are theoretical $t \rightarrow m$ transformation temperatures and solid ones correspond to the Y_2O_3 - ZrO_2 phase diagram in Figure 15. Solid dots are from experiments.

Figure 24 – Grain size and yttria concentration dependency of the $t \rightarrow m$ transformation temperature [45]

It is important to note that the effect of stabilizer content on critical grain size appears to level out at 3 mol% Y_2O_3 [46]. This is not surprising, since the formation of the metastable t' phase beginning at about the same concentration certainly interrupts the trends of Figure 24. Stabilization via grain size control is therefore restricted to low yttria compositions.

The thermodynamic relation of $d_{critical}$ to surface and interfacial energy has recently been refined in a study [50] that separately investigated the phase

changes within 1) loose powder particulate and 2) grains within sintered solids. It was found that $d_{critical}$ varies differently in those two physical formats because of the added requirement for geometric compatibility in the case of sintered grains. There is no constraint imposed on t phase in a loose powder, so in that case $\Delta U_{SE}^{t \rightarrow m}$ is zero and $d_{critical}$ depends primarily on the surface energy difference between t and m ($\Delta\gamma_s$). On the other hand, a t-ZrO₂ particulate in a sintered body is constrained, and the $\Delta U_{SE}^{t \rightarrow m}$ term suppresses the transformation to a lower temperature (Figure 23). In that case, $d_{critical}$ depends on both ΔU_{SE} and $\Delta\gamma_i$, the change in interfacial energy.

For powders, critical particle size $d_{critical}$ was found to be [50]

$$\frac{1}{d_{critical}} = -\frac{\Delta H_{\infty} T}{6\Delta\gamma_s T_{\infty}} + \frac{\Delta H_{\infty}}{6\Delta\gamma_s} \quad (7)$$

For the sintered solid, $d_{critical}$ is

$$\frac{1}{d_{critical}} = -\frac{\Delta H_{\infty} T}{6\Delta\gamma_i T_{\infty}} + \frac{\Delta H_{\infty} + \Delta U_{SE}}{6\Delta\gamma_i} \quad (8)$$

As described, in these relations $\Delta\gamma_i$ is the difference in interfacial energy in sintered pellets, while $\Delta\gamma_s$ is the difference in surface energy in powder grains. ΔU_{SE} is the total strain energy involved in the t $\rightarrow$ m transformation (per unit volume), T is the transformation temperature, T_{∞} is the transformation temperature for an infinitely large grain, and ΔH_{∞} is the enthalpy change of the transformation for an infinitely large grain. It can be seen that powders therefore have larger critical sizes than sintered solids, and higher transformation temperatures.

Regardless, the dominant factor governing the stability of tetragonal grains is the stress state, related to the strain energy term ΔU_{SE} . An illustration of this is provided in Figure 25, which is a schematic of test results [51] after annealing tetragonal grains in humid air long enough for water ingress to occur. A clear explanation for the results came only twenty years later [52] in 2005. The penetration of water radicals caused the grains to contract, and for grains that were constrained (in positions 1, 2 and 3) this destabilized the t phase by reduction of ΔU_{SE} (Figure 23). Protruding grains (position 4) were unconstrained, making ΔU_{SE} nearly zero. So although grains in position 4 contracted, they did not form tensile stresses, and therefore maintained stability.

Figure 25 – Schematic of a TEM foil edge of t-ZrO₂ before and after annealing in humid air which infused the lattice with water causing large internal strain (non-hatched represents t phase, hatched m phase) [51].

In situ experiments [26] have shown that the stress induced t → m transformation initiates as m lathes at t grain boundaries where atomic coordinations are small and lattice reorientations are least restricted. The transformation then continues by propagation of isolated laths and not by forming new ones, suggesting that the nucleation barrier of m-ZrO₂ is the controlling factor for this reaction. As the m plates continue to grow through the tetragonal grain, they cause microcracks along the grain boundaries (due to the large

transformation strains ahead of the advancing lath) which can initiate other m laths in adjacent grains if crack impingement occurs [26].

On the topic of a nucleation barrier, TTT diagrams for 100% t-ZrO₂ clearly show the incubation time necessary for the t → m transformation to begin (Figure 26). The appearance of a nose temperature (at 300°C) indicates at least two opposing factors controlling the rate of monoclinic nucleation and growth [53].

Figure 26 – TTT diagrams for 2 mol% Y₂O₃ + ZrO₂ ceramics sintered at a) 1600°C and b) 1450°C [53]

The consistent nose temperature in Figure 26 for both sintering times suggests a dependency only on composition. Meanwhile, between sintering at 1600°C and 1450°C, incubation time changes from 10^{2.35} (= 224) to 10^{0.30} (= 2) seconds. This was explained by the authors not on the basis of sintering temperature, but instead on porosity, where higher degrees of porosity mean less constrained grains, a higher transformation temperature (by Figure 23), and ultimately a larger driving force on cooling that expedites the transformation.

2.3.4 PHASE MORPHOLOGIES

All of the phase transformations reviewed previously involve changes to the shape of unit crystal cells, which interact with the parent matrix and translate to strain energy changes that hinder transformation by their effect on free energy (Equation 5). A natural mechanism for minimizing strain energy is therefore not surprising. It occurs in the form of morphological features that accompany transformations as they occur, ensuring that the strain imposed by a transformed crystal is mutually accommodated by a differently oriented neighbour. All phases but cubic fluorite display this type of behaviour. f-ZrO₂ is exempt because it has equal lattice parameters in all three dimensions, so cannot accommodate strain with an ordered arrangement of orientations. It is therefore omitted from the following discussions, but often appears in micrographs as the parent matrix to t and m particles.

2.3.4.1 Monoclinic (m)

Due to the large shear strains that accompany the t → m transformation (Figure 22), m-ZrO₂ particles usually contain twin domains. Twins are crystallographically identical but differently oriented variations of the same phase, so it is possible for neighbouring domains to mutually accommodate their shear components of strain. This ordered morphology arises from randomly oriented m-ZrO₂ nuclei, which only survive and grow if an appropriate twin is nearby. Only then is ΔU_{SE} minimized in Equation 5 such that the pair of orientations is competitive. Monoclinic particles thus usually appear similar to Figure 27 and Figure 28, having a lamellar morphology consisting of two adjacent twin domains.

Figure 27 – Predicted morphologies of m-ZrO₂ particles (arrows show direction of reference and twin lattice parameters) [54]

Figure 28 – Twinned monoclinic particles in a cubic matrix of PSZ [54]

Figure 27 schematically shows the most common monoclinic particles, with twin boundaries being either perpendicular or parallel to the longitudinal axis. Although in both illustrated cases the normal component of twin strain acts in the same direction, shear strains (normally 8% [32]) are completely cancelled (assuming equal domain thicknesses) [54]. The two cases shown in Figure 27 have twin planes of $(100)_m$ (left) and $(001)_m$ (right) and originate from the assumption that parent c_t axes become c_m axes (see Figure 4). This is most common when the $t \rightarrow m$ reaction is stress-induced. Meanwhile, c_t axes generally become a_m or b_m during athermal initiation at high temperatures. In cases where twin planes are 1° offset from $(100)_m$ and $(001)_m$, shear strain is not perfectly cancelled but the remaining component is very small, near 0.09% [54]*.

* Kelly and Ball [54] report 0.05° , but shear strain is quoted here as $\tan\theta = \tan(1^\circ) = 0.087\%$.

With twinning accounted for, the free energy change associated with the $t \rightarrow m$ transformation (from Equation 5) becomes [32]

$$\Delta G_{t \rightarrow m} = \Delta G_c + \Delta U_{SE} f_T + \frac{6\gamma_T g_T}{d} + \Delta U_S \quad (9)$$

Particle diameter is taken as d and volume is $\frac{4}{3}\pi d^3$. The total area of the twin planes, A_T , is normalized by particle surface area, and $g_T = A_T/\pi d^2$. The variable γ_T is twin plane energy per unit area, and while f_T appears independently, $(1 - f_T)$ is the fraction of strain energy relieved. Accumulatively, the new term $6\gamma_T g_T/d$ represents the energy of the twin plane per unit volume of transformed material. These changes to Equation 5 can equivalently be considered a loss of constraint [32], discussed in detail in section 2.3.3.3.

While twinning is one method of increasing the $t \rightarrow m$ driving force through a loss of constraint, another is by microcracking. Microcracking expands Equation 5 to [32]

$$\Delta G_{t \rightarrow m} = \Delta G_c + \Delta U_{SE} f_c + \frac{A_c \gamma_c}{V} + \Delta U_S \quad (10)$$

where $(1 - f_c)$ is the fraction of strain energy relieved, A_c is the area of the crack surface, γ_c is fracture energy per unit area, and V is the monoclinic particle volume. The term $A_c \gamma_c/V$ represents energy per unit volume of transformed material associated with the crack surface.

With these morphological additions to the thermodynamics of the $t \rightarrow m$ transformation, Lange [32] went on to show the effect on critical grain size, $d_{critical}$, below which the tetragonal phase is retained and monoclinic is not formed at all. With some practical assumptions for parameter values, a major result was the

ability to predict the morphology of monoclinic particles according to normalized grain size ($d/d_{critical}$, where $d_{critical}$ here is with reference to unconstrained particles) and temperature or alloy composition (plotted in $\Delta U_{SE}/|\Delta G_c|$ space).

Figure 29 is the plot which was produced.

Figure 29 – Regions indicating the transformed phase and accompanying morphologies as a function of normalized grain size ($D = d$ in the text, and $D_{uc} = d_{critical}$ for unconstrained particles) and temperature or alloy composition [32]

2.3.4.2 Tetragonal (t)

The early stage of t phase precipitation is characterized by very small particles in a cubic matrix, which nucleate with enough Y_2O_3 content for coherency within the f matrix [26]. Although tetragonality in PYSZ t- ZrO_2 is small, it is enough to favour the growth of particles that offer the lowest long range

strain energy, which are those that form neighbouring twin domains. Twin tetragonal pairs are arranged in long colonies in a repeating pattern, accumulatively producing an invariant plane strain that makes the $f \rightarrow t$ transformation nearly stress free [55]. Example colonies are shown in Figure 30. Interestingly, although most strain is accommodated, there is evidence suggesting that the resistance of newly formed $t\text{-ZrO}_2$ to stress-induced transformation is primarily controlled by the stress fields imposed by neighbouring particles [55].

Figure 30 – Tetragonal colonies in a cubic matrix (in PYSZ), where two $t\text{-ZrO}_2$ twins appear as light or dark contrasts [56]

The two twins in each colony differ only by the orientation of their c_t axis and share the same habit plane with the parent cubic matrix [57]. It is well established that there are three possible variants of t phase domains, each one occurring with its c_t axis nearly parallel to one of the three original cubic axes, i.e. parallel to $(001)_f$, $(100)_f$ or $(010)_f$. These three tetragonal variants are appropriately designated t_1 , t_2 and t_3 , and are separated by $\{110\}$ type twin planes [58]. Due to their tetragonality in a cubic matrix, they are not perfectly orthogonal at 90° , but are instead tilted by a small angle which experiments have

revealed to be 0.5° [55] such that variants meet at 89.4° when $c_t/a_t = 1.01$ [59].

This means that twin planes are stress free, with all the transformation strain concentrated at the colony-matrix interface [26].

Each combination of the three possible domains can be separated by one of two twin planes, so there are six potential colony types that occur in pairs of (t_1, t_2) , (t_1, t_3) or (t_2, t_3) [57]. But additionally, each type can have layers stacked in two different orientations, so the total number of colony variants is twelve. The four variants originating from (t_1, t_2) appear in Figure 31.

Figure 31 – Schematic of four tetragonal colony variants in the (001) plane consisting of the (t_1, t_2) pair (redrawn from [58])

The directions that colony variants grow have been explained on the basis of varying domain thicknesses [26], which would require thickness ratios of roughly 4:1 to be solely accountable [56]. The minimum overall strain energy is theoretically obtained when the relative thickness of the two repeating twin domains is given by [26]

$$\eta = \frac{-\varepsilon_{11}^o}{\varepsilon_{33}^o - \varepsilon_{11}^o} \quad (11)$$

where

$$\varepsilon_{11}^o = \frac{a_t - a_f}{a_f} \quad \text{and} \quad \varepsilon_{33}^o = \frac{c_t - a_f}{a_f}$$

With common values of $a_f = 5.128 \text{ \AA}$, $a_t = 5.090 \text{ \AA}$ and $c_t = 5.180 \text{ \AA}$, an example value for η is 0.423, which agrees with stable configurations observed experimentally [26]. In some colony structures that exhibit layers with equal thickness, directional growth has been explained by specific shifts of twins along twin planes [56].

Direction changes like those in Figure 30 occur by a reversal of domain thickness, as illustrated in Figure 32. They can also occur by changes in the way that twin planes are shifted [56]. Such variations in behaviour are a function of bulk Y_2O_3 content, and also of heat treatment [56].

Figure 32 – Model of precipitate colonies changing direction by angle α due to thickness changes of lamellae [56]

2.3.4.3 Non-transformable Tetragonal (t')

Much of the morphological discussion for equilibrium $t\text{-ZrO}_2$ applies to non-transformable $t'\text{-ZrO}_2$ as well, including the existence of colonies for reduced coherency strains, twin variants and twin planes. Even so, the most important differences between equilibrium (low-yttria) $t\text{-ZrO}_2$ and non-transformable (high-yttria) $t'\text{-ZrO}_2$ are in their morphologies.

As explained in previous sections, equilibrium $t\text{-ZrO}_2$ forms from a cubic matrix in a diffusion-controlled reaction. Yttria is displaced out of growing t

precipitates and into the f-ZrO₂ matrix, which is enriched to stability as tetragonal colonies form. The resulting morphology is similar to Figure 30 with low-yttria tetragonal colonies in a high-yttria cubic matrix. However, since t' zirconia is produced via quenching, there is no displacement of yttria and therefore no matrix/colony morphology. Instead, the entire volume of material is retained in a metastable, high-yttria, tetragonal state (t'), with no cubic matrix. Twin domains still form into colonies that minimize coherency strain [59], but colonies are tightly packed, i.e. immediately adjacent to one and other. This produces a t' morphology that is so highly regular that it is commonly referred to as "herringbone" (with reference to the weaving pattern by the same name). An example micrograph is shown in Figure 33.

Figure 33 – t'-ZrO₂ domains forming colonies (C) in a herringbone pattern [59]

As the previous subsection (2.3.4.2) pointed out, the morphology of equilibrium t-ZrO₂ concentrates all transformation strain along the colony-matrix

interface, allowing the $\{110\}$ twin planes (offset by 0.5°) to be stress free throughout the full thickness of colonies. However, in t' -ZrO₂, since every colony exists immediately adjacent to another, the strains at their boundaries are intimately entangled with those of their neighbours. To prevent domain misfits between neighbours, slight deviations occur from ideal domain orientations near colony boundaries. In particular, the twin t_1 is thought to deviate very slightly (below what can be experimentally measured), and twins t_2 and t_3 tilt mutually toward each other by 0.5° each [59]. This behaviour can be seen on close examination of Figure 33, where twin planes are not perfectly horizontal or vertical throughout the thickness of any colony, but instead tilt slightly near the colony boundary.

Figure 33 represents the common planar structure in t' -ZrO₂, where two types of colonies are stacked repeatedly in a single longitudinal direction with a single plane describing their intersections. Another structure can occur that is considered 'three-dimensional', as three colonies (each composing of two repeating twins) join along their longitudinal axes in a helical arrangement [59]. This is shown in Figure 34, where colonies C_1 and C_2 intersect along the (011) plane and the t_1 domain is common to both, while t_2 adjoins t_3 . The colonies C_1 and C_3 share t_2 and have a colony boundary along $(10\bar{1})$, where t_1 adjoins t_3 . Finally, along $(\bar{1}10)$ between C_2 and C_3 , t_3 is common and t_1 adjoins t_2 . In this helical assembly, the three colonies mutually accommodate strain very efficiently.

Figure 34 – Three-dimensional shape of the colonies created of tetragonal domains, differently arranged with respect to the $\langle 111 \rangle$ longitudinal colony axis (modified from [59])

The most cited characteristic of the t' phase is the existence of a domain substructure, pictured in Figure 35. Instead of domains consisting of a uniform twin lattice like for equilibrium t phase, they contain tiny sub-domains of variants that are separated by anti-phase domain boundaries[†] (APBs) [59]. Variants in this case are differentiated by the reversed displacement of oxygen sub-lattices [42], and not by different tetragonal orientations such is the case between twin domains. As illustrated in Figure 36, APBs occur between cells with a common, contiguous Zr-Zr lattice, but with O^{2-} displacements that are symmetric where continuity is otherwise expected. Previous discussions of the tetragonal crystal

[†] Although zirconia literature commonly uses the term 'anti-phase domain boundary' (APB), the International Tables for Crystallography [24] define APBs as separating translational but not rotational twins. As is discussed further in the text, APBs (in the context of t' -ZrO₂) occur within a contiguous Zr-Zr lattice and are defined by the symmetry of oxygen displacements [42] where continuity is otherwise expected. This means that the tetragonal cells bordering an APB behave simply as rotated variants, with there being no associated translation. Thus when the term 'APB' is applied to t' -ZrO₂, it is a technical misnomer.

structure (sections 2.1.2.2 and 2.3.3.1) introduced this digression of O^{2-} from the ideal cubic fluorite structure, but Figure 36 clarifies the symmetry about APBs.

Figure 35 – Small anti-phase domain boundaries inside the domains of t'-PYSZ [59]

Figure 36 – A schematic of APBs showing the different displacements of oxygen anions in a) adjacent sub-domains and b) as viewed from the (001) direction (O^{2-} is black, Zr^{4+} is white, and image is modified from [42])

Zhou *et al.* [42] documented that oxygen displacement in t'- ZrO_2 reduces with increasing yttria concentration until a critical point at 16 mol% $YO_{1.5}$ where tetragonality suddenly becomes negligible and cubic fluorite is instead identified

upon quenching. This correlates well with the earlier work of Scott [37] (Figure 21).

The sudden loss of tetragonality at 16 mol% $\text{YO}_{1.5}$ is not caused by a discontinuous reduction of O^{2-} displacement. Oxygen displacement in fact continues to reduce gradually [42]. Rather, the sudden loss of tetragonality is the result of reaching a critical point where the Zr-Zr cation lattice collapses, likely out of thermodynamic necessity. Since the driving force for oxygen displacement reaches zero at still higher concentrations of yttria, this gives rise to a cubic phase, referred to as $\text{f}'\text{-ZrO}_2$, in which O^{2-} anions are not in their equilibrium f lattice positions.

2.4 STRENGTH AND TOUGHNESS OF ZIRCONIA CERAMICS

Zirconia ceramics are mechanically superior to many others due to two strengthening mechanisms, namely transformation toughening and ferroelasticity, each which increases fracture toughness. Transformation toughening occurs as the $t \rightarrow m$ reaction is activated in the high stress regions at cracks tips, which closes the crack and hinders propagation. Ferroelasticity also acts to close crack tips, but by the reorientation of t phase rather than a phase transformation. These two toughening mechanisms are now discussed.

2.4.1 TRANSFORMATION TOUGHENING

In section 2.3.3.3, it was established that strain energy change (ΔU_{SE} in Equation 5) is the dominant factor governing the $t \rightarrow m$ reaction due to the large

volume increase between tetragonal and monoclinic crystallography. It follows that, since t-ZrO₂ precipitates are thermodynamically unstable at room temperature (having no stable region in the Y₂O₃-ZrO₂ phase diagram below 585°C), they only require tensile strain for transformation to m phase. At locations near cracks then, where tension is high, the monoclinic transition occurs readily and the associated 4% volume expansion [32] closes the crack tip.

This added resistance to failure is called transformation toughening since it increases the observed fracture toughness (K_c) of materials containing t-ZrO₂. As reported by Lange [47], transformation toughening improves K_c according to the relation

$$K_c = \left[K_0^2 + \frac{2h_{tt}V_tE(|\Delta G_c| - \Delta U_{SE}f_P)}{(1-\nu^2)} \right]^{1/2} \quad (12)$$

where K_0 is critical stress intensity (in MPa $\sqrt{m}$) without the effect of transformations. The term $(|\Delta G_c| - \Delta U_{SE}f_P)$ is the work done per unit volume by the stress field to induce the transformation, V_t is the volume fraction of transformable t-ZrO₂ precipitates, E and ν are elastic properties of the matrix in which the t particles are dispersed, and h_{tt} ($\approx d$) is the size of the transformation zone around the crack. The loss of constraint on t particles near the propagating crack is given by $(1 - f_P)$, but f_P appears independently in the equation. Finally, the terms ΔG_c and ΔU_{SE} are as they appear in Equation 5. In other work [60], experiments have shown that $\Delta U_{SE}f_P$ can be neglected (set equal to zero).

A good example of the effect is shown in Figure 37. High strength is measured in the figure when grain size is small enough to retain the tetragonal

phase to room temperature ($d < d_{critical}$) and enable transformation toughening. Lower strengths are measured in the absence of t-ZrO₂ when $d > d_{critical}$. In the figure, $d_{critical} \approx 0.3 \mu\text{m}$.

Figure 37 – Bulk strength vs. grain size for TZP [61]

Equation 12 reveals a number of trends and methods for improving the high strength in Figure 37, as well as toughness. The most intuitive method is to maximize the fraction of transformable t-ZrO₂ particles, V_t , since the larger this fraction the greater is K_c . The maximum value of $V_t = 1$ represents a purely tetragonal material (i.e. TZP). In this case, individual grains (of size d) are considered to exist in a matrix defined by other differently oriented tetragonal grains. Since transformation strains among neighbours are anisotropic, each grain is constricted from undergoing stress free transformation [47].

Changes to the term $(|\Delta G_c| - \Delta U_{SEFP})$ in Equation 12 are governed primarily by temperature and stabilizer content because chemical free energy, ΔG_c , is highly sensitive to both [47]. For $T < T_0$ in Figure 23, $|\Delta G_c|$ decreases at higher

temperatures and the $t \rightarrow m$ reaction loses driving force. Dopants like Y_2O_3 and CeO_2 are tetragonal stabilizers and also reduce $|\Delta G_c|$, so driving force is lost with increasing stabilizer concentration as well. Thus, fracture toughness is highest at low temperatures and when alloy content in the $t\text{-}ZrO_2$ is minimized. The combination of high temperature and stabilizer concentration at which the contribution of transformation toughening disappears depends on ΔU_{SEFP} [47]. Also, increasing the matrix elastic properties (E and ν) is favourable, and since it is assumed that $h_{tt} \approx d$, the contribution of transformation toughening is best when tetragonal particles are large (but still $< d_{critical}$). Figure 38 is an example micrograph of crack hindrance by $t \rightarrow m$ transformation.

Figure 38 – TEM image of t phase (background) transformed to m phase (foreground lamellae) at a crack tip in PYSZ [55]

The highest values of toughness emerge from PYSZ that has been processed in the two-phase ($t + f$) field of the $Y_2O_3\text{-}ZrO_2$ phase diagram, because these materials exhibit transformation toughening [62]. This is in contrast to PYSZ that is quenched from the cubic region, since t' does not transform to monoclinic and so does not exhibit transformation toughening. Although less

tough, non-transformable t' phase is used for TBCs because, although the ability for $t \rightarrow m$ transformations enables transformation toughening, it is also what degrades coating integrity with thermal cycling. In any case, t' -ZrO₂ is very tough in its own right compared to other ceramics. To illustrate this, a histogram of ceramic toughness levels is shown in Figure 39, including a number of YSZ materials.

Figure 39 – Toughness of PYSZ, YSZ and other ceramics [62]

Non-transformable t' -ZrO₂ is actually stronger than predicted, and so are some PYSZs at high temperature. For example, at 1500°C where the $t \rightarrow m$ transition does not occur, PYSZ strength has been measured to be 700 MPa, whereas stabilized f phase at such temperatures is only 350 MPa [63]. The large difference is due to the second zirconia strengthening mechanism, ferroelasticity.

2.4.2 FERROELASTICITY

Not technically a phase transformation, ferroelasticity in zirconia is a toughening mechanism that does not involve any change of crystal structure, but instead only a change of crystal orientation. A crystal is ferroelastic if it has two or more stable orientation states and can be readily transformed from one to another by the application of mechanical stress [64]. It is characterized by a hysteresis loop between the strain, ϵ , and the applied stress, σ , such that a symmetric σ - ϵ relationship exists as illustrated in Figure 40 [63]. In the figure, ϵ_s is the spontaneous strain that occurs at coercive stress, σ_c , and the area enclosed by the full loop represents the mechanical energy dissipated in one cycle.

Figure 40 – Schematic showing a hysteresis loop for ferroelastic materials, where the shaded region is energy absorbed in reorientation of domains during fracture (redrawn from [63])

Non-transformable tetragonal (t') zirconia is well known to exhibit this behaviour with its three orthogonal variants, which gives it relatively high strength even in the absence of transformation toughening. Stress that exceeds coercive stress ($|\sigma| > \sigma_c$) can cause variant domains to switch if the direction of principle

stress is closely parallel to a_t axes. In tension, a_t axes are stretched to become c_t axes and c_t axes become a_t , effectively accomplishing a 90° rotation [63, 64]. Compressive stress leads to the reverse process. Assuming equal proportions of all three variants prior to domain switching, upon reaching coercive stress (σ_c) the spontaneous strain (ϵ_s) caused by a single switched variant is given by [62]

$$\epsilon_s = \frac{1}{3}(c_t/a_t - 1) \quad (13)$$

where c_t and a_t are lattice parameters and c_t/a_t is tetragonality. If two of the three variants switch, the coefficient in Equation 13 becomes $2/3$. On unloading, ϵ_s is permanent. Coercive stress has shown to be inversely proportional to temperature [65], and to illustrate the spontaneous strain that occurs when it is reached, an experimental σ - ϵ curve is shown in Figure 41. The curve was acquired at 500°C , and it is noted that.

Figure 41 – A compressive stress/strain response at 500°C for a 3 mol% YSZ single crystal [62]

In Figure 41, which includes plastic yield stress (σ_y) and eventual failure, it is clear that ferroelasticity is a deformation mechanism. Moreover, since toughness is taken as the area beneath the curve, the domain switching that occurs at σ_c is an important contributor.

If reorientation occurs in response to tension ($> \sigma_c$) at a crack tip, toughening occurs as the crack is closed by ε_s . Stress will decrease with distance from the plane of an extended crack, and become less than coercive stress at some distance h (beyond which domain switching does not occur). Recognizing that the energy absorbed during domain switching is represented by the shaded region of Figure 40, Virkar and Matsumoto [63] have given toughness including ferroelasticity as

$$K_c = \left[K_0^2 + \frac{2h_f E}{(1-\nu^2)} \int_{\text{shaded}} \sigma d\varepsilon \right]^{1/2} \quad (14)$$

which has a similar format as Equation 12 describing the effect of transformation toughening. Process zones h_f (for ferroelasticity, Equation 14) and h_t (for transformation toughening, Equation 12) are both proportional to K_c^2 and inversely proportional to σ_c^2 .

The ferroelastic process zone in YSZ observed by Mercer *et al.* [62] in 2007 is shown in Figure 42. In those experiments, the contribution of toughness by domain switching was found to be 35 J m^{-2} , a factor of 5.8 more than that of 20 wt% f-YSZ (non-toughened). Further, Equations 13 and 14 suggest that greater tetragonality should further improve the toughness contributions of ferroelasticity (since the shaded region grows with increasing c/a_t). This was raised in 2007

[62] and was hastily demonstrated the same year by Schaedler *et al.* [12] who added 15.2 mol% TiO_2 to t' -YSZ. Ti^{4+} substituted Zr^{4+} in the cation lattice and increased tetragonality from 1.013 (for 7YSZ) to 1.023, for a 77 J m^{-2} toughness advantage over f-YSZ, or a factor of 8 more.

Figure 42 – The ferroelastic process zone ($h_f \approx 3 \mu\text{m}$) near a crack in YSZ containing three t' variants, with a darker contrast due to twin planes which are not present in the virgin single-variant material [62]

Whether or not ferroelastic domain switching occurs in equilibrium tetragonal (t) materials is still debated, but in some direct experiments [63] the evidence is very strong. It has been noted by Virkar and Matsumoto [63] and others that contributions of transformation toughening in t- ZrO_2 should become negligible above $\sim 800^\circ\text{C}$ as the driving force (ΔG) to transform to m- ZrO_2 decreases. However on the contrary, strengths up to 700 MPa (compared to 350 MPa for stabilized f- ZrO_2) have been reported at up to 1500°C as was previously mentioned, and high toughness ($K_{\text{IC}} \approx 6 \text{ MPa m}^{1/2}$) can occur without measurable

quantities of m phase that would indicate a $t \rightarrow m$ reaction [63]. Ferroelasticity can account for these discrepancies, but to date, accounts are rarely predicted and are instead usually developed to explain unexpected experimental results. To remedy this, research in this area continues.

2.5 BOND COAT INTERLAYER AND THERMALLY GROWN OXIDE

Simple mechanical interlocking between the superalloy substrate and ceramic TBC would not provide adequate bonding between the two. Further, zirconia is very oxygen diffusive at high temperatures, so the substrate requires alternative oxidation resistance. The bond coat (BC) serves both of these issues.

As illustrated in Figure 3, a thermally grown oxide (TGO) forms atop the BC during deposition. It then grows during operation as the BC is oxidized somewhat sacrificially in protection of the substrate. The TGO also has an important mechanical purpose, though. While the BC composition is similar to that of a superalloy, the TGO is a ceramic (like the TBC top coat). The BC/TGO pair thus makes each interface a separation of similar materials, enabling chemical bonds that are much stronger than mechanical interlocking.

There is no universal bond coat for all substrates. Instead, optimization for each new system offers the best overall performance [66]. Typical bond coat materials are M-based MCrAlY alloys where M is one of Ni, Co or NiCo [8]. Here, cobalt is used for its superior hot-corrosion resistance, and nickel for its resistance to oxidation [3]. Since superalloy substrates are also Ni or Co based,

their use in MCrAlY bond coats avoids thermal expansion mismatches which could otherwise crack and delaminate the coating during operation.

Al and Cr oxidize selectively over the more abundant Ni and Co, which is an important reason for their inclusion in MCrAlY systems. Therefore, the TGO which forms from the BC consists primarily of alumina (Al_2O_3) and chromia (Cr_2O_3). The most preferential oxide produced is Al_2O_3 , which also has the slowest oxygen diffusion rate of any oxide so is best able to hinder further oxidation once produced [67]. The TGO is the source of many failure modes as it grows with time, at a rate depending largely on the content of yttria.

The growth of Al_2O_3 and Cr_2O_3 occurs as micro-sized scales [3]. Yttrium is added to MCrAlY alloys (at levels near 0.1 wt%) as a reactive element to reduce the rate of scale growth, but more importantly, to improve the adherence of scales to the MCrAlY bond coat [3]. The mechanism by which this occurs is still debated, but the improved adherence provides resistance to coating spallation [68]. Yttrium can be substituted by other reactive elements from groups 3 and 4 of the periodic table, including La, Zr and Hf [3]. Stecura [69] has additionally shown that replacing Y with Yb improves the cycle lifetime by delaying coating spallation even further [8].

The surface roughness of bond coats has significant effects on the adhesion of the TBC. A roughness amplitude in the order of 15 μm has been reported to be best for TBC top coats applied with plasma spraying [70]. In contrast, smoothness is preferred for TBCs deposited with electron beam physical vapour deposition (EB-PVD), where experiments show that reducing

roughness from 3.76 to 0.82 μm improves cycle lifetime by 38% [71]. The growth of the TGO is also affected by BC surface roughness [72].

Bond coats are generally produced as dense as possible in a vacuum or in low pressure, preferring the processes of vacuum plasma spraying (VPS), low pressure plasma spraying (LPPS) or EB-PVD. When modified MCrAlY systems are used, plasma spraying is always the application process of choice. It allows better control of composition, which is necessary because some additives (like Si or Hf) have low vapour pressures that make control with EB-PVD difficult [3].

Studies in 2008 [66] show that small additions of hafnia (< 1 wt%) change the evolution of the TGO microstructure and produce an undulated interface with the bond coat. Hafnium oxide particles form throughout the TGO thickness during thermal cycling, and stresses are reduced via introduction of short-distance cracking which can be seen in Figure 43. It is speculated that these cracks delay the critical crack driving force for spallation during TGO growth. This is a subject of continued research, but regardless of the precise mechanism, this modification increased TBC life by an impressive factor of 15.

Figure 43 – A modified TGO microstructure by addition of hafnia [66]

2.6 COATING DEPOSITION TECHNOLOGIES

In industry, the selection of an appropriate coating application process is equally important as the proper design of zirconia ceramics. The method employed significantly affects both thermo-mechanical properties, life cycle expectancy, and the ultimate modes of failure. By far, the two most common application technologies are plasma spraying (PS) and electron beam physical vapour deposition (EB-PVD), each of which tolerates the strain of operation by different mechanisms. By either method, in the thermally cyclic conditions of gas turbines (say, between a temperature difference ΔT), the primary tolerated strain ($\Delta \varepsilon$) comes from the thermal expansion mismatch between the coating and substrate, which is

$$\Delta \varepsilon = (\alpha_1 - \alpha_2) \Delta T \quad (15)$$

where α_1 ($\approx 10 \times 10^{-6} \text{ K}^{-1}$) and α_2 ($\approx 13 \times 10^{-6} \text{ K}^{-1}$) are roughly the thermal expansion coefficients of the coating and substrate, respectively.

Plasma sprayed ceramics will generally retain the same uniform composition as the feedstock material [73], since deposition cooling rates are very rapid. The deposition temperature of substrates is generally elevated for EB-PVD, so cooling rate is reduced, and precise composition control is difficult [3]. Even so, EB-PVD is used to produce smoother, more strain tolerant coatings on vital surfaces such as turbine blades. Plasma spraying, on the other hand, is a simpler process with greater flexibility, producing relatively dense coatings with compositions otherwise unattainable [74]. These technologies are now further described in terms of process control, microstructure, and performance.

2.6.1 PLASMA SPRAYING (PS)

Thermal spraying, in general, is a deposition process which melts a solid feedstock and accelerates molten particles at high velocity towards the target surface, where they spread and solidify to form thin lamellae. Resultant coatings therefore consist of stacked lamellae, accompanied by a characteristic pore structure.

Plasma spraying in particular melts and deposits powder feedstock using an electric arc and plasma gas, accomplished with a spray torch similar to that shown in Figure 44. The electric arc reaches temperatures of about 15,000 K to form a region of ionized plasma [8]. It is produced at a high frequency by direct current passing through a tungsten cathode, with a water-cooled and annular copper anode completing the circuit on the opposite side of the inert gas stream [3]. The gas stream is typically nitrogen or argon, and generally contains a small percentage of an enthalpy-enhancing gas, such as hydrogen [8].

Figure 44 – Schematic cross section of a plasma spraying torch [3]

Example feedstock powder is shown in Figure 45a. The powder is injected into the plasma stream where it melts and is propelled out of the nozzle at 100 to 300 m/s [8]. The molten particles flatten on impact with the target surface, and produce characteristic 'splats' (Figure 45b) which cool quickly and accumulate to form complex lamellar microstructures (Figure 45c). A complete PS TBC system is shown in Figure 46 with a complementary labelled schematic in Figure 47. It can be seen from these images that TBC thickness is generally around 100 μm .

Figure 45 – Plasma spray a) powder feedstock [75], b) splat structure [76] and c) fracture surface cross section of a deposited microstructure [77]

Figure 46 – Cross section of a typical plasma sprayed microstructure [3]

Figure 47 – Schematic cross section of a typical YSZ microstructure produced by plasma spraying [8]

2.6.1.1 Optimal Process Parameters

Porosity in PS coatings can exceed 20 vol%, depending on processing parameters [78]. In 2005, Li *et al.* [75] used a uniform design of experiments to find optimal parameters that minimized porosity and maximized hardness in their atmospheric plasma sprayed YSZ coatings. They reported that a lower argon flow rate of 30 l/min, a higher hydrogen flow rate of 14 l/min, and a powder feed rate of 56 g/min would produce a minimum porosity of 4.3% by volume. A maximum hardness value of 702 kg/mm² was achieved at the same settings with the additional requirement that arc current be 620 A. It was stressed that these exact settings were only valid for the experimental setup employed, however the 'higher' and 'lower' trends generally apply universally.

2.6.1.2 Microstructure Development

The lamellar microstructure of PS coatings (consisting of accumulated splats) itself contains columnar grains that are perpendicular to the substrate surface (Figure 48). These columns are formed due to the sharp temperature gradient that exists between the cold substrate and the hot molten ceramic. This initially causes very rapid cooling, leading to the formation of a thin layer of fine equiaxed grains [79], but subsequent splats grow columns because they are shielded from the cold substrate by previously deposited material and therefore cool less rapidly. Columns grow through the thickness of their parent lamella (splat) but are generally constrained from trans-lamellar growth.

Figure 48 – A transverse fracture surface of plasma sprayed 8YSZ showing lamellae, columnar grains, and very little inter-lamellar contact [80]

Air is trapped between lamellae and between splat globules, forming inter-lamellar and globular (spherical) porosity. Inter-lamellar porosity (which reduces contact area) and the lack of trans-lamellar grain growth leads to very weak interfacial bonding, having important effects on mechanical properties. Another important characteristic is the presence of microcracks which form within lamellae during cooling. These features are pictured in Figure 49.

a)

b)

Figure 49 – Plasma sprayed zirconia exhibiting globular voids (spherical porosity), microcracking and inter-lamellar pores in a) a SEM image of a fracture surface [81] and b) a schematic illustration [80]

Stecura [7] recognized 7YSZ as being the optimal yttria-zirconia composition because it yields primarily t' -ZrO₂ crystallography in PS coatings, but enough equilibrium m phase (typically between 5 and 10% [82]) that sufficient microcracks are introduced. The importance of having some microcracks is explained in the discussion of PS coating stiffness, section 2.6.1.4.

2.6.1.3 Stress State

According to experiments [83], the net stress state of cooled and relaxed PS coatings is in compression (about -20 MPa), however the upper surface is in tension (about 30 MPa). Residual stress is combinations of [84]

1. quenching stress (σ_q) generated during solidification,
2. phase transformation stress ($\sigma_{pt} = 0$ if t' -ZrO₂ is retained), and
3. thermal stress (σ_{ts}) generated as the sprayed specimen cools down.

Analytically, the magnitude of tensile quenching stress (σ_q) can be estimated from [85]

$$\sigma_q = \alpha_c (T_m - T_u) E_c \quad (16)$$

where α_c is the coating coefficient of thermal expansion ($= \alpha_1$ in Equation 15), E_c is Young's modulus of the coating, T_m is the melting temperature of zirconia and T_u is the temperature of the underlying material.

Since initially deposited material cools very quickly against the cool substrate, and later deposited material cools more slowly, thermal stress varies with distance from the substrate/coating interface. At the interface it follows Equation 15, so

$$\sigma_{ts \text{ (interface)}} = E_c(\Delta\varepsilon) = E_c(\alpha_1 - \alpha_2)\Delta T \quad (17)$$

But at the (top) coating surface, thermal stresses are roughly [85]

$$\sigma_{ts \text{ (surface)}} \approx \sigma_{ts \text{ (interface)}} \frac{1+\nu}{1-\nu^2} \quad (18)$$

where ν is Poisson's ratio of the coating.

At a critical level of tension, zirconia will form the microcracks in Figure 49. Widjaja *et al.* [85] quote this level to be about 30 MPa, which explains the same measured value [83] at the top surface of zirconia PS coatings.

2.6.1.4 Coating Stiffness

Atmospheric PS zirconia coatings (APS) have very low Young's moduli (stiffness). This might be expected due to the high porosity visible in earlier figures, but such porosity only accounts for about 33% of lost stiffness in some zirconia coatings that demonstrate a 99.6% loss [86]. This massive difference of macro-elasticity is attributed to low inter-lamellar bonding. Unlike high-density material, APS bonding is minimally chemical and is instead mainly held together by weak mechanical interlocking between splats. Thus, when loads are applied, deformation occurs primarily by lamellae sliding against one and other along their boundaries [86].

Low stiffness values are preferred in TBCs since they reduce the stresses that arise during thermal cycling (Equation 15). While the weakly bonded lamellar microstructure reduces stiffness, it also acts as residual stress relief since it allows shearing to occur (but over short distances only, due to the distorted shapes of splats) [82]. Far more mechanically important though are the

microcracks that result from the PS process. They greatly enhance strain tolerance by opening and closing during substrate heating and cooling [80]. This lowers the apparent tensile stiffness on a stress-strain curve. The effect of microcracks and their relation to tensile and compressive stiffness is illustrated in Figure 50.

Figure 50 – Schematic representation of the variation of coating stiffness with imposed strain, and the associated behaviour of microcracks [80]

From the size (between 0.1 and 0.2 μm) and spacing (about 10 μm) of microcracks [87], it can be estimated that 2% of strain is accommodated during their closing in compression [80], at which point stiffness increases dramatically as shown in Figure 50.

2.6.1.5 Performance Evolution

The high temperature operating conditions that TBCs are exposed to cause changes in PS microstructures and properties over time. During isothermal heating, the effects of sintering (section 2.7.2) lead to the repair of microcracks and to the reduction of inter-lamellar porosity [80], allowing columnar grains to grow and become trans-lamellar (Figure 51) [80, 81]. The opening and closing of microcracks is thus prevented, and so is the sliding of lamellae, which increases

stiffness and unifies it in tension and compression. The net effect is detrimental to coating performance with the removed ability for strain compliance.

Figure 51 – A transverse fracture surface showing sintered lamellar interfaces bridged by trans-lamellar grain growth [76]

Such isothermal behaviour is not directly transferrable to industrial applications, however, since thermal cycling impedes the repair of microcracks by repeatedly fracturing them [81]. In some thermally cycled experiments, stiffness actually reduces with time. Investigations show that the reduction of stiffness is generally due to inter-lamellar cracking from repeated thermal stresses (Equation 15) [86].

As discussed, weak inter-lamellar bonding reduces stiffness and allows PS coatings to accommodate the thermal strain of substrates. In cyclic conditions, the repeated stress caused by the sliding of lamella boundaries can break the weak bonds that exist, or induce excessive microcracking, which can lead to failure by spallation [86]. Figure 52 is evidence of this, showing much wider spacing between lamellae after thermal cycling (which indicates broken bonds). If cracking does not lead to premature failure, a balance with the effects of

sintering can be reached and stiffness can become stable. In Figure 52c, this is shown to occur after about 700 cycles. It is not a sign of permanent stability, however, because the bond coat continues to be oxidized, ensuring growth of the TGO. Associated crack nucleation and propagation inevitably degrades the coating integrity until failure. Growth of the TGO is to date unavoidable, but isothermal heat treatments prior thermal cycling have shown to reduce the growth rate [88, 89]. This is attributed to the suppression of detrimental mixed oxides that initiate cracks, accomplished by the production of an initial layer predominantly of Al_2O_3 .

Figure 52 – A thermally sprayed YSZ top coat and underlying bond coat
a) before and b) after 1374 thermal cycles to 1121°C , and
c) the effect on Young's modulus [86]

Thermal conductivity is also affected by pore architecture. It is considered to be predominately controlled by the free path of phonons, and so inter-laminar porosity acts to scatter phonons and reduce their mean free path, improving thermal insulation. Sintering therefore increases thermal conductivity as porosity

is reduced and lamellar contact rises. Under isothermal conditions, the effect is shown in Figure 53 for a number of stabilized zirconia-based TBCs.

Figure 53 – The effect of isothermal sintering at 1400°C on thermal conductivity for yttria (Y-), dysprosia (Dy-) and ytterbia (Yb-) stabilized zirconia (SZ) [81]

Raising the deposition temperature of the substrate during plasma spraying has shown to significantly influence the residual stress [83] and microstructure of PS coatings [76], providing an important modification to the process that allows increased control of thermo-mechanical properties. Another method of control of course is the use of an entirely different deposition process. EB-PVD is one process that offers a range of advantages, but at some expense.

2.6.2 ELECTRON BEAM PHYSICAL VAPOUR DEPOSITION (EB-PVD)

EB-PVD is an expensive process used for coating vital aerodynamic surfaces like rotating blades in hot sections of gas turbines, and in such applications it is the preferred process for many reasons. It provides smoother

(more aerodynamic) surfaces, it leaves cooling holes open, the microstructure is strain tolerant, erosion and spallation resistance is superior, and, in general, overall thermal cycle life is improved. A disadvantage however is an increase in thermal conductivity by about a factor of two [2, 3].

The EB-PVD process always takes place in a vacuum, and unlike PS, there is no 'bulk delivery' of feedstock material to the substrate surface (such as molten drops). Instead, a solid feedstock ingot is vaporized by an electron beam and expanded as a vapour stream into the vacuum where a substrate rotates. EB-PVD is thus a line of sight process, and the vapour stream can contact substrate surfaces at different angles. Typical EB-PVD equipment is shown schematically in Figure 54, including approximate process parameters.

Figure 54 – Schematic of a typical EB-PVD process [3]

Opposite to plasma spraying, EB-PVD coatings require the adjoining surface to be smooth or preferably polished prior to coating deposition. Adhesion is therefore by strong chemical means (not by weaker mechanical interlocking as in PS coatings) and can be improved with raised deposition temperatures of 850 to 1050°C [3] or post-coating heat treatments in the same temperature range [8]. Zirconia EB-PVD coatings usually deposit 7YSZ or a near-equivalent, and a specific oxygen partial pressure is maintained to achieve the correct oxygen stoichiometry in the deposited ceramic coating [8]. With 7YSZ, the t' phase is usually attained at the time of deposition, even when substrate temperatures are $> 850^{\circ}\text{C}$ [90], with a tetragonality of about 1.011 [62].

2.6.2.1 Microstructure Development

At the start of deposition as ZrO_2 vapour begins to condense on substrate surfaces, nuclei form and grow into grains immediately adjacent to one and other with random orientations [91]. This leads to an initial layer that is very dense, compacted further by oxygen deficiencies in the vacuum that commonly exist at the commencement of the EB-PVD process [8]. As condensation continues, nucleation ends and competitive grain growth begins. To survive, grains must have tips that are able to propagate with a steady state shape along the average direction of the vapour flux [92]. Further, there is an added constraint that tip facets be in the $\{111\}$ family of planes since they are most energetically favourable at the surface [91]. In a simplified case where the average incident vapour stream is normal to the substrate, the result is that competitive grains grow preferentially in the $\langle 100 \rangle$ crystallographic direction, perpendicular to the

substrate surface. This is because a square pyramidal morphology exists that allows four {111} facets to capture equal amounts of integrated flux (in the form of condensed zirconia), and therefore grow with a steady state shape [92].

Conventional rotation of a substrate within equipment like that of Figure 54 is illustrated schematically below in Figure 55, along with the associated flux pattern at pyramidal column tips. Following Figure 55b, the flux (J) that reaches the rotating flat surface in the vapour stream is [92]

$$J = J_0 (\cos \xi)^v (L/l)^2 \quad (19)$$

where J_0 is the flux arriving on a stationary sample located directly above the source at distance L . The angle ξ is between the plume axis and the line of sight, the variable l is the distance between the point and the source, and v is an empirical exponent reflecting the spread of the vapour plume. Equation 19 accounts for flux decay both with distance from the plume axis of symmetry (the line of sight axis) and with distance from the source.

Figure 55 – Schematics showing a) conventional rotation, b) related geometric variables and c) the associated flux pattern at square pyramidal grain tips [92]

As columns grow they competitively coarsen and coalesce, becoming thicker with increased distance from the substrate [91]. A representative microstructure of a completed coating is shown in Figure 56 with an accompanying schematic. The preferred square pyramidal tips are most clearly seen on the coating surface when the rate of substrate rotation is zero, such as in Figure 57a. In a more common scenario where the substrate rotation is non-zero, the vapour stream incidence angle varies and grain tips cast 'sunrise, sunset' shadowing on their neighbours [93] which acts to round tips [91], as seen in Figure 57b.

Figure 56 – a) The columnar microstructure of EB-PVD coatings [3] and b) an accompanying schematic [8]

Figure 57 – Columnar tips as viewed at the coating surface, produced at a) 0 rpm, clearly displaying {111} facets, and b) 5 rpm, with rounded tips due to shadowing of the incident vapour stream [91]

Another effect of shadowing is inter-columnar gap width, where gaps are widest in the plane of vapour incidence since that is where shadowing is most pronounced [92] during ‘sunrise, sunset’ motion of the vapour source. This translates into anisotropic strain tolerance, to be discussed further in the following performance subsection.

As mentioned previously, the average incident vapour stream location is normal to the substrate (Figure 55c) and leads to the $\langle 100 \rangle$ growth direction of columnar grains. It follows that regions of the substrate that do not lie in the plane of incidence grow columnar grains with axes that are slightly tilted from the substrate normal. Further, to support steady state growth, competitive pyramidal tips have diagonal edges (corresponding to {100} planes, Figure 55c) that are either parallel or perpendicular to the rotation axis [92]. Common variations to this are tips with rectangular bases (elongated in a {110} direction, making tips reminiscent of a ‘roof top’) which have their top ridges oriented at $\pm 45^\circ$ to the rotation axis [92].

More changes arise in non-conventional rotation modes not yet discussed, where the substrate might rotate on a plane parallel (instead of normal) to the vapour stream axis and away from (instead of above) the stream centre. In such cases, 'sunrise, sunset' shadowing is eliminated. The incident stream still averages (roughly) normal to the substrate, but it does so in circles above columnar tips instead of the plane shown in Figure 55c [92]. These sorts of conditions satisfy the equal flux and steady state growth condition for all orientations of the pyramid diagonal edges, and therefore, no alignment of grains is observed and there is a loss of grain packing efficiency [92]. This leads to complications during the EB-PVD coating of complex surfaces since it further contributes to anisotropic behaviour.

As in plasma sprayed coatings, those produced via EB-PVD have a complex substructure and a system of porosity. A clear example appears in Figure 58. Columnar grains of EB-PVD coatings are separated by inter-columnar gaps (labelled '1' Figure 58) and are composed of many layers often referred to as 'feather arms' ('3' in Figure 58). Feather arms are a network of nano-scale sub-columns which grow incrementally. Each increment represents a single rotation of the substrate and is accompanied by the formation of a nano-pore between sub-columns ('2' in Figure 58). Two increments are indicated in Figure 58a between three lines. Since nano-pores form incrementally with sub-column growth, they are arranged in layers parallel to the rounded surface of the grain tip at the moment of their formation [93]. They are either globular or elongated spheroids and range from 18 to 25 nm [93].

Figure 58 – a) A cross section and b) a fracture surface, revealing inter-columnar gaps (1), globular and elongated spheroid nano-pores arranged in layers (2), and 'feather arms' (3) in a columnar grain of a EB-PVD zirconia coating [93]

Sub-columns do not appear in EB-PVD coatings applied to stationary or slowly rotated substrates. They only appear on substrates rotated roughly more than 10 rpm [91]. They originate at the sides of columnar grains and are a result of substrate rotation and shadowing. At high angles of incidence, very little vapour stream reaches the sides of columnar grains because they are in the shadow of the macroscopic grain tips. However, a fraction of vapour does penetrate inter-columnar gaps, and it impinges the sides of columns. As the angle of incidence changes with the rotating substrate, so does the local angle of incidence, which ultimately yields sub-columns [91].

The interface between sub-columns is sometimes loosely bonded (which makes 'feather arms' better defined in micrographs), leading to open porosity aligned at $\sim 45^\circ$ toward the main column axis [93]. This is seen quite clearly in Figure 58a. During continued deposition at elevated temperatures, this open porosity may subsequently close into lines of nano-scale pores as driven by

minimization of surface energy, trapping gas in the process [93]. During condensation, gas entrapment can also occur within the sub-column structures, and even if they are absent altogether [91].

Established above is that porosity arises from three primary sources, each illustrated and summarized in Figure 58. Total porosity can be controlled by a number of process parameters, one of the simplest being substrate rotation. Since nano-pores accompany growth increments of sub-grains, and increment thickness represents one rotation of the substrate, nano-porosity can be increased by selecting a faster rpm. Also, the number of inter-columnar gaps (a form of open porosity) can be controlled by the substrate rotation speed since it affects column widths (a faster rpm creates wider columns [91]). Finally, the sub-columnar interfaces that can close and trap gas can be encouraged by selecting a fast rpm (greater than about 10 rpm, as discussed previously) such that feather arms appear. This control of porosity is very important for minimizing the thermal conductivity of EB-PVD coatings. Porosity also affects coating strength, strain tolerance and resistance to failure, properties that will now be discussed further.

2.6.2.2 Stress and Stiffness

The columnar grain structure of EB-PVD coatings and their chemical adhesion to substrates are the primary benefits over coatings produced via plasma spray. These respectively lead to improved strain tolerance and resistance to spallation, and both relate to stiffness. Thermal conductivity, on the other hand, is in general higher than for PS coatings, because the open inter-columnar gaps that account for much of the porosity are less efficient insulators.

As in PS specimens but in a different manner, EB-PVD coatings display a strong correlation between residual stress and stiffness [94]. Also as in PS, residual stress is primarily imposed by thermal stresses upon cooling from the application process, according to Equation 17. Since deposition temperatures are typically very high, in excess of 850°C [90], these thermal stresses on cooling have potential to produce much more compression, as much as -300 MPa [94] compared to the -20 MPa for PS. Most of this compression is restricted to the bottom of the coating where the density of material is highest and inter-columnar gaps least developed, as discussed in the previous subsection. Microcracks, however, are not commonly observed at the bond coat interface after deposition.

The bottom of EB-PVD coatings have small inter-columnar gaps and cannot accommodate much strain [95]. In a similar way and recalling the anisotropic nature of EB-PVD microstructures, any direction with fewer or narrower gaps will tend to be under an increased state of residual compression since it is less able to accommodate strain upon cooling. Since 'sunrise, sunset' shadowing is most prevalent in the plane of vapour incidence during the coating process, columnar grains near this plane are the thinnest [93] and are separated by the widest gaps [91]. With large and abundant inter-columnar gaps, this direction is the most strain tolerant, under the least amount of compressive residual stress (often in tension), and therefore displays the lowest stiffness values, near 20 GPa [94]. Directions perpendicular to the plane of incidence follow the opposite trend, being in residual compression and measuring stiffness values near 80 GPa [94]. Figure 59 shows the correlation between residual stress and stiffness for one set

of experiments, where elastic modulus properties were obtained using flexural resonance techniques.

Figure 59 – Residual stress vs. in-plane elastic modulus (stiffness) for EB-PVD coatings, where open symbols designate properties measured perpendicular to the plane of incidence and closed symbols designate properties parallel to it [94]

Residual stress and stiffness are important properties to understand, because coatings with a higher compressive residual stress require less applied compressive strain before failure [94]. In a similar way, they fail with shorter thermal cycle lifetimes.

2.6.2.3 Performance Evolution

The microstructure and consequential thermo-mechanical properties of EB-PVD coatings are not immune to the effects of sintering, which become apparent at temperatures above 900°C [96]. Since the driving force for sintering is surface area reduction, porosity is inevitably reduced and causes thermal conductivity to increase by roughly 20% [93]. Nano-porosity conglomerates to form larger (less

numerous) pores, and interfaces between 'feather arms' close to become lines of nano-porosity. This can happen quite quickly, shown to have begun after only an hour at 1100°C in Figure 60a below, and to be nearly complete after an hour at 1400°C in Figure 60b. Given enough time, inter-columnar gaps also reduce, and columns sinter together at contact points.

Figure 60 – Sintered columnar grains for 1 hour at a) 1100°C and b) 1400°C [96]

The loss of strain tolerance with sintering causes substantial stiffness increase since columns no longer expand and accumulate stress instead, eventually necessitating through-thickness cracking [97]. In 2009, Vecchione *et al.* [95] measured Young's modulus before and after annealing for 80 hours at 1100°C using nano-indentation of EB-PVD coatings. They reported a 36% increase at the top surface (from 152 to 206 GPa), and a 97% increase in the bottom 20 µm of cross sections (from 66 to 129 GPa). On the topic of thermal conductivity, Zhu *et al.* [97] found a typical increase of roughly 20% from 1.55 to 1.80 W/m·K during their thermal tests lasting 200 hours in 2 hour cycles.

2.7 PRESSING AND SINTERING OF CERAMIC POWDERS

In materials research, PS and EB-PVD processes are often avoided. Instead, a common processing technique is to press and sinter ceramic powders into dense samples. This was employed in the current thesis research because it allows a more controlled study of material properties in the absence of complex microstructures.

In general, there are three basic powder pressing procedures. In order of increasing complexity, they are [98]

1. uniaxial,
2. isostatic (or hydrostatic), and
3. hot pressing.

With the exception of hot pressing, these operations create green bodies that require a subsequent firing operation to sinter, during which time the green body shrinks, reduces in porosity, and improves in mechanical integrity to form ceramics as they are known [98].

Uniaxial pressing involves powder compaction in a metal die by pressure applied in a single direction. It produces simple geometries because green bodies take on the form of the die, which is designed for uniform pressure distribution along only one axis. Isostatic methods allow more intricate geometries since pressure is applied omnidirectionally by immersion into a fluid. Finally, hot pressing combines pressing and sintering in the same process and produces materials with very low porosity.

Uniaxial pressing and pressureless sintering in a furnace were applied in the current thesis research. Although the content of this section (2.7) is written primarily with that in mind, it generally applies to all three pressing methods.

2.7.1 COLD POWDER PRESSING

Overall, the success of this process is largely defined by the attained packing density of the pressed green body. Packing density is controlled by a number of things, including particle shape, size, size distribution, and additives.

2.7.1.1 Definition of Packing Density

Green body density is determined solely by the powder packing that occurs during a pressing process. Packing density is a quantity given by [99]

$$\text{Packing Density} = \frac{\text{volume of solids}}{\text{volume of solids} + \text{voids}} \quad (20)$$

It depends on particle shape, size distribution, shaking (in the die) prior to pressing, and on the extent to which surface and frictional forces prevent rearrangement [100]. Inter-particulate contact and friction prevent rearrangement and increase packing density, therefore smooth and spherical particulate is preferred.

2.7.1.2 Effect of Particle Shape

Industrially produced ceramic powders are often spherical and with a uniform size distribution. However, since mechanical milling is often used, particulate size and shape can vary greatly. The further the particulate is from spherical, the lower the packing density will be. If sizes are remain uniform,

Figure 61 might be used to estimate the expected random packing density (random is in contrast to ordered, which is unlikely if shapes are aspherical).

Figure 61 – Effect of relative roundness on random packing density [99]

Similarly, if particulate size is uniform but is not spherical, Table 2 provides a list of expected packing densities for different randomly packed geometries. Note that if packing were ordered for some of the listed shapes, such as for a cube, there would be zero pores and a packing density of 1.

Table 2 – Dense random packing density for various particle shapes [99]

Particle shape	Aspect ratio	Packing density
Sphere	1	0.64
Cube	1	0.75
Rectangle	2:5:10	0.51
Plate	1:4:4	0.67
Plate	1:8:8	0.59
Cylinder	5	0.52
Cylinder	15	0.28
Cylinder	60	0.09
Disk	0.5	0.63
Tetrahedron	1	0.50

2.7.1.3 Effect of Particle Size

As will be seen in section 3.4, the milling of ceramic particles sometimes leads to a combination of two distinct fine and coarse sizes. Such bimodal mixtures are beneficial and improve packing density, because the smaller particulate can occupy the interstitial space between the larger. The data in Figure 62 can be used to estimate packing that results from bimodal powders. At its top is the theoretical packing maximum of 0.868, calculated specifically for the case when many small particles fill each interstitial (as opposed to each interstitial being filled by one perfectly sized particle).

Figure 62 – Particle size ratio versus packing density for bimodal, spheroid powders [99]

Some powders have such size variations that they cannot be considered to have only two (coarse and fine) nominal sizes. These 'multiple mixtures' have particle size distributions which can be quantified statistically. The Andreassen equation is a well known method of not only describing size distributions, but also

identifying distributions that optimize packing density. In 1994, Funk and Dinger [101] published a modification to the Andreasen equation, and showed that packing density is optimized if the particle size distribution can be described by

$$W = \frac{d^m - d_s^m}{d_L^m - d_s^m} \quad (21)$$

Here, the minimum particle size is d_s , the largest is d_L , and W is the mass fraction of particles that are less than size d . The exponent m is an empirical constant for data fitting, and experiments show that maximum packing occurs when $1/3 < m < 1/2$ [99].

2.7.1.4 Additives

Ceramic forming can be aided with combinations of four categories of additive: binders, solvents, dispersants and plasticizers. For a given system, it is possible to formulate chemical principles and practical guidelines for the selection of additives, but there is a wide range of additives available and, in many cases, their chemical structures and process reactions are not well understood [99]. For this reason, most successful additives to date have been found by trial-and-error.

Binders can be added in solid or liquid form (if in solid form, they require a solvent). Their function is to form bridges between powder particulate in order to increase green body strength, but their complete removal is usually preferred prior to sintering. Liquid organic chemicals are usually selected for advanced ceramics because they can be removed almost entirely with pyrolysis (a debinding heat treatment) [99]. Binder selection criteria include burnout

characteristics, viscosity effects and compatibility with other additives. Concerns for viscosity usually relate to the effect that binders have on solvents, since providing fluidity to powders during pressing enables maximum rearrangement and packing density.

The primary function of (liquid) solvents is to dissolve solid additives and maximally influence the flow of particles. In selecting a solvent, evaporation rates are also taken into consideration and boiling temperature is often used as a rough guide [99]. This way, there is at least a qualitative account for how difficult it will be to thermally remove the solvent from pressings before they are fired.

The last two common additives are dispersants and plasticizers. Dispersants are liquid additives that increase the repulsion between particles. This effectively stabilizes slurries against the agglomeration (grouping) of small particles, thereby maximizing packing density. Finally, plasticizers are commonly solids and are added to dry powders before adding the solvent. Once dissolved by the solvent, plasticizers soften the effect of binders such that green body strength is reduced but flexibility is improved [99].

2.7.1.5 Pressing Pressure

A review of literature has revealed that uniaxial pressings of zirconia are usually performed in the range of 30 to 200 MPa (sometimes as high as 300 MPa but mostly less than 100 MPa), but no one method of numerically deciding an applied pressure could be identified. It is often found that the applied pressure (P) relates to green packing density (ρ_G) by the logarithmic relation [100]

$$\rho_G = c_1 \cdot \log P + c_2 \quad (22)$$

where c_1 and c_2 are constants obtained experimentally. The origin of this behaviour is not understood, but the experimental results in Figure 63 are a perfect example of it. In the figure, plots of green density versus the log of applied pressure yield straight lines. The authors who produced it further noted that increasing applied pressure up to 150 MPa did not improve green density.

Figure 63 – Logarithmic compaction curves for two YSZ powders, one averaging 102 μm particle diameter (solid dots) and the other 256 μm (open dots) [102]

The ultimate objective of pressing is to prepare a properly shaped specimen that can then be sintered. Sintering transforms the weak green body of loosely bound powder to a hard and dense ceramic. The green body porosity is reduced and isolated (closed), and a continuous grain boundary network is formed. It is a continuous process, but one that consists of several stages.

2.7.2 SOLID STATE SINTERING

As was well established in discussions of zirconia phases and transformations, systems tend toward lower free energy. At temperatures

roughly $> 0.4T_m$ (T_m , absolute melting temperature), increased atomic mobility enables sintering to occur with the driving force of reducing surface free energy. This involves loss of surface area and therefore porosity, with corresponding densification and grain growth. Sintering effectively transitions green bodies, with densities of about 50% theoretical, to ceramics with densities up to 99%. Figure 64 illustrates this with a plot of sintered density versus temperature.

Figure 64 – Effect of sintering temperature on sintered density of 8YSZ [102]

2.7.2.1 Driving Forces and Sintering Mechanisms

Sintering can be interpreted [103] as minimum free energy being attained by surface area (A_s) reduction (i.e. pore size reduction), which itself is a means to minimize surface tension (γ_s). In that case, the increasing interface area (A_i) and its corresponding interface tension (γ_i) acts as resistance. Hence, the total free energy minimized with sintering is a combination of those two driving forces:

$$\Delta G = \Delta G_s + \Delta G_i = \gamma_s dA_s + \gamma_i dA_i \quad (23)$$

Externally applied pressure and chemical reactions can also act as driving forces, but there are no chemical reactions to occur in co-doped YSZ and an external pressure is assumed absent during sintering (this is obviously not a valid assumption in the case of hot pressing).

Reducing surface area requires both grain growth (coarsening) and pore reduction (densification), and plastic flow can also contribute. Coarsening and densification are traditionally regarded as competitive sintering mechanisms, and excluding plastic flow, a sintering process may be presented in a plot of surface area per unit volume against fractional density, such as Figure 65.

Figure 65 – A plot illustrating the competitive nature between coarsening and densification (redrawn from [104])

There are two extremes in the above plot. Pure coarsening is presented as a straight vertical line as some grains grow at the expense of others (section 2.7.2.4 below). This occurs at a constant volume fraction of porosity. The other extreme is pure densification, which is presented as a straight line connecting the

initial and final stages to indicate simultaneous surface area and pore volume reductions [104]. Real sintering occurs in between these two extremes which indicates that both mechanisms contribute. Their interference with each other makes the process very complicated, as they compete for transporting material.

Generally speaking, the material transport necessary for sintering occurs by six methods, illustrated in Figure 66. Four methods involve diffusion (1, 2, 4 and 5 in the figure), and the other two methods are vapour transport (3) and plastic flow (6). Only methods 4, 5 and 6 contribute to densification, because only they displace material that reduces the distance between sphere centres.

Figure 66 – The six methods of material transport which support coarsening and densification during sintering [99]

With zirconia ceramics, plasticity is very low and the melting temperature is high (2680°C), indicating that plastic flow is minimal and the partial pressure of zirconia gas is small during sintering. It follows that the contributions of vapour

transport and plastic flow are not appreciable, and indeed, zirconia literature focuses mostly on sintering via diffusional methods. Diffusion is discussed in section 2.7.3. But first, the current topic is continued with models based on the energetic stability of grains and pores during the different stages of sintering.

2.7.2.2 Stages of Sintering

Sintering has been classified as occurring in three stages, identified according to the state of pores and grain boundaries [103]. The first stage includes no grain growth, only the formation of necks at particle interfaces. The second (intermediate) stage is considered to start when grain growth begins, and continues while interstitial pores remain connected and grain boundaries are disconnected. Most densification occurs in the second stage. As pores become isolated and grain boundaries connect to form a continuous network, the second stage ends and the third begins. The third stage is characterized by very rapid grain growth with only a slight increase in density.

Most available theory applies to the first and intermediate stages of sintering because of the increasing interactions of driving forces and sintering mechanisms as the process nears completion. Theory that does exist for the third stage is notoriously inaccurate, albeit insightful and complex (such as the original work by Coble [105] in 1961). Therefore, this short review of literature will omit it, and focus on the initial and intermediate stages.

2.7.2.3 Initial Stage (Neck Formation)

At the time of green body insertion into the furnace, compacted particles have only singular points of contact with each other, with zero effective contact

area. The chemical potential for neck formation between particles ($\Delta\mu_n$), according to the Gibbs-Kelvin relation, is given by [103]

$$\Delta\mu_n = \gamma_s V_A (1/\rho_n - 1/r) \quad (24)$$

where V_A is atomic volume and ρ_n and r are the radii of the neck and particles, respectively. Inspection of Figure 66 reveals that the neck's centre of curvature lies outside the particle, so it is concave such that $\rho_n < 0$.

The driving force for necking is highest when the chemical potential is most negative which, following Equation 24, is at the very beginning of sintering when ρ_n is infinitely small. At this point, the contact angle between spheres (ϕ) is zero, as illustrated in Figure 67a. As interface area grows, the concave neck radius follows, and ϕ becomes non-zero (Figure 67b). Even when $|\rho_n| = r$, concavity ensures that the potential remains negative, encouraging further growth.

Figure 67 – Contact angle, ϕ , and neck radius, ρ_n , a) before, b) during and c) after active necking (neck material omitted for clarity) (redrawn from [103])

The chemical potential for necking remains negative unless mass transport is allowed to transform the two particles into one sphere, since only then is ρ_n convex and equal to r . This on-going driving force explains grain growth into the

third stage of sintering. However, in reality, the two particles never become one sphere. Impeding neck formation is the second component to Equation 23, namely interface tension which rises during the necking process. The contact angle ϕ increases only to a constant value, ϕ_e (the dihedral angle), where the system reaches equilibrium. This equilibrated state appears in Figure 67c, and the dihedral angle is given as [103]

$$\cos(\phi_e/2) = \gamma_i / 2\gamma_s \quad (25)$$

As Figure 66 illustrates, porosity is associated with the empty space between neighbouring particles. Figure 68 shows the relation of ϕ_e to the coordination of pores, n , of which there is a critical value (n_c) beyond which pores are unstable and shrink. When pores begin to shrink appreciably, the second (intermediate) stage begins.

Figure 68 – Dihedral angle (ϕ_e) in three pore configurations (based on [103])

2.7.2.4 Intermediate Stage

As calculated by Shi [103] in his update to Coble's original work [105], the critical coordination (n_c) at which pores are unstable depends on ϕ_e by

$$n_c = 2\pi / (\pi - \phi_e) \quad (26)$$

which is itself derived from the free energy change accompanying changes in pore radius, r_p . From combination of pore geometry with Equation 23, the free energy change is

$$\frac{dG}{dr_p} = \frac{\phi_e - \pi + \frac{2\pi}{n}}{\sin \frac{1}{2}(\phi_e - \pi + \frac{2\pi}{n})} \cdot \sin\left(\frac{\pi}{n}\right) n\gamma_s - n\gamma_i \quad (27)$$

So, from the perspective of the pore centre, if particle interfaces appear concave (if $n < n_c$) then the pore is unstable and, as it shrinks, free energy decreases according to Equation 27. On the other hand, pores are at equilibrium if particles appear planar ($n = n_c$), and if they appear convex they are stable and free energy decreases with growth.

It is of interest to note that similar conclusions are drawn from analysis of grain growth. In essence, grain boundaries move toward the centre of curvature [106]. If pores are conceptually replaced with grains in Figure 68, then grains with less than six sides shrink, while those with more than six grow. This is the same behaviour that is described here for pores.

An accurate estimate for a critical pore size requires upgrading to three dimensions and the introduction of n_s , the pore coordination in space. It is generally assumed that $n_s \gg 1$. Also, let D_{eff} be the effective diffusion coefficient, Ω_a be diffusion volume, and d_p and d be pore and grain diameters, respectively. With $R = d_p/d$, the rate of a single pore's volume change can be expressed as [103]

$$\frac{dV_p}{V_p dt} = -\frac{48\Omega_a \rho \gamma_s D_{eff}}{d^3 R^2 (R+1) kT} \left[1 - (R+1) \cos \frac{\phi_e}{2} \right] \quad (28)$$

where k and T have their usual meanings, and ρ is relative solid density. From Equation 28, the critical R (when $dV_p/V_p dt = 0$) is

$$R_c = \cos(\phi_e/2)^{-1} - 1 \quad (29)$$

so that pores with $R < R_c$ tend to shrink.

When $R > R_c$, pores should theoretically grow. Shi [103] and others [99, 107] point out, however, that pore growth is not usually observed. With that in mind and assuming a broad range of pore sizes, the densification rate of a sintering body during the intermediate stage can be written as [103]

$$\frac{d\rho}{\rho dt} = \frac{48\Omega_a \rho (1-\rho) \gamma_s D_{eff}}{d^3 \bar{R}^2 (\bar{R}+1) kT} \cdot \left[1 - \int_{R_{min}}^{R_c} (R+1) f(R) \cos\left(\frac{\phi_e}{2}\right) dR \right] \cdot \int_{R_{min}}^{R_c} f(R) dR \quad (30)$$

The function $f(R)$ is the frequency distribution of R , and $\bar{R} = \int_{R_{min}}^{R_{max}} R f(R) dR$, i.e. R calculated with average d_p and d values.

Note that Equation 28 is negative and Equation 30 is positive. This is expected since densification increases with porosity reduction, and vice-versa. So there should exist a relation between rate of densification, $d\rho/\rho dt$, and pore shrinkage, $dV_p/V_p dt$. If ρ is the relative density of a sintered sample and V_T is the total volume of solid phase (V_S) and pores (V_P), then [103]

$$\rho = V_S/V_T, \quad V_T = V_S + V_P, \quad V_T = 1/\rho \quad \text{and} \quad V_P/V_T = 1-\rho \quad (31)$$

and

$$\begin{aligned} d\rho/\rho dt &= -dV_T/V_T dt = -(V_P/V_T) dV_P/V_P dt \\ &= -(1-\rho) dV_P/V_P dt \end{aligned} \quad (32)$$

Therefore Equation 30 also gives the rate of porosity loss (with application of Equation 32).

From the discussion of driving forces and sintering mechanisms in section 2.7.2.1, both grain growth and pore reduction reduce surface area and they are traditionally regarded as competitive forces. Now having reviewed a sintering model, it is instructive to revisit this concept quantitatively. Figure 69 acts to illustrate the competitive nature of grain growth and pore reduction, as well as the effect of pore size distribution. In Figure 69a, sample powder “S-3” has the largest distribution. Because of the larger average R value which would approach or surpass R_c , the driving force for pore reduction by Equation 30 is small, and densification is limited. Meanwhile, the opposite is true for small distributions, the smallest being “S-1” which densifies the most and coarsens less than “S-2”, which has a slightly higher spread of particle size.

Figure 69 – The effect of a) pore size distribution (and therefore particle size distribution) on b) grain growth and densification [108]

2.7.2.5 Effect of Agglomerates and Green Density

The concept of a critical coordination number and pore radius means that particle agglomeration in green bodies can be highly detrimental to densification. Agglomerates, which are groupings of particles, introduce a secondary and very large pore structure if close together. They become problematic when about 100 times the size of single particles [103]. At those sizes, the large secondary pores they introduce have high coordinations and it is likely that $R > R_c$. Since they are thermodynamically stable, these pores are inherently difficult to remove.

Zhao and Harmer [107] documented this sort of behaviour by impregnating MgO-doped Al_2O_3 with large pores and firing them at 1620°C . The resultant microstructure after 5 minutes is shown in Figure 70. The large pores are stable, with high coordination numbers and shapes like that in Figure 68c. It has been estimated that large pores like these remain stable until grains grow to average 68% their size [107].

Figure 70 – Microstructure of pore-impregnated and sintered MgO-doped Al_2O_3 for 5 minutes at 1620°C [107]

In another example involving agglomerates [109], complete densification between primary zirconia particles was achieved at 1250°C after 2 hours. However, initial densification of the secondary pore structure introduced by agglomerates was only observed at 1600°C. Worse, it stopped entirely at 1800°C when grain growth became dominant (the third stage of sintering).

Similarly, lower green body densities will have larger average R values and be unfavourable for densification due to a smaller driving force for pore shrinkage (note that R is in the denominator of Equation 28). Diffusion distances will also be longer, retarding the sintering process [103].

2.7.3 DIFFUSION

As stated, the mass transport required for neck formation, grain growth and pore shrinkage (densification) is accomplished by diffusion. It is therefore appropriate to briefly review the primary methods of diffusion.

Diffusion through a crystal lattice (or volume diffusion) occurs by motion of ions by point defects, namely vacancies and interstitials. For example, a Zr^{4+} cation in ZrO_2 requires enough energy (generally provided by high temperatures) to either jump to a neighbouring vacancy in the cation lattice or to move to some nearby interstitial location. The relation between point defect concentration C_{defect} and the diffusivity of the diffusing species D_i is given as [110]

$$D_i = (C_{defect} / C_i) \cdot D_{defect} \cdot j \quad (33)$$

where C_i is the concentration of the diffusing species, and D_{defect} is the diffusion coefficient of defects. The correlation factor j depends on the crystal structure and diffusion mechanism ($j \approx 0.653$ for vacancies in a fluorite lattice).

Other diffusion paths are more energetically favourable. Atoms along line and area defects such as dislocations, grain boundaries and free surfaces, are lesser coordinated and therefore easier to move along (and across). Grain boundaries are the most common of these defects, and free surfaces can be treated similarly. Diffusion along them can be described mathematically by application of Fick's laws, which is the subject of the following subsection.

2.7.3.1 Fick's Laws

Solid state diffusion is modelled based on Fick's first and second laws which describe linear flow in one dimension, relating concentration, position, and in the second law only, time. As mentioned, these laws describe diffusion that occurs as point defects through an otherwise uniform crystal lattice.

Fick's first law applies only to steady state diffusion where concentration at any position does not vary. It is not relevant to the current discussion, but Fick's second law (for non-steady state diffusion) can be used to derive much insight.

Fick's second law applies to non-steady state conditions, where concentration (C) and concentration gradient (dC/dx) change with time at every position (x) according to the partial differential equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (34)$$

where D is the diffusion coefficient, assumed independent of composition. This is not a completely accurate assumption, but it simplifies matters greatly. For zirconia with varying concentrations of $\text{YO}_{1.5}$, diffusion coefficients as they relate to temperature are plotted in Figure 71.

Figure 71 – Diffusion coefficient (D) plotted against temperature for a number of $\text{YO}_{1.5}$ concentrations (mol%, as labelled) [110]

Equation 34 requires boundary conditions to be solved, and as such, can yield the diffusion behaviour for many situations. For an introductory example, if the diffusion medium is semi-infinite and the concentration of the diffusing species at the surface is constant, say with concentration C_1 , then the boundary conditions are [111]

$$\begin{cases} C(x, 0) = C_0 & (x > 0, t = 0) \\ C(0, t) = C_1 & (x = 0, \forall t) \end{cases} \quad (35)$$

Application of Equation 35 to 34 yields

$$\frac{C(x, t) - C_1}{C_0 - C_1} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (36)$$

which allows computation of concentration $C(x, t)$ at any position x and time t .

2.7.3.2 Diffusion in a Sphere

For a case more pertinent to sintering, consider a sphere. If the diffusing species originates at the sphere's surface and strictly moves along the radial axis, x_r , and if D is assumed constant, then Fick's second law becomes [112]

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x_r^2} + \frac{2}{x_r} \frac{\partial C}{\partial x_r} \right) \quad (37)$$

Letting $u = C \cdot x_r$,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 u}{\partial x_r^2} \quad (38)$$

which is equivalent to linear flow in one dimension (Equation 34).

If a dopant particle is adjacent to one composed of zirconia, and the zirconia particle has radius r , dopant ions will diffuse inward such that the zirconia surface concentration C_s (mol% dopant) decays with time from an initial value, C_0 , as the dopant ions are depleted from their parent particle. This will occur approximately logarithmically, so say $C_s(t) = C_0[1 - \exp(-\lambda t)]$. An equation can then be derived (see Crank [112]) to show that at any radial location, x_r , and time, t , concentration $C(x_r, t)$ is

$$\begin{aligned} \frac{C(x_r, t)}{C_0} = 1 - \frac{r}{x_r} \exp(-\lambda t) \frac{\sin[(\lambda r^2 / D)^{1/2} x_r / r]}{\sin[(\lambda r^2 / D)^{1/2}]} \\ - \frac{2\lambda r^3}{\pi D x_r} \sum_{n=1}^{\infty} (-1)^n \frac{\exp(-D n^2 \pi^2 t / r^2)}{n(n^2 \pi^2 - \lambda r^2 / D)} \sin \frac{n \pi x_r}{r} \end{aligned} \quad (39)$$

2.7.3.3 Grain Boundary Diffusion

While Equation 39 describes diffusion through a crystal lattice, dislocations, grain boundaries and free surfaces are all energetically easier for a diffusing

species to move along. The most typical of these high diffusivity paths are grain boundaries. With diffusion coefficient D_{gb} and thickness δ (generally < 1 nm [111]), grain boundary diffusion is commonly modelled based on Fick's second law as [111, 113]

$$D_{gb} \cdot \delta = 0.66 \left(\frac{4D}{t} \right)^{1/2} \left[-\frac{\partial \ln \bar{C}}{\partial x^{6/5}} \right]^{-5/3} \quad (40)$$

where $\bar{C}$ is the average concentration of the diffusing species away from the grain boundary, and D is the diffusion coefficient through the grain volume.

In pure zirconia, cation diffusion is difficult because the oxygen sublattice is tightly packed and largely disallows interstitial defects. The same applies to stabilized zirconia. Since one O^{2-} vacancy is produced for every two Y^{3+} cations (section 2.2.1.1), this translates to only 2.8 mol% O^{2-} anions lost in 7YSZ. So by and large, the oxygen sublattice is tightly packed (with only 2.8% of unit cells lacking an O^{2-} anion).

The only means for cation diffusion through crystal lattices is therefore via single cationic vacancies, as shown by Kilo *et al.* [110] in 2000 using a ^{96}Zr tracer species. However, between these vacancies remains the barrier of the tight oxygen sublattice. Most diffusion in YSZ therefore occurs along grain boundaries according to Equation 40, highlighting its importance.

3 EXPERIMENTS

Zirconia (section 2.1) is a well understood ceramic which is routinely stabilized (section 2.2) to avoid harmful crystallographic transformations to the monoclinic phase. However, thermal protection systems with yttria stabilized zirconia (section 2.3), considered to be very strong and tough (section 2.4), require further improvement to provide increased reliability and longer service lives. While research continues to optimize bond coats (section 2.5) and deposition techniques (section 2.6), zirconia ceramics themselves can be further developed with the addition of co-dopant oxides for improved stability. In support of efforts to select the most appropriate co-dopants, this thesis research is primarily an investigation into the cooling rate sensitivities of atomic stabilizing mechanisms. To accomplish this and other objectives, analyses were conducted on co-doped samples made from cold pressed and sintered ceramic powders (section 2.7). The following subsections are a documentation of that process.

3.1 OVERVIEW

In summary from section 1.4, there are three objectives for the current research: 1) Examine the cooling rate sensitivity of differently co-doped 7YSZ samples to infer the sensitivity of their atomic stabilizing mechanisms; 2) conduct microstructural analyses to observe associated effects of stability; and 3) quantify the effect of co-dopants on hardness and stiffness.

Co-dopant oxides were selected to be Yb_2O_3 , CeO_2 and Nb_2O_5 (section 3.2), and precise molar mixtures were chosen which defined three co-doped

compositions: Yb:7YSZ, Ce:7YSZ and Nb:7YSZ (section 3.3). All oxides were obtained commercially in powder form, and then mechanically alloyed with 7YSZ (section 3.4). Mixed powders were cold pressed into small disks (section 3.5), sintered in a furnace at 1400°C, and cooled by one of three schemes, namely fan, air or furnace (section 3.6).

For each combination of composition and cooling rate, four samples were produced for a total of twelve samples of each composition. The exception was the 7YSZ reference composition, of which only six samples were produced.

Below is a tabulated summary.

Table 3 – Summary of samples produced

Composition	Number of Samples Produced		
	Fan Cooled	Air Cooled	Furnace Cooled
7YSZ	2	2	2
Yb:7YSZ	4	4	4
Ce:7YSZ	4	4	4
Nb:7YSZ	4	4	4

Various analyses were conducted on the sintered materials, which required further specimen preparation. Fractured pieces of samples were used for measuring bulk density (section 3.7). Other pieces were ground and polished (section 3.8) for scanning electron microscopy (section 3.9), which also analyzed fracture and as-pressed surfaces. Ground and polished specimens were further used for quantifying the porosity (section 3.10) and average grain size (section 3.11) of each composition. X-ray diffraction (section 3.12) provided the amounts of monoclinic, tetragonal and cubic phases that were retained to room temperature by each cooling scheme for each composition.

To aid in the interpretation of results, energy dispersive X-ray spectrometry was also conducted (section 3.13) to provide maps that revealed the distribution of elements within the theoretical worst case composition (Yb:7YSZ). Finally, hardness and stiffness measurements were made of each composition, utilizing a nano-indentation technique.

Every sample in Table 3 was analyzed for the amounts of phases retained to room temperature. However, all other analyses were conducted on only select samples, since either composition or cooling rate was considered to have an insignificant effect on the property being measured. Further, different types of surfaces were investigated for each analysis technique, and there were additional preparation steps required. Table 4 is a list of the analyses and techniques applied in the current experiments, along with the prepared samples and surfaces they investigated.

Table 4 – Analysis techniques and prepared samples investigated

Analysis	Technique*	Compo- sitions [†]	Cooling Scheme [‡]	Surface	Additional Preparation
Bulk Density	Water immersion	All four	Fan		Fractured 1 g specimens [§]
Phase Content	XRD	All four	All three	Pressed	
Microstructural	SEM	All four	Furnace	Pressed	Carbon coated
			Furnace	Fractured	Carbon coated
			Furnace	Polished	Etched, carbon coated
Porosity	SEM, software	All four	Furnace	Polished	Etched, carbon coated
Grain Size	SEM, software	All four	Furnace	Polished	Etched, carbon coated
Elemental Map	EDS	Yb:7YSZ	Furnace	Polished	Etched, carbon coated
Hardness and Modulus	Nano-indentation	All four :	Air	Polished	
		7YSZ : All	All	Polished	

* XRD = X-Ray Diffraction, SEM = Scanning Electron Microscopy, EDS = Energy Dispersive X-ray Spectrometry

[†] All four compositions = 7YSZ, Yb:7YSZ, Ce:7YSZ and Yb:7YSZ

[‡] All three cooling schemes = Fan, air and furnace

[§] Specimen mass ranged within 1 ± 0.6 g

Processing and analyses were performed in the laboratories of Carleton University and the National Research Council Canada, Institute for Aerospace Research (NRC-IAR). Precise locations are specified in the sections that follow.

3.2 CO-DOPANT SELECTION

Following section 2.2, the microstructural stabilizing mechanisms for zirconia ceramics are based two point defects, namely oxygen vacancies and lattice distortions. To induce variations of these defects so that their cooling rate sensitivities could be studied, three co-dopant cations were selected and, when mixed with 7YSZ, each was expected to substitute Zr^{4+} in the cation network. The co-dopants selected were Yb^{3+} , Ce^{4+} and Nb^{5+} , with corresponding oxides Yb_2O_3 , CeO_2 and Nb_2O_5 . Ionic properties for the elements involved are given in Table 5, and a discussion on the stabilizing mechanisms contributed by each co-dopant follows.

Table 5 – Ionic properties for relevant elements

Ion	Atomic Number	Mass (g/mol)	Radius* (Å)
Zr^{4+}	40	91.224	0.84
Y^{3+}	39	88.90585	1.019
Yb^{3+}	70	173.04	0.985
Ce^{4+}	58	140.115	0.97
Nb^{5+}	41	92.90638	0.74
O^{2-}	8	15.9994	1.42

*Assuming eightfold coordination (from [21])

3.2.1 YTTERBIA

As discussed in section 2.2.1.1 on oversized trivalent dopants, Yb^{3+} cations were expected to substitute Zr^{4+} in the cation network of 7YSZ and impose

compressive lattice strains which would provide some high temperature stability by a reduction of t-ZrO₂ tetragonality. Moreover, Yb³⁺ was selected for its 3+ valence which would produce oxygen vacancies in addition to those from Y³⁺ (by Equation 4). The fact that Yb³⁺ is oversized relative to Zr⁴⁺ was of primary consideration, since only oversized trivalent dopants leave all oxygen vacancies available to Zr⁴⁺, and consequently have the greatest effect on stabilization.

It is of interest to note that Stecura [114] has predicted the optimum ytterbia concentration in ZrO₂ to be between 12.4 and 14.7 wt% Yb₂O₃ (without yttria), which maximizes cycles to failure in PS coatings.

3.2.2 CERIA

Tetravalent Ce⁴⁺ shares a valence state with Zr⁴⁺ so was not expected to form (or annihilate) oxygen vacancies. It was selected for its larger ionic radius which would dilate the lattice in compression. By this deformation, it was expected to further stabilize high temperature phases (by the method reviewed in section 2.2.1.2) and provide data on the stability achieved with a O²⁻ vacancies (by Y³⁺) plus two sources of dilative lattice deformations (Y³⁺ and Ce⁴⁺).

3.2.3 NIOBIA

According to the review of pentavalent dopants in section 2.2.1.3, Nb⁵⁺ was expected to annihilate oxygen vacancies produced by Y³⁺ in the maintenance of charge balance. Thus, by a reduced concentration of seven-coordinated Zr⁴⁺, tetragonal and cubic phases would be destabilized. This would allow observation of only lattice deformations (by both oversized Y³⁺ and undersized Nb⁵⁺).

The manner in which niobium annihilates O^{2-} vacancies can be shown in the same way that Y^{3+} was shown to produce them (section 2.3). In Kröger-Vink notation, the most probable dissolving reaction for Nb_2O_5 in yttria-zirconia ceramics is [17]

The two free electrons may then annihilate a single O^{2-} vacancy introduced by Y_2O_3 , by

Two Nb^{5+} cations are thus needed to annihilate a single O^{2-} vacancy.

3.3 CO-DOPED COMPOSITIONS

The selected co-dopant oxides were carefully and separately added to a standard 7YSZ molar mixture of $3.95 \cdot Y_2O_3 + 96.05 \cdot ZrO_2$ (or, with unit cations, $7.59 \cdot YO_{1.5} + 92.41 \cdot ZrO_2$). Table 6 is a summary of the chosen compositions, which the following subsections explain.

Table 6 – Co-doped sample compositions

Composition	Co-dopant Cation	Cation Concentration			
		Zr ⁴⁺ (mol%)	Y ³⁺ (mol%)	Co-dopant (mol%)	Total Dopant (mol%)
7YSZ	-	92.41%	7.59%	-	7.59%
Yb:7YSZ	Yb ³⁺	87.95%	7.23%	4.82%	12.05%
Ce:7YSZ	Ce ⁴⁺	87.95%	7.23%	4.82%	12.05%
Nb:7YSZ	Nb ⁵⁺	85.89%	7.06%	7.06%	14.11%

3.3.1 YB:7YSZ

Yb^{3+} was added at a concentration of 5 mol% so that the total dopant cation concentration would be comparable to industrially available materials (at roughly 12 mol%). This was to maintain an industrial context for comparative purposes and for later research. The molar mixture with 7YSZ was

For the calculation of this, see Appendix A. The resultant concentrations of cations are given in Table 6. Expanded concentration information can be found in Appendix B. Also, the ternary $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Yb}_2\text{O}_3$ phase diagram at 1400°C , as given by Corman and Stubican [14], appears in Figure 72 below.

Figure 72 – The zirconia-rich portion of a ternary $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Yb}_2\text{O}_3$ phase diagram at 1400°C (F_{ss} is f- ZrO_2 , T_{ss} is t- ZrO_2 , and C_{ss} is a rare-earth type) [14]

3.3.2 CE:7YSZ

Like Yb^{3+} , Ce^{4+} was added at a concentration of 5 mol% so that the total dopant cation concentration would be comparable to industrially available materials (at roughly 12 mol%). This was to maintain an industrial context for comparative purposes and for later research. The molar mixture with 7YSZ was

For the calculation of this, see Appendix A. The resultant cation concentrations are given in Table 6. Expanded concentration information can be found in Appendix B. Also, the CeO_2 - Y_2O_3 - ZrO_2 ternary phase diagram at 1600°C appears below in Figure 73.

Figure 73 – A ternary ZrO_2 - Y_2O_3 - CeO_2 phase diagram at 1600°C [15]

3.3.3 NB:7YSZ

Nb^{5+} was added to 7YSZ to annihilate all oxygen vacancies. Since two Y^{3+} cations are required to produce one O^{2-} vacancy (Equation 4), and two Nb^{5+} cations annihilate one O^{2-} vacancy (Equations 41 and 42), this required equal concentrations of Nb_2O_5 and Y_2O_3 . The resultant molar mixture with 7YSZ was

For the calculation of this, see Appendix A. The resultant cation concentrations are given in Table 6. Expanded concentration information can be found in Appendix B. Also, the ternary phase diagram for Nb_2O_5 - Y_2O_3 - ZrO_2 at 1500°C and the location of Nb:7YSZ is provided in Figure 74.

Figure 74 – The ternary ZrO_2 - Y_2O_3 - Nb_2O_5 phase diagram at 1500°C (C_{ss} is f- ZrO_2 , T_{ss} is t- ZrO_2 and NT_{ss} is t'- ZrO_2 [16])

3.3.4 SUMMARY OF ACCUMULATIVE STABILIZING MECHANISMS

Overall, each co-dopant allowed an investigation into the cooling rate sensitivity of its stabilizing mechanisms. For each composition, Table 7 summarizes the mechanisms of yttria and co-dopants, including the amount of theoretical oxygen vacancies. Based on O^{2-} vacancies, equivalent Yb:7YSZ, Ce:7YSZ and Nb:7YSZ compositions can be located on the Y_2O_3 - ZrO_2 binary phase diagram. Along a tie line drawn at the sintering temperature of 1400°C, these equivalent compositions appear in Figure 75.

Table 7 – Summary of (co-)dopant stabilizing effects

Dopant Cation	Effect on O^{2-} Vacancies	Lattice Distortions	Dopant Cation Concentration*	Effective Stabilizing Mechanisms in 7YSZ
Y^{3+}	+1 vacancy per 2 cations	Compressive	7.59 mol%	3.80 mol% O^{2-} vacancies, compressive distortions
Yb^{3+}	+1 vacancy per 2 cations	Compressive	4.82 mol% Yb^{3+} (+ 7.23 mol% Y^{3+})	6.03 mol% O^{2-} vacancies, compressive distortions only
Ce^{4+}	None	Compressive	4.82 mol% Yb^{3+} (+ 7.23 mol% Y^{3+})	3.80 mol% O^{2-} vacancies, compressive distortions only
Nb^{5+}	-1 vacancy per 2 cations	Tensile	7.06 mol% Yb^{3+} (+ 7.06 mol% Y^{3+})	0 mol% O^{2-} vacancies, compressive + tensile distortions

*From Table 6

Figure 75 – 7YSZ and equivalent co-doped compositions located on the binary $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram

3.4 POWDER PREPARATION

The powders used to achieve the co-doped 7YSZ compositions listed in Table 6 were obtained commercially from a number of suppliers. These suppliers and the purity of their product are listed in Table 8, along with particulate sizes as determined from the as-received microstructures shown in Figure 76. Between the four powders, particle sizes ranged from less than 1 μm to about 65 μm , and took on a number of shapes including spheroids and elongated polyhedrons.

Table 8 – Basic information of commercially obtained powders

Powder Name	Formula	Purity	Size (μm)	Supplier
7YSZ	7 wt% Y_2O_3 + ZrO_2	97.8%	25 to 65	Praxair
Ytterbium Oxide	Yb_2O_3	99.9%	1 to 20	Metall
Cerium (IV) Oxide	CeO_2	99.9%	1 to 40	Metall
Niobium (V) Oxide	Nb_2O_5	99.9%	< 1	Sigma-Aldrich

Figure 76 – SEM micrographs of commercially obtained a) 7YSZ, b) Yb_2O_3 , c) CeO_2 and d) Nb_2O_5 powders

As discussed in section 2.7.2, smaller powder particulate lead to smaller pore sizes and therefore faster densification during sintering (Equation 30), generally providing ceramics with low porosity. Further, for reasons covered in section 2.7.3, diffusion in zirconia is slow but can be improved with an increase in grain boundary area (Equation 40). Also, smaller particles correlate to smaller diffusion distances between them. All together, particulate reduction was of interest in order to aid sintering and help ensure adequate diffusion such that the desired compositions of Table 6 were attained uniformly throughout the material.

Long duration mechanical alloying was therefore undertaken, following the careful mixing of powders for each desired composition. A ball milling method was employed at NRC-IAR using a Turbula Type 12C shaker-mixer made by WAB Co. A small and dense grinding media was preferred to maximize the rate of milling, so ZrO_2 balls were used with a diameter of 10 mm and a density of 6.27 g/cm^3 . This also avoided contamination by a foreign material.

Each composition of powder was milled for a total running time of 70 hours, in a one hour on, one hour off cycle (i.e. 70 hours on). This was to avoid excessive heating by friction. Following ball milling, the powder was separated from the grinding media and 9 g samples were prepared for pressing.

Figure 77 shows the final microstructures of milled powders. Inspection revealed that particulate sizes had been reduced so that the reference 7YSZ powder varied between about 1 and $25 \mu\text{m}$, Yb:7YSZ varied similarly but with more particles near $25 \mu\text{m}$, Ce:7YSZ had particles ranging from 1 to $30 \mu\text{m}$, and Nb:7YSZ contained what could only be large 7YSZ particulate (about $55 \mu\text{m}$).

Figure 77 – SEM micrographs of 70 hours ball milled a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ powders

3.5 UNIAXIAL COLD PRESSING

Subsequent to ball milling, the 9 g powder samples were compacted into disks with a diameter of 2.54 cm using a uniaxial press and the die sets shown in Figure 78. These dies were manually machined of 17-4 precipitation hardened

(PH) stainless steel (SS) on a mill at Carleton University, with the dimensions given by the drawings in Appendix C. Tolerances were established experimentally. The choice of material was so that dies would survive repeated pressings without yielding (the yield strength of 17-4 PH SS is about 1170 MPa).

Figure 78 – Three-part die sets with a common radius of 2.54 cm, not including tolerances (see Appendix C)

As can be seen in the figure above, the pressing faces of dies were finely polished, but a release agent was also required for the removal of green bodies. In the following subsections, the selection of additives and pressing pressure is outlined, followed by the 12 step pressing process that was developed.

3.5.1 ADDITIVE SELECTION

A description of possible additives was given in section 2.7.1.4. Based on a minimalist approach in order to preserve the purity of the specimens, and based on requirements of the implemented processing, a number of options were eliminated.

Since uniaxial cold pressing was being employed (requiring a relatively dry powder), a dispersant was not necessary in the absence of a wet slurry. Further,

pressed disks would be handled carefully by hand, negating the need for a plasticizer. Finally, without solid additives, a solvent was not required to dissolve them, however the function of providing fluidity to powders during pressing remained of interest to improve packing density. A liquid binder was therefore desired with the ability to provide green body strength and adhere well to zirconia to provide maximum fluidity. Additionally, the need for minimal contaminants required that the binder be organic, such that it could be easily removed with heat.

Propylene carbonate ($C_4H_6O_3$), an organic liquid, was selected for its high chemical affinity to zirconia ceramics, high boiling point of $240^{\circ}C$ and flash point of $135^{\circ}C$. It would not evaporate from green bodies quickly but could be easily removed at high temperatures. Later, while optimizing the pressing process, it was iteratively determined that 35 drops should be added to each 9 g sample of powder for good green body strength after the pressing pressure was applied.

3.5.2 PRESSING PRESSURE AND GREEN INTEGRITY

Following literature (section 2.7.1.5), the initial uniaxial pressing pressure was chosen to be 100 MPa, but the resulting green bodies could not maintain their shape and crumbled when removed from the die. In an iterative manner, pressure was then gradually increased to 540 MPa which provided adequate green body integrity, allowing limited handling. This pressure was held for 10 minutes, and disks emerged about 4 mm thick. Many disks appeared in good condition, but some displayed cracks on their circumferential surface as seen in Figure 79 below.

Figure 79 – Pressed green disks

The observed cracks, combined with the dark metallic residual also visible in the figure, were the first evidence to suggest that the pressing axis was not perfectly perpendicular to the pressing surface. However, repeated attempts to remedy this by aligning the press plates failed, and experiments moved forward regardless. With that, it is noted that the effective applied pressure was probably less than 540 MPa since an off-axis component was lost at the expense of dies which sometimes exhibited deep striations. For this reason, dies had to be repeatedly repaired or replaced as a working balance between pressing pressure and die tolerances was being established on the misaligned press. One damaged die set is shown in Figure 80. This sort of damage was avoided once a working (twelve step) process was established.

Figure 80 – A damaged die set (insert not shown)

3.5.3 TWELVE STEP PRESSING PROCESS

Successful pressing was a manual process performed at Carleton University, and was composed of 12 steps. The 12 steps were as follows:

1. Polish the pressing surfaces of the insert and the indenter to a mirror finish.
2. Polish the circumferential surfaces of the insert, indenter and inner ring wall to a smooth finish.
3. Clean the die set with alcohol, then spray a minimal amount of Teflon release agent on all polished surfaces.
4. Empty a 9 g sample of powder into a small beaker, add 35 drops of propylene carbonate binder, and mix well.
5. Place the insert inside the ring, mirror side up.
6. Empty the powder/binder mixture on top of the insert inside the ring.

7. Place the indenter (mirror side down) into the ring and manually push down until it is snug, gently compressing the powder/binder mixture.
8. Place the assembly between the upper and lower plates of the uniaxial press.
9. Press and hold at a pressure of 540 MPa for 10 minutes, then release.
10. Flip the assembly upside down, place spacers on the ring's (now) upper surface, and apply uniaxial pressure until the green body is fully exposed. Remove the insert which lies on top.
11. Remove the green body and store it. Remove the indenter from the ring.
12. Wash all three parts well in water, and return to step 1.

With the completion of cold pressing, each composition of green body was transported in plastic bags inside of a rigid box (Figure 81) to the NRC-IAR, where furnace sintering was conducted.

Figure 81 – A collection of 12 green disks (two layers of 6) in a rigid box

3.6 SINTERING AND VARIABLE COOLING

Green bodies were sintered in air for 250 hours at 1400°C in a LINDBERG/BUE furnace with a 2416 "P" model controller. 7YSZ compacts are shown loaded in the furnace (at NRC-IAR) in Figure 82. The air atmosphere ensured equilibrium with oxygen and therefore the correct ZrO_2 stoichiometry which would otherwise complicate the study [99]. The average ramping rate during the heat up cycle was nearly 1°C/min. A separate debinding cycle was not necessary since the binder ablated during ramping at about 200°C.

Figure 82 – Green disks (7YSZ) loaded in the furnace on crafted alumina holders

Sintering was conducted over such a long period of time to allow adequate diffusion of elements across the largest observed powder size, and the homogenous distribution of dopant cations was later established using energy

dispersive X-ray analysis (see section 3.13). While sintering, samples rested on crafted alumina holders (Figure 82) to simplify their removal at high temperatures.

When sintering was complete, samples were removed from the hot furnace so that they could cool in still air, in the wash of a table fan, or remain inside the closed furnace while it cooled. The three cooling schemes appear in Figure 83 for the first two hours. The fan and air cooled data was acquired using two thermocouples and a spare controller (temperature indicator) that had to be manually switched between the two channels to obtain data points. As a result, these points should be considered with ± 10 s. Furnace cooled data is accurate, taken directly from the furnace controller.

Figure 83 – Fan, air and furnace cooling schemes

To reach 25°C, the average fan cooling rate was 39°C/min. For air cooling it was 9°C/min, and for furnace cooling it was about 1°C/min. Furnace cooled

specimens experienced accelerated temperature changes initially because the furnace door was open while removing the other two sample sets. Once at room temperature, disks were manually fractured and these pieces were prepared subsequent characterization methods.

3.7 BULK DENSITY MEASUREMENTS

Bulk density was assumed unaffected by cooling rate, so air cooled samples were physically measured by implementing an Archimedeian buoyancy method at NRC-IAR. Dry specimens were weighed (W_{dry}), immersed into distilled water, and then weighed again ($W_{immersed}$). The density of water at the measured temperature was known (ρ_{water}), so bulk density ($\rho_{specimen}$) was

$$\rho_{specimen} = \frac{W_{dry}}{W_{dry} - W_{immersed}} \cdot \rho_{water} \quad (46)$$

The buoyancy of samples (including that from pores) made $W_{immersed} < W_{dry}$. To immerse specimens, the commercially obtained setup in Figure 84 was used.

Figure 84 – The measurement of bulk density, showing a) the scale and configurations for b) zeroing the balance, c) reading W_{dry} and d) reading $W_{immersed}$

Following Figure 84, a thin wire was suspended from a simple frame, the base of which was inserted into the balance port. After zeroing the balance, specimens were hung from the wire and w_{dry} was read. Specimens were then immersed into a beaker of water to obtain $w_{immersed}$, while the beaker was placed on a prop to separate it from the base.

For consistency, a standard immersion time was required because scale readings were not constant as connected pores filled with water. An immersion time of 30 seconds was chosen. The small intake of water during that time was negligible, on the order of 10 μg . For comparison, the dry sample weights were in the range of 1 ± 0.6 g.

3.8 GRINDING AND POLISHING

Cross sectional microstructural analyses required that some samples be ground and polished prior to microscopic examination. For use in the available grinding equipment at NRC-IAR, these samples were first mounted in resin epoxy and cold-cured. This process was chosen to avoid cracking that might develop using an alternative hot mounting press method. The resin epoxy was Hysol RE2038, a silica-filled option with low shrinkage properties and extremely low viscosity [115]. A Hysol hardener (HD3404) was also used to aid curing.

Polishing followed at a 140 rpm on a Buehler Ecomet 4 grinder-polisher in which the mounted specimens were installed. Rough grinding began using 180 grit silicon carbide paper and continued through 240, 320, 400, 600, 800 and 1200 grit stages. Diamond suspensions on TEXMET 2000 and 1500 surfaces were used for the fine polishing stages starting at 9 μm and progressing through

6, 3, and 1 μm . The final polishing stage was with a combination of colloidal silica and 0.05 μm Al_2O_3 on a nylon surface.

Figure 85 – Example resin mounted specimens of (from the left) 7YSZ, Yb:7YSZ, Ce:7YSZ, and Nb:7YSZ

Finally, the polished samples were etched in 10% hydrofluoric acid for 30 minutes at room temperature to reveal grain boundaries. Samples intended for scanning electron microscopy (SEM) were then carbon coated. The carbon coating added conductivity to surfaces and avoided charging by the SEM electron beam that would otherwise produce low quality images.

3.9 SCANNING ELECTRON MICROSCOPY (SEM)

Images with magnifications ranging from 300X to 2000X were acquired on a Hitachi S-570 scanning electron microscope at NRC-IAR, which had a tungsten filament thermionic emission gun as an electron emission source. Specimens were mounted in the SEM according to the surface prepared for observation, but all were carbon coated (in an Edwards E306 vacuum coater). Pieces for imaging as-pressed faces were mounted on a single large stub with double sided carbon tape. Pieces for cross sectional analysis resided in resin (following section 3.8), and they were placed in a mounting bracket sized specifically for such samples.

Finally, fracture surfaces were produced from detached disk tops which were broken and mounted perpendicularly on stubs, as pictured in Figure 86. This allowed the incident electron beam better access to the fracture surface and was required due to spatial limitations within the SEM.

Figure 86 – Mounted specimens for observing fracture surfaces in the SEM

3.10 POROSITY MEASUREMENTS

To quantify pore volumes, image analysis techniques were conducted on three lower magnifications (1000X, 600X and 300X) of pore structures as they appeared in SEM images of polished and etched specimens. The software ImageTool [116] was employed for this process. First, greyscale SEM images were thresholded to binary images, where the zero level (black) was assigned to the pore network and the one level (white) to the solid material. The resultant black and white pixels were then quantified to find an area percent porosity. This process is summarized graphically in Figure 87. Afterward, the porosity values obtained at the three magnifications were averaged.

Figure 87 – a) An SEM image of a polished microstructure (Nb_2O_5 co-doped specimen at 1000X) and b) digitally isolated pores

A normal assumption is that pores are spherical, and therefore that area percent porosity equals volume percent. The pores shown in Figure 87 are clearly not spherical, so they were instead assumed to be equally misshapen in all directions. In this way, it was maintained that area percent porosity was equal to volume percent.

3.11 GRAIN SIZE MEASUREMENT

With ASTM Standard E 112 – 96 (2004)⁶² section 13 as a reference [117], ImageTool [116] was used for measuring the average grain size of specimens with the mean lineal intercept method. Three straight lines were digitally drawn on 2000X SEM images of polished and etched specimens, and the number of intersections that each line made with grain boundaries was divided by the line

length. Intercepts occurring at the beginning or end of lines were counted as $\frac{1}{2}$ intercepts, and those coinciding with junctions (between three grains) were counted as $1\frac{1}{2}$, following the quoted standard. An example of one line with tagged grain boundary intersections is shown in Figure 88.

Figure 88 – Example measurement of average grain size in ImageTool (line shown is drawn on a Nb:7YSZ microstructure at 2000X)

ASTM Standard E 112 – 96 could not be followed precisely. The standard states that a magnification of 100X is ideal for grain size measurement, however grains appearing in the sintered, polished and etched specimens of the current research were not adequately apparent until viewed at 2000X. Also, due to high porosity, it was difficult to randomly select test lines that were not interrupted by appreciable voids. As a result, lines were not selected randomly but rather consciously and carefully to avoid porous regions. Grain structures were equiaxed in all cases, so line direction was deemed insignificant although was still attempted to be selected in a non-biased way.

The above issues led to an average of only 41 intersections per test (50 are required by the ASTM standard). This theoretically reduced the precision of

measurements, however no standard deviation exceeded 30% its corresponding grain size, and most were below 9%. These results are presented and further discussed in section 4.5.

3.12 X-RAY DIFFRACTION (XRD)

A cobalt source was used to acquire X-ray diffraction data on a Bruker AXS D8 Discover diffractometer with General Area Detector Diffraction Software (GADDS) version 4.1 [118]. The output data consisted of properties for each ZrO_2 phase, which was obtained with a Rietveld quantitative analysis [119, 120] as has been recommended for determining the phase content of zirconia polymorphs [2].

During acquisition, as-pressed and sintered sample surfaces were cyclically displaced 3 mm in order to increase their effective gate volumes and achieve finer (less coarse) data. Three frames of 2θ ranges were merged to produce a single raw data file for each sample, with a complete 2θ range of 20 to 95°. Raw data files were analyzed using TOPAS software [121] in which the peaks for cubic, tetragonal and monoclinic polymorphs were isolated and iteratively compared to reference data using a least squares method. Results were in the form of converged iterated variables.

Results for the tetragonal phase were reported for the bct interpretation (Figure 7) of the cation lattice. This complicated later comparisons with literature, since values for the (near) fcc interpretation (Figure 4) are usually quoted. The c_t lattice parameter corresponds to the same dimension in each interpretation, but a_t does not. Figure 7 clarifies this. Following the figure, and Table 1,

$$a_t = \sqrt{2} \cdot a_{t|bct} \quad (47)$$

An important note is that, throughout this thesis, “ a_t ” refers to $a_{t|fcc}$ (the near fcc interpretation).

Calculation of a_t by application of Equation 47 to XRD data produced lower numbers than Figure 21 predicts. The discrepancy was small, in the range of 0.05 Å. To rule out invalid data, a comparison was made to published figures. Li *et al.* [9] have directly measured both a_t and $a_{t|bct}$, but Equation 47 does not accurately relate them. Instead, there is a similar discrepancy of roughly 0.05 Å, which serves to validate the current data.

Without an accurate method for correcting the obtained $a_{t|bct}$ values to the standard fcc interpretation, the measured values for a_t in the current research were not overly useful. With the data validated, however, experiments resumed with only c_t for comparison to literature.

3.13 ENERGY DISPERSIVE X-RAY SPECTROMETRY (EDS)

To ensure that the selected 250 hours of sintering was adequate for a uniform distribution of co-dopants, an EDS system equipped on a Philips XL-30 S FEG scanning electron microscope was used. The emission source was a Schottky-based thermionic field emission electron gun, and in this study an acceleration voltage of 20 kV was used. EDS was performed at NRC-IAR and allowed the acquisition of a map that showed the distribution of co-dopant cations throughout the ceramic microstructure.

Only one specimen was analyzed with EDS. Polished, etched, and resin-mounted Yb:7YSZ (furnace cooled) was selected since Yb^{3+} was the largest co-dopant cation and would have diffused the slowest during sintering. A uniform distribution of Yb^{3+} would therefore imply the same conclusion for all co-dopants. Here, cooling rate was considered insignificant relative to 250 hours of sintering.

3.14 HARDNESS AND MODULUS TESTING

It was of interest to establish the effects of the following on hardness and Young's modulus properties:

1. Co-dopants to standard 7YSZ
2. Cooling rate

To document the effect of co-dopants, polished and air cooled specimens of each composition (not etched or carbon coated) were tested following the procedure described below, and results from co-doped specimens were compared to those for standard 7YSZ. Then, since 7YSZ produced the most consistent results while testing air cooled specimens, it was selected for further testing in order to document the effect of cooling rate. This required testing two additional 7YSZ specimens, one that had undergone fan cooling and another that had undergone furnace cooling. The effect of all three cooling rates was thus documented for one composition, which would provide enough insight to draw conclusions for the other three compositions.

Tests were performed using a CSM Instruments Nano-Hardness Tester with Indentation Software, all mounted on a vibration table. The maximum load applied was 100 mN at equal loading and unloading rates of 200 mN/minute. A

conventional triangular nano-indenter yielded Vickers hardness values. The Oliver and Pharr method [122] was used for analysis and a Poisson ratio of 0.25 was assumed in all cases for the calculation of Young's moduli.

Measurements were difficult due to the high porosity of samples.

Depending on the location of attempted indents, the underlying porous structure allowed for varying degrees of material collapse. As a result, inconsistent measurements were produced as well as non-conventional plots of force vs. penetration depth. To circumvent this issue, as many as ten indentations were performed for each test, which were then averaged. Young's modulus values were then corrected with the use of Mackenzie's equation, which is [123]

$$E = E_0(1 - 1.9V_p + 0.9V_p^2) \quad (48)$$

where E is the effective modulus (with porosity), E_0 is the modulus of dense material, and V_p is volumetric porosity ($0 < V_p < 1$). The equation is not generally applicable to indentation techniques, but its application in this case provided a method to account for porosity so that results could be better compared. Corrected values of E would not be accurate, but qualitative trends were expected to be revealed.

4 RESULTS AND DISCUSSION

Following a documentation of sintered sample conditions, this section details the results of experiments and relates them to the thesis objectives.

4.1 CONDITION OF SINTERED DISKS

The condition of ceramic disks that emerged from the furnace varied appreciably. Figure 89 shows two samples that represent the best and worst cases.

Figure 89 – A display of ideal and worst case conditions of ceramic disks after sintering

Nearly all of the sintered samples displayed a small amount of cracking on their underside, shown in Figure 90. Other than that, the Yb:7YSZ disks were mostly pristine in appearance. All other compositions had a large portion of samples with detached or partially detached tops, like the Nb:7YSZ sample in Figure 89. The fracture pattern that led to this corresponded with the cracking in

green bodies pictured in Figure 79, re-emphasizing the problems with the uniaxial press used.

Figure 90 – Typical underside cracking displayed on nearly all sintered disks, as viewed with a stereomicroscope (shown here is a 7YSZ, furnace cooled sample)

Similar to Yb:7YSZ, the 7YSZ reference samples also emerged from the furnace in quite good condition although some had the detached tops described above. Ce:7YSZ disks were in good condition. Lastly, the Nb:7YSZ disks were in the worst condition due to furnace contamination where, upon reaching a high temperature, drips of a dark glassy substance fell on three samples. The remaining Nb:7YSZ samples were in fair condition although had an intrinsic brown-grey colour, best seen in Figure 85 in relation to the other compositions. This colour difference was not significant compared to otherwise co-doped 7YSZ, and was taken to be unrelated to the furnace contamination. The Nb:7YSZ disk in Figure 89 was not ruined by contamination, but did make contact along its underside as indicated in the figure. Most Nb:7YSZ disks did not make contact and were in better condition.

4.2 PHASE RETENTION OF SINTERED SAMPLES

The phases present in the sintered samples were measured with XRD, and the results revealed important trends that can be explained on the basis of transformation kinetics (section 2.3.3) and the reviewed mechanisms of phase stabilization (section 2.2). As expected, the four compositions tested retained different quantities of low and high temperature phases, due to the different stabilizing mechanisms their co-dopants imposed and also due to cooling rate.

4.2.1 XRD RESULTS

The X-ray spectra obtained over a 2θ range of 20 to 95° are shown in Figure 91 to Figure 94 with dominant peaks labelled. As described in section 3.12, these X-ray spectra were compared to those known for m, t and f phases, which were iteratively combined by software until a fit was made with the experimental spectra. The converged phase amounts, lattice parameters and densities are summarized in Table 9, categorized by sample composition and cooling method. An important note is that the mass per unit cell was internally calculated assuming pure ZrO_2 , without accounting for dopants or O^{2-} vacancies. The densities listed in Table 9 must therefore be interpreted appropriately.

In these experiments, the tetragonal a_t lattice parameter was reported for the bct interpretation of the tetragonal phase (see section 3.12). This prevents the calculation of standard tetragonality, c_t/a_t , which is a valuable parameter since it indicates stability (section 2.2.1). So where it is necessary, trends of tetragonality are inferred from the c_t lattice parameter, with lower c_t values corresponding to lower tetragonality (as in Figure 21).

a) Fan cooled

b) Air cooled

c) Furnace cooled

Figure 91 – 7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples

a) Fan cooled

b) Air cooled

c) Furnace cooled

Figure 92 – Yb:7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples

a) Fan cooled

b) Air cooled

c) Furnace cooled

Figure 93 – Ce:7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples

a) Fan cooled

b) Air cooled

c) Furnace cooled

Figure 94 – Nb:7YSZ X-ray spectra (intensity versus 2θ) for a) fan, b) air and c) furnace cooled samples

Table 9 – Phase contents, lattice parameters and densities

Composition	Cooling	Phase	Phase Content*	Lattice Parameters (Å)				Density (g/cm ³)
				a [†]	b	c	β (°)	
7YSZ	Fan	m	39.1%	5.1736	5.2162	5.3325	99.1888	5.7615
		t	14.0%	3.6071	-	5.1923	-	6.0576
		f	46.9%	5.1440	-	-	-	6.1067
	Air	m	40.9%	5.1735	5.2187	5.3321	99.1981	5.7594
		t	13.2%	3.6089	-	5.1914	-	6.0525
		f	45.9%	5.1439	-	-	-	6.1072
	Furnace	m	42.1%	5.1726	5.2212	5.3300	99.2351	5.7605
		t	12.3%	3.6091	-	5.1888	-	6.0550
		f	45.7%	5.1429	-	-	-	6.1108
Yb:7YSZ	Fan	m	6.3%	5.1780	5.2024	5.3337	99.1850	5.7705
		t	22.5%	3.6173	-	5.1611	-	6.0598
		f	71.2%	5.1395	-	-	-	6.1229
	Air	m	6.9%	5.1770	5.1976	5.3308	99.2010	5.7804
		t	22.7%	3.6193	-	5.1554	-	6.0598
		f	70.5%	5.1377	-	-	-	6.1295
	Furnace	m	8.3%	5.1770	5.2059	5.3259	99.2020	5.7765
		t	17.8%	3.6153	-	5.1631	-	6.0641
		f	73.9%	5.1376	-	-	-	6.1296
Ce:7YSZ	Fan	m	22.4%	5.1890	5.2121	5.3529	99.1444	5.7262
		t	25.9%	3.6159	-	5.1939	-	6.0262
		f	51.7%	5.1620	-	-	-	6.0433
	Air	m	21.0%	5.1885	5.2118	5.3547	99.1514	5.7254
		t	25.5%	3.6155	-	5.1986	-	6.0221
		f	53.5%	5.1616	-	-	-	6.0446
	Furnace	m	37.3%	5.1869	5.2285	5.3436	99.1856	5.7212
		t	15.4%	3.6234	-	5.1991	-	5.9954
		f	47.3%	5.1622	-	-	-	6.0424
Nb:7YSZ	Fan	m	73.5%	5.1672	5.2108	5.3369	99.1188	5.7686
		t	16.2%	3.6316	-	5.1355	-	6.0422
		f	10.3%	5.1523	-	-	-	6.0773
	Air	m	76.5%	5.1689	5.2114	5.3367	99.1476	5.7668
		t	12.1%	3.6149	-	5.1848	-	6.0401
		f	11.4%	5.1515	-	-	-	6.0802
	Furnace	m	78.4%	5.1667	5.2129	5.3332	99.1749	5.7719
		t	11.3%	3.6207	-	5.1632	-	6.0458
		f	10.4%	5.1497	-	-	-	6.0867

* wt%, with an internal accuracy of ± 0.2 wt%† For t phase, a is reported for the bct interpretation ($a_t|_{bct}$), cannot be corrected, so is not considered further (section 3.12)

4.2.2 ANALYSIS OF 7YSZ

It is first important to discuss and validate the results from the 7YSZ reference sample. The 7SYZ phase contents given in Table 9 are graphed for clarity in Figure 95 to show the proportion of m, t and f phases under fan, air and furnace cooling schemes.

Figure 95 – Measured phase content versus cooling scheme for 7YSZ

7YSZ has 7.59 mol% $\text{YO}_{1.5}$ and sintering was conducted at 1400°C . When this point is located on the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram (Figure 75) application of the lever rule (which assumes equilibrium was reached) estimates phase contents of 63 mol% tetragonal and 37 mol% cubic, prior to cooling. When cooling begins, these two components undergo changes. From section 2.3.3.1, it is expected that the brief time spent at high temperatures allows limited displacement of yttria while some cubic phase undergoes the diffusion controlled transformation to tetragonal. As this happens, neighbouring f- ZrO_2 becomes yttria-rich, enough that much of it has sufficient Y_2O_3 content to retain its fluoritic

structure to room temperature. Less than the 37 mol% cubic content is therefore expected once cooled. The roughly 46 wt% that is reported by XRD in Table 9 indicates the limitations of Scott's $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram. Although it is the accepted standard, there have been many proposed modifications. The solubility trends that it illustrates, however, are agreed upon.

An increasing cubic lattice parameter (a_f) indicates an increasing content of the oversized dopant cation, Y^{3+} . Based on this, it follows that the Y_2O_3 concentration in f- ZrO_2 can be calculated from a_f . An empirical relation is [90]

$$[\text{Y}_2\text{O}_3] = 77059a_f^2 - 76316a_f + 18877 \quad (\text{mol}\%) \quad (49)$$

where a_f is in nm. Using this equation, relative errors have been reported in the range of 2.5% [90], but regardless, the trend of increasing a_f with Y^{3+} content is widely accepted. From Table 9, a_f is 5.14402 Å for fan cooling, 5.14388 Å for air, and 5.14288 Å for furnace cooling of the 7YSZ samples. By Equation 49, the concentrations of $\text{YO}_{1.5}$ in the cooled cubic phase are therefore 18.89, 18.82 and 18.33 mol%, respectively. These concentrations are consistent with the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram which indicates that the cubic phase is stable only above 18 mol% at room temperature.

Similarly, although a literature review revealed no reliable equation for $\text{YO}_{1.5}$ in the tetragonal phase (something also noted by Schulz [90] in 2000), obtained values for c_t were enough to correlate with Figure 21 and extract estimates. Accordingly, fan, air and furnace cooled samples are estimated to have t- ZrO_2 $\text{YO}_{1.5}$ concentrations of roughly 0.46, 0.60, and 2.00 mol%, respectively. Since a higher presence of yttria in t- ZrO_2 indicates improved stability (section 2.2.1), this

estimated trend in yttria concentration means that slower cooled t phase is more stable. This should translate to reducing tetragonality, then, because Y^{3+} is an oversized trivalent dopant (as in section 2.2.1.1) and its addition to ZrO_2 causes lattice dilatation and O^{2-} vacancies that reduce oxygen overcrowding. Indeed, this is shown to be the case in Table 9 since c_t reduces with cooling rate.

However, the decreasing concentration of yttria in f- ZrO_2 with decreasing cooling rate was in fact opposite what was expected, since more time at high temperatures should allow more $f \rightarrow t$ transformations, necessitating more displacement of yttria and the further enrichment the f phase that remains (section 2.3.3.1). An explanation for this apparent discrepancy comes from the fact that the amount of cubic fluorite in fan and furnace cooling (the two extreme cooling rates) differed by less than 1.5 wt%. This indicates that, under both cooling schemes, nearly equal amounts of f- ZrO_2 was enriched with Y_2O_3 and stabilized to room temperature. Considering the large difference in cooling rates, this must have occurred quickly at the start of cooling, such that cubic retainment was about equal in both cases.

The decreasing yttria concentrations in the cubic phase with decreasing cooling rate could thus not be the result of $f \rightarrow t$ transformations. Instead, it was likely caused by yttria diffusion from the cubic to tetragonal phase after the cubic had been enriched to stability by $f \rightarrow t$. All three calculated concentrations in f- ZrO_2 were > 18 mol% $YO_{1.5}$, which is more than is necessary for stability, especially when cooling is rapid (which requires as little as 14 mol% $YO_{1.5}$). These high yttria concentrations may have caused enough of a chemical

potential for diffusion to occur into neighbouring t phase. This is possible since the estimated contents of the t phase (the maximum was 2.00 mol% when furnace cooled) were all lower than is soluble (up to 4.6 mol% $\text{YO}_{1.5}$).

The increasing amounts of yttria in t- ZrO_2 with decreased cooling rate was expected, because the t phase solvus line in the phase diagram shows an increasing solubility of $\text{YO}_{1.5}$ in equilibrium conditions. Therefore, slower cooling rates (which more closely approximate equilibrium) will result in t- ZrO_2 with more yttria content. Further, since the t $\rightarrow$ m transformation is not diffusion controlled, it does not displace yttria as preferred by the lower-soluble monoclinic phase. m- ZrO_2 thus usually forms with more yttria than is stable, which will diffuse outward and into the low-yttria t- ZrO_2 if time and temperature allow it.

The tetragonal phase in pure zirconia should transform to monoclinic in a diffusionless reaction upon cooling to room temperature (section 2.3.3.3), but the internal yttria content in some of it was enough for retention to room temperature (sections 2.2 and 2.2.1.1 discussion the mechanisms of stabilization in more detail). The increased presence of the tetragonal phase under rapid fan and air cooling was due to the cubic matrix more quickly contracting around t- ZrO_2 precipitates. With an increase in strain energy, this suppressed more t $\rightarrow$ m transformations and retained more t phase (as described in section 2.3.3.3).

For an external validation of the 7YSZ results in Table 9, a comparison to similar experiments is justified. One was conducted by VanValzah and Eaton [124] who were studying the effects of aging and quenching on PS coatings. In one case, they aged 4.24 mol% $\text{Y}_2\text{O}_3 + \text{ZrO}_2$ at 1371°C for 100 hours and then

applied either fan cooling (with a similar scheme as in the current work) or furnace cooling (roughly six times more rapid than the current work). 6 vol% m-ZrO₂ was documented for fan cooling and 31 vol% for furnace, with differences being attributed mostly to stress effects on t-ZrO₂. In another experimental comparison Shimbo *et al.* [125] sintered 7YSZ at 1500°C, and though the cooling rate was not specified, the authors also found all three phases present at room temperature in amounts comparable to those in Table 9. These are typical results for yttria stabilized zirconia, within the range of experimental variability.

4.2.3 STABILITY OF CO-DOPED COMPOSITIONS

The effect of each co-dopant on the retention of phases is a strong indicator of the stabilizing effects imposed. With the analysis of 7YSZ as a reference, each composition is now examined according to Table 9 and the expected effects for which co-dopants were selected (sections 3.2 and 3.3).

4.2.3.1 Yb:7YSZ

The low amount of m phase in Yb:7YSZ under all three cooling schemes (Table 9) makes it clear that this composition had the most success stabilizing high temperature phases, most notably the cubic phase. Figure 96 emphasizes this, plotting the proportion of m, t and f phases under fan, air and furnace cooling schemes. The high cubic phase content was due to the increased number of oxygen vacancies provided by trivalent Yb³⁺, which gave some high temperature Zr⁴⁺ sevenfold coordination and thereby avoided a large amount of t → m transformations in just the same way that Y³⁺ does (section 2.2.1.1).

Figure 96 – Measured phase content versus cooling scheme for Yb:7SYZ

The stabilizing effect of Y^{3+} and Yb^{3+} is so similar at low concentrations that the ZrO_2 - Y_2O_3 - Yb_2O_3 ternary phase diagram at $1400^\circ C$ (Figure 72) is nearly symmetric along the $[Y_2O_3] = [Yb_2O_3]$ tie line. It follows that 5 mol% $YbO_{1.5}$ + 7YSZ can be thought of as equivalent to having 12 mol% $YO_{1.5}$ stabilized ZrO_2 (by adding the cationic concentrations of Y^{3+} and Yb^{3+} in Table 6). This equivalent composition is located in Figure 75 within the $t + f$ two-phase field of the Y_2O_3 - ZrO_2 phase diagram, and predicts a higher cubic presence at $1400^\circ C$ since it is closer to the cubic single phase field than 7YSZ. The ternary phase diagram (Figure 72) agrees, since Yb:7YSZ falls just inside the cubic single phase region at $1400^\circ C$. On cooling, it follows that more f- ZrO_2 will be retained in Yb:7YSZ than in 7YSZ, which is demonstrated consistently for all three cooling schemes by comparing Figure 95 with Figure 96.

4.2.3.2 Ce:7SYZ

Cerium is known to be a tetragonal stabilizer at low concentrations [13]. The effect is to decrease the $t \rightarrow m$ transition temperature (M_s) with increasing CeO_2 concentrations. When added to pure ZrO_2 (without Y_2O_3), the difference in the start temperature M_s is 1170°C (with no CeO_2 , discernable from the phase diagram in Figure 15) versus 200°C with about 12 mol% CeO_2 [13]. The additional presence of Y_2O_3 in Ce:7YSZ alters the thermodynamics, but the effect of CeO_2 would be the same: the nucleation of m- ZrO_2 is delayed on cooling until lower temperatures. In Table 9, and Figure 97 below, the Ce:7YSZ composition behaves accordingly when fan and air cooled, however when furnace cooled, the result was unexpectedly different.

Figure 97 – Measured phase content versus cooling scheme for Ce:7SYZ

When cooled quickly, insufficient time at the lowered $t \rightarrow m$ transition temperature resulted in retaining about 26 wt% t- ZrO_2 and prevented any more than ~21 wt% m- ZrO_2 from forming. However, when cooled slowly in the

furnace, Ce:7YSZ retained only 15 wt% t phase which is very close to that of 7YSZ, and it produced a 37 wt% m phase. From this large jump of ~21 to 37 wt% m phase, it is clear that Ce:7YSZ is highly sensitive to cooling rate.

However, a literature investigation has revealed a likely explanation which is not due to the stabilizing mechanisms that Ce:7YSZ was selected for (in section 3.2.2).

Figure 73 shows the ternary phase diagram that applies to Ce:7YSZ at 1600°C. Near the Ce:7YSZ composition is a two-phase t + f region, revealing that ceria can also stabilize the cubic phase. Some literature describes this as occurring by a stoichiometric shift [126]. In high temperature conditions, Ce^{4+} (in CeO_2) can reduce to Ce^{3+} which has the preferred stoichiometry of Ce_2O_3 . When this happens, ionic radius grows by 10% and the oxygen vacancies that trivalent Ce^{3+} now forms (like in section 2.2.1.1) stabilize f- ZrO_2 [126].

The high sensitivity of Ce:7YSZ originates, then, from the retention (or not) of oxygen vacancies that are formed at high temperatures. Regardless of cooling rate, the behaviour of cerium reverts from Ce^{3+} back to Ce^{4+} when temperature is lowered. The corresponding stoichiometric shift from Ce_2O_3 to CeO_2 , which annihilates the oxygen vacancies formed at high temperatures, necessitates ingress of oxygen from the surrounding atmosphere. When cooling is rapid, the diffusion of oxygen is prevented and vacancies are retained. But when cooling is slow, longer time at high temperatures allows more oxygen diffusion and vacancies are lost. This destabilizes the cubic phase and enables $f \rightarrow t$ and $t \rightarrow m$ transformations, leading much more m phase as Table 9 shows.

4.2.3.3 Nb:7YSZ

The equal parts Nb^{5+} and Y^{3+} in Nb:7YSZ were expected to annihilate the O^{2-} vacancies introduced by Y^{3+} and produce an equivalent Y_2O_3 composition near zero (Figure 75). During sintering, along a 1400°C tie line in the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram, Nb:7YSZ is positioned inside the tetragonal single phase field. Since the tetragonal phase would transform to monoclinic on cooling, the phase content was expected to be mostly m-ZrO₂ in the absence of high temperature stabilization. The available ternary $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram is at 1500°C (Figure 74), but appears to also predict the Nb:7YSZ composition to be within the single t-ZrO₂ phase field. Figure 98 illustrates the phase contents measured in Yb:7YSZ, and indeed, all three cooling rates resulted in a high monoclinic presence. However, there was a surprising amount of f phase.

Figure 98 – Measured phase content versus cooling scheme for Nb:7SYZ

While t phase could be hindered by strain energy from transforming to monoclinic (section 2.3.3.3), the presence of cubic phase indicates that many

oxygen vacancies (by Y^{3+}) were not annihilated by Nb^{5+} . An imperfect mixing of powders (in section 3.4) could have resulted in less Nb_2O_5 additions than intended, but another explanation could be Nb^{5+} segregation. If Nb^{5+} was not uniformly distributed in 7YSZ, many O^{2-} vacancies would remain. The issue of segregation is important, and is investigated closely in section 4.3 by mapping the distribution of elements.

4.2.4 STABILIZING MECHANISMS

With a detailed account on the effect of co-dopants in section 4.2.3, observations can now be made on the cooling rate sensitivity and relative effectiveness of stabilizing mechanisms. Sensitivity is indicated by the changes in monoclinic content with cooling scheme, and the relative effectiveness of mechanisms originates similarly.

4.2.4.1 Cooling Rate Sensitivity

Theoretically, the stabilities of all compositions but Nb:7YSZ were affected by oxygen vacancies. Based on this concept, equivalent compositions are illustrated on the Y_2O_3 - ZrO_2 phase diagram in Figure 75. Accordingly, Yb:7YSZ has the most vacancies since it includes both Y^{3+} and Yb^{3+} which are both trivalent dopants and produce vacancies according to section 2.2.1.1. At room temperature and at equilibrium, 7YSZ and Ce:7YSZ have equal amounts of oxygen vacancies since Ce^{4+} does not produce them. However, cerium's unique shift to 3+ valence at high temperatures (section 4.2.3.2) provides additional vacancies which then become unstable at low temperatures.

For Nb:7YSZ with no vacancies, Table 9 and Figure 98 show that the two extreme cases of fan and furnace cooling influenced the monoclinic phase content differently by 4.9 wt%. For 7YSZ, the two cooling schemes produced a difference of 3.0 wt%, and in the same way, the results of Yb:7YSZ differed by only 2.0 wt%. An increasing concentration of oxygen vacancies (Nb:7YSZ < 7YSZ < Yb:7YSZ) clearly produces less sensitive stability, and from this, it is inferred that oxygen vacancies themselves are insensitive.

The co-dopant cation Ce^{4+} was selected for its large size and equal valence to that of Zr^{4+} . However, with the interfering effects of its shift to Ce^{3+} , it could not contribute to observations on the cooling rate sensitivity of oversized dopants. This limits the discussion on the cooling rate sensitivity of lattice distortions to only that of undersized dopants, which were investigated via Nb:7YSZ.

In Figure 98, Nb:7YSZ shows the expected increasing trend of monoclinic content with decreasing cooling rate. The difference in content between fan and air cooling is 3.0 wt%, and the difference between air and furnace is 1.9 wt%. The same numbers for 7YSZ are 1.8 and 1.2 wt%. Since Nb:7YSZ theoretically contains no oxygen vacancies, this is a direct sensitivity comparison of the stabilizing mechanisms by tensile lattice distortions (by the undersized Nb^{5+}) and oxygen vacancies (by the oversized Y^{3+}), where the rigid dilative distortions imposed by Y^{3+} (expanded in section 2.2.1) are roughly equal in both cases (due to nearly equal Y^{3+} cation concentrations in Table 6). It follows that tensile lattice distortions impose stability that, per dopant cation added, is more sensitive to cooling rate than oxygen vacancies.

4.2.4.2 Relative Effectiveness

The behaviours of Ce:7YSZ and Nb:7YSZ provide insight into the effectiveness of O^{2-} vacancy and lattice distortion stabilizing mechanisms. Theoretically without vacancies and with added tensile lattice distortions, Nb:7YSZ loses most of its ability for high temperature phase stabilization. Further, the small amount of remaining f and t phases in Nb:7YSZ is later shown to probably be due to segregation (section 4.3). The large difference in monoclinic phase content between 7YSZ and Nb:7YSZ therefore suggests that tensile lattice distortions are much less effective than oxygen vacancies in stabilizing high temperature phases.

Ce:7YSZ, with its unique shift to Ce^{3+} at high temperatures, shows that when O^{2-} vacancies are retained by rapid cooling they stabilize against more than 21 wt% m phase formation. This places Ce:7YSZ between 7YSZ and Yb:7YSZ in terms of stabilizing success, with roughly a 19 wt% m phase improvement over 7YSZ (comparing values from fan and air cooling). However, when the vacancies are lost during slow cooling, this leaves only cerium's compressive, rigid lattice deformations that differentiate Ce:7YSZ from 7YSZ. In that case, Ce:7YSZ offers only about a 5 wt% m phase improvement over 7YSZ. With a drop in m phase improvement from 19 to 5 wt%, this provides a crude estimate that O^{2-} vacancies are roughly four times more effective than compressive lattice distortions at preventing m phase development in this research.

4.3 ELEMENTAL DISTRIBUTIONS

In any composition, co-dopant segregation would affect the amounts of retained phases. Of particular relevance is the unexpected cubic presence in Nb:7YSZ (section 4.2.3.3). The purpose of EDS elemental mapping was to investigate such issues. As discussed in section 3.13, it was performed only on Yb:7YSZ since Yb^{3+} has the largest cationic radius and thus represents the worst case for diffusion. Because of this, Ce^{4+} and Nb^{5+} should be more uniformly distributed relative to a map of Yb^{3+} . The EDS results appear in Figure 99.

Figure 99 – Elemental maps of a) a polished region showing concentrations of b) Zr^{4+} , c) Y^{3+} and d) the co-dopant, Yb^{3+} (dashed white lines border porosity)

In the above elemental maps, the density of yellow dots indicates the density of the indicated element. Zr^{4+} (in Figure 99b) shows to be quite uniformly distributed, but with a higher density in large central regions away from pore boundaries. Y^{3+} (in Figure 99c) is similarly distributed, but in the central regions where it and Zr^{4+} are rich, the density of the co-dopant (Yb^{3+} , Figure 99d) is low.

4.3.1 ORIGIN OF SEGREGATION

Explaining the observed segregation in Figure 99 requires referencing Figure 76 in section 3.4, which shows the original Yb_2O_3 powder to be quite fine, and 7YSZ to be quite coarse. After mixing and ball milling these powders together, Figure 77b shows that Yb:7YSZ had both large and small particulate. The larger was probably 7YSZ, based on the original size difference. The reason for the non-uniform distribution of Yb^{3+} in Figure 99 is thus apparent. The mass transport supporting sintering apparently occurred primarily along pore surfaces (mechanisms '1', '2' and possibly '3' in Figure 66), displacing cations in the adjacent lattice but minimally affecting the composition of large central regions. In Figure 99, the large central regions rich with Zr^{4+} and Y^{3+} but lean in Yb^{3+} represent large 7YSZ particulate in the original mixed powder (Figure 77b).

Grain boundary diffusion has been reported as the primary contributor to sintering with many zirconia powders [108, 127]. The current results are thus significant. They show that with micro-scale particulate, diffusion along pore boundaries is favoured over the grain boundaries inside the particulate. Therefore, grain boundary diffusion can only be predominant if porosity is low and not part of a connected network.

4.3.2 EFFECT OF SEGREGATION

The effect on the XRD results discussed in section 4.2 is readily apparent, most easily from Nb:7YSZ data. Nb^{5+} was added in the same concentration as Y^{3+} so that, theoretically, all O^{2-} vacancies would be annihilated. This was expected to destabilize the cubic phase (as discussed in section 3.2.3), yet roughly 10 wt% f phase remained after all three cooling rates (Figure 98). The unexpected cubic phase can be accounted for if Nb^{5+} was concentrated at grain boundaries similar to Yb^{3+} . In that case, O^{2-} vacancies would not be annihilated near the centres of large grains, and the cubic phase would remain stabilized in those regions. Based on where co-dopant cations are scarce in Figure 99, those regions appear to account for much of the volume.

By Equation 41, two Nb^{5+} cations are required for one O^{2-} vacancy annihilation. Therefore, with Nb:7YSZ having a consistent f phase presence of roughly 10 wt% in Table 9, about 20% of 7YSZ was deprived of Nb^{5+} . Compared to the size of deficient Yb^{3+} regions in Figure 99, this estimate seems reasonable.

4.4 SINTERED MICROSTRUCTURES

SEM micrographs of as-pressed, fractured and polished surfaces revealed many properties of the sintered ceramics and the processing methods applied. They are now discussed.

4.4.1 AS-PRESSED SURFACES

As-pressed surfaces (furnace cooled) are shown in Figure 100. Yb:7YSZ was revealed to have superior integrity since its pressed surface was the most

tightly packed and ordered (Figure 100b). Sintered Yb:7YSZ disks were already noted to be in the best condition when inspected visually (section 4.1). From Figure 100, increasing disorder was shown according to Yb:7YSZ < 7YSZ < Nb:7YSZ < Ce:7YSZ with grains appearing more loosely bonded and a network of grain boundaries being more difficult to distinguish.

Figure 100 – As-pressed and sintered surfaces of a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ ceramic disks

Explaining the pressed surfaces above was not straight forward. From Figure 77, Yb:7YSZ powder had a small distribution of particulate size which likely aided sintering (discussed further in section 4.5), but 7YSZ had an even smaller distribution and yet exhibited greater disorder, and Ce:7YSZ had comparable distribution but showed the most disorder. Because these trends are inconsistent and because Yb³⁺ was actually suspect of diffusing the slowest of all the co-dopants (so should have been the least successfully sintered), reasons for the improved quality of the Yb:7YSZ samples are likely linked to the troubled pressing process and releasing of green bodies from dies. Although the same release agent was used throughout sample fabrication, its efficiency may have varied with the condition of the cylindrical dies and the chemistry of powders.

The as-pressed surfaces in Figure 100 also provide an initial three-dimensional perspective of porosity and its scale. It is clear from the figure that much if not all of the porosity was connected and was significant in size. Porosity is discussed further below as it was quantified from polished surfaces.

4.4.2 FRACTURE SURFACES

The (furnace cooled) fracture surface topographies in Figure 101 also reveal (to some extent) the aforementioned three-dimensional and connected pore network. More importantly, however, Figure 101 shows the fracture behaviour of each composition. Combined with the measured phase contents (Table 9), this allows a study of the propagating crack's interaction with each phase.

Figure 101 – Fracture surfaces of a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ specimens

Yb:7YSZ (Figure 101b) was mostly cubic fluorite and exhibited predominantly transgranular fracture, producing a smooth, near-planar surface. In contrast, Nb:7YSZ (Figure 101d) was mostly monoclinic and fractured along grain boundaries (intergranular). Nb:7YSZ was also the easiest composition to

fracture by hand. 7YSZ and Ce:7YSZ retained intermediate amounts of monoclinic and cubic phases, and on close inspection, contained both transgranular and intergranular fracture paths.

The intergranular fracture behaviour of highly monoclinic compositions was due to the presence of microcracks around m-ZrO₂ grains which formed with the $t \rightarrow m$ transformations that occurred on cooling [46]. Cracking of the bulk material therefore occurred along grain boundaries since strength was already compromised there.

In the absence of the monoclinic phase there was an absence of intergranular microcracks, and fracture was observed to have propagated in a transgranular manner. Through cubic grains, the result was a smooth fracture surface because there was no accompanying phase transformation. However, transgranular fracture through tetragonal grains stress-induced the $t \rightarrow m$ transformation (see sections 2.3.3.3 and 2.4.1). According to Lange [46], tetragonal grains can be identified based on this fact, since the transgranular crack path interacts with newly formed monoclinic twins (section 2.3.4.1) and the resultant fracture surface is irregular, not smooth. In the current experiments, tetragonal grains were observed in this manner as pictured in Figure 102. To summarize the observations, grain polymorphs effected crack propagation as follows:

- m-ZrO₂ caused local intergranular fracture.
- t-ZrO₂ grains displayed transgranular fracture with an irregular surface.
- f-ZrO₂ grains displayed transgranular fracture with a smooth surface.

Figure 102 – Tetragonal grains (arrows) surrounded by monoclinic and cubic grains in a 7YSZ specimen

The above fractography suggests that the three phases were present as separate grains instead of (for example) as tetragonal precipitates within a cubic matrix, which is the case when quenching is performed from the f phase [46].

4.4.3 POLISHED SURFACES

The primary reasons for producing polished and etched surfaces were to establish the level of porosity in sintered samples and to measure grain size. Figure 103 shows polished and etched surfaces for each composition. Porosity was high and much of it was connected, as was already noted from micrographs of as-pressed surfaces.

Figure 103 – Polished and etched surfaces of a) 7YSZ, b) Yb:7YSZ, c) Ce:7YSZ and d) Nb:7YSZ specimens

4.5 POROSITY, GRAIN SIZE AND BULK DENSITY

Volume percent porosity and average grain size were measured from the micrographs in Figure 103 according to sections 3.10 and 3.11, respectively.

Together with bulk density (section 3.7), the results are given in Table 10.

Table 10 – Bulk density, porosity and grain size

Sample	Bulk Density (g/cm ³)	Porosity (m ³ /m ³)	Average Grain Size (μm)
7YSZ	5.57	10.63%	2.67 ± 0.22
Yb:7YSZ	5.86	14.30%	2.52 ± 0.71
Ce:7YSZ	5.68	7.64%	2.90 ± 0.18
Nb:7YSZ	5.57	15.68%	3.00 ± 0.15

Overall, there was a large amount of porosity which made it clear that sintering had been hindered and complete densification had not been achieved. The high porosity probably originated from low green body densities and the large particle size distributions seen in Figure 77. Both of these would have increased the size of average green interstitials. This would raise the likelihood of there being pores with greater than critical coordination (n_c , Equation 26) and greater than critical size (R_c , Equation 29), such that they are stable and hinder densification (by Equation 30) as well as lower the expected density (Figure 69). Further, maps of elemental distributions (section 4.3) suggest that sintering occurred primarily by mechanisms '1' and '2' in Figure 66, but since only mechanisms '4' and '5' contribute to densification (section 2.7.2.2), this accounts for porosity being largely unchanged by sintering.

A large particulate size distribution was especially present in the mixed Nb:7YSZ powder (Figure 77d), which Table 10 shows to be the composition with the lowest bulk density and highest pore volume. Not all expected trends were observed, however. For example, by further inspection of Figure 77, 7YSZ appears to have the smallest particle size distribution, but it had the identical low density as Nb:7YSZ, and had a higher pore volume than Ce:7YSZ. Also

Yb:7YSZ, which appeared the most successfully sintered in Figure 100, displayed the second highest pore volume.

One contributing factor to these inconsistencies was aspherical powders which would have reduced packing density (according to Figure 61) in a largely unpredictable way. Also contributing to density is phase content. For example, m phase is the least dense in Table 9, and most prevalent in Nb:7YSZ.

In some small regions there was very low porosity, and a network of grain boundaries was visible. These regions probably originated either as large powder particulates (naturally composed of many grains), or as agglomerates of smaller particles. Meanwhile, other regions contained large resin-free pores. Magnified views of both artefacts are shown in Figure 104. Note that the pore shown is highly coordinated and comparable to the stable pores in Figure 70. It is perhaps beyond critical coordination, so did not shrink during sintering.

Figure 104 – Magnified views of a) open porosity (in Yb:7YSZ) and b) a region of enhanced local sintering (in Nb:7YSZ)

Resin-free pores like that shown above are easily distinguished in Figure 103 by their bright perimeters caused by the etching process, which rounded the pore edges and led to an amplified signal in the SEM. They could be a network of disconnected (closed) porosity, or the result of grain pull-out during polishing. Regardless, they are of interest since most pores were filled with resin.

Explicit quantitative testing for connected porosity was not conducted, but connected behaviour was noted on several occasions. This included during extended periods of water immersion (while measuring bulk density), on studying the three-dimensional pore structure on as-pressed surfaces, and on inspection of Figure 103 which shows a presence of resin inside nearly all pores. The Ce:7YSZ composition contained the most that were resin-free.

Ce^{4+} was not the smallest co-dopant cation (Table 5), so the sinterability of Ce:7YSZ was not expected to be the best. But on that note, closed porosity is a sign of progression through the stages of sintering (section 2.7.2.2), so more of it indicates better sinterability. Therefore, it is not likely that the resin-free pores in Figure 103 represent closed porosity. It is more likely that they are pulled-out grains, occurring most easily with a high t phase content of which Ce:7YSZ exhibits the second highest (after Yb:7YSZ). More t phase would allow more $t \rightarrow m$ transformations during polishing, but Ce:7YSZ, with a higher m phase content than Yb:7YSZ, had more microcracks to support grain pull-out.

4.6 MECHANICAL PROPERTIES

Nano-indentation provided Vicker's hardness and Young's modulus values for air cooled specimens of each composition. 7YSZ specimens cooled by all

three schemes (fan, air and furnace) were also tested to reveal trends associated with cooling rate. Averaged results are tabulated in Table 11. The table also includes corrected Young's moduli (see section 3.14), co-dopant radii, and wt% retained m and t phases. Further, to illustrate the force-penetration curves from which hardness and Young's modulus values were calculated, those for variably cooled 7YSZ appear in Figure 105.

Table 11 – Maximum values for hardness and Young's modulus

Composition	Cooling Method	Avg. Hardness (Vicker's)	Avg. Modulus* (GPa)	Corrected Modulus† (GPa)	Co-dopant Radius (Å)	Phase Content (wt%)‡	
						m	t
7YSZ	Fan	980.75	158.17	195.71	0.84 (Zr)	39.1%	14.0%
7YSZ	Air	726.87	153.26	189.63	0.84 (Zr)	40.9%	13.2%
7YSZ	Furnace	957.65	152.94	189.24	0.84 (Zr)	42.1%	12.3%
Yb:7YSZ	Air	1120.53	132.63	177.62	0.985	6.9%	22.7%
Ce:7YSZ	Air	1079.23	167.78	195.08	0.97	21.0%	25.5%
Nb:7YSZ	Air	507.67	118.40	163.49	0.74	76.5%	12.1%

* Young's modulus, E

† By Equation 49, using porosity from Table 10. For investigation of trends only.

‡ From Table 9

Figure 105 – Force-penetration curves for variably cooled 7YSZ samples (the curves shown correspond to maximum hardness values measured)

4.6.1 EXPECTED EFFECT OF CO-DOPANT PROPERTIES

Co-dopant radii are included in Table 11 because co-dopants with larger ionic radii have been documented to reduce Young's modulus. This is because they increase lattice parameters and interatomic distances, and therefore cause lower bond strengths. Oxygen vacancies, on the other hand, reduce lattice parameters (section 2.2.1.1) and have shown to increase Young's modulus [128, 129]. Therefore, co-dopant trivalence should increase E , and pentavalence should decrease it.

4.6.2 EXPECTED EFFECT OF RETAINED PHASES

Also included in Table 11 are the amounts of m and t phases in the indented samples. Higher m-ZrO₂ content should reduce Young's modulus since, as discussed in section 4.4.2, fracture is aided by microcracks at grain boundaries produced as a result of $t \rightarrow m$ transformations. On the other hand, due to the effects of transformation toughening and ferroelasticity (sections 2.4 and 2.4.2), more t-ZrO₂ should increase E .

4.6.3 OBSERVED EFFECT OF POROSITY

As mentioned in section 3.14, the high degree of porosity in samples caused solid material to crack and collapse under the applied force during indentation. Evidence of this was seen in force-penetration curves as flat regions where depth increased substantially without resistance, and so without a corresponding increase in the measured force applied. Two example curves like this appear in Figure 106, one displaying a moderate amount of cracking and

collapse occurring several times (sample 1), and the other displaying a single extensive event (sample 2). Smaller but more numerous occurrences likely occurred erratically during all indentations of all samples.

Figure 106 – Sample force-penetration curves (both Yb:7YSZ, furnace cooled) showing moderate (sample 1) and extensive (sample 2) cracking and collapse (indicated by arrows) of indented material

4.6.4 NET PROPERTIES OF COMPOSITIONS

With the substantial effects of porosity, neither hardness nor Young's modulus values were considered accurate. Corrected moduli were considered equally inaccurate, but with the correction for porosity, expected trends were revealed. They are now discussed according to composition.

4.6.4.1 7YSZ

The 7YSZ composition was the only one selected to have all three cooling schemes characterized by nano-indentation. Since only phase content differed

between the three measured samples, this allowed an investigation into the trends associated uniquely with phase content.

In Table 11 for 7YSZ, increasing m phase content occurs in the order of fan, air and furnace cooling. As expected (section 4.6.2), Young's modulus is seen to decrease accordingly. Hardness, however, does not vary expectedly.

4.6.4.2 Yb:7YSZ

Compared to air cooled 7YSZ, air cooled Yb:7YSZ has a far lower presence of m-ZrO₂ which should act to increase its relative mechanical properties (section 4.6.2). However, there are also ionic effects of Yb³⁺ to consider. Ytterbium is oversized relative to zirconium, which should lower E due to increased bond lengths and decreased bond strengths (section 4.6.1). It is also trivalent and introduces oxygen vacancies, which raises E . According to the nano-indentation results in Table 11, the net effect is a reduced Young's modulus and significantly improved hardness.

4.6.4.3 Ce:7YSZ

Without imposing new O²⁻ vacancies, the possible contributions of CeO₂ in 7YSZ are a reduction in E due to the Ce⁴⁺ cation being oversized, and an increase in E since air cooled Ce:7YSZ contains only about half as much m-ZrO₂ as air cooled 7YSZ. Nano-indentation results indicate that the two contributions roughly balance, with a small increase in both Young's modulus and hardness.

4.6.4.4 Nb:7YSZ

Nb^{5+} is pentavalent, undersized, and Nb:7YSZ results in nearly twice as much m phase as the equivalently cooled 7YSZ. Influences to E are thus a reduction, improvement, and dramatic reduction, respectively. The nano-indentation data in Table 11 confirms that the net effect on Young's modulus is a significant reduction, and the same is observed for hardness as well. These final observations verify that the expected trends of mechanical properties can be extracted from even very porous ceramics when using nano-indentation, and the final conclusions of this thesis reflect that.

5 CONCLUSIONS

In support of the objectives of this research (section 1.4), the following conclusions were drawn from experimental results.

1. To impose variations of stabilizing mechanisms, co-dopant cations Yb^{3+} , Ce^{4+} and Nb^{5+} were added to 7YSZ and expected behaviours were observed. Trivalent and oversized Yb^{3+} produced oxygen vacancies and dilated the ZrO_2 lattice in compression, preferentially stabilizing the cubic phase overall. Tetravalent and oversized Ce^{4+} induced compressive dilative strains on the ZrO_2 lattice and lowered the $t \rightarrow m$ transition temperature, preferentially stabilizing the tetragonal phase. Pentavalent and undersized Nb^{5+} annihilated oxygen vacancies and introduced large tensile lattice strains, with a net effect which destabilized the cubic phase and produced large amounts of monoclinic.
2. The stabilizing mechanisms investigated that were most sensitive to cooling rate were compressive (dilative) and tensile lattice deformations. No appreciable difference in cooling rate sensitivity could be identified between these two types of lattice strains. The mechanism of oxygen vacancies showed to be minimally affected by cooling rate.
3. Additionally, oxygen vacancies are far more effective than lattice distortions at stabilizing high temperature phases. A crude estimate based on results obtained with Ce^{4+} is that they are roughly four times more effective.

4. Doping 7YSZ with tetravalent Ce^{4+} produces a zirconia alloy which is highly cooling rate sensitive. This is due to the production of oxygen vacancies at high temperatures, which become metastable on cooling and are annihilated if cooling rate was slow.
5. Slower cooling schemes result in more monoclinic formation, so are therefore not ideal in general.
6. Large particulate size distributions in mixed powders, combined with aspherical particulate shapes, resulted in high amounts of sintered porosity in the current experiments. Further, as indicated by the distribution of elements in a polished sample, sintering occurred primarily by mass transport mechanisms along free surfaces, which do not contribute to densification.
7. From observation of fracture surfaces, crack paths are intergranular for f and t phases and transgranular for m phase.
8. The effect of co-dopants on hardness and Young's modulus was not conclusive due to the interfering effects of porosity. Numerical manipulation to account for porosity revealed expected trends, however measured values remained inaccurate.

6 RECOMMENDED FUTURE WORK

The presented experimental procedures and results reveal a number of directions for continued research, and also ways in which it can be improved.

1. Continue the current investigations by conducting differential scanning calorimetry (DSC) to obtain $t \rightarrow m$ transformation temperatures for variably cooled and co-doped compositions. Additionally, make new samples with a range of co-dopant concentrations to establish the effect on the $t \rightarrow m$ start temperature.
2. Analyze the Nb:7YSZ composition with EDS to confirm that segregation occurred in that mixture.
3. Confirm the results for Nb:7YSZ (repeat experiments for this composition) so that effects of furnace contamination can be ruled out.
4. Perform a wet analysis to confirm that the target mixtures of 7YSZ and co-dopants were attained. The imperfect mixing of powders is one possible source of discrepancy, but contamination might have also resulted from ball milling, pressing, or sintering on Al_2O_3 holders. Mixtures with discrepancies may have contributed to unexpected results in the current research such as the presence f- ZrO_2 in the Nb:7YSZ composition.
5. Conduct explicit tests for connected and disconnected porosity. For example, mercury immersion can measure total porosity with little error, while extended immersion within a highly wetting chemical (such as

propylene carbonate) can reveal connected porosity. Disconnected (closed) porosity is simply the difference.

6. Manufacture sintered disks with lower porosity, and repeat the nano-indentations performed in the present study. With lower porosity, the same trends should appear but with accurate values. If penetration curves indicate that material collapse occurs, conduct more measurements (~20) for improved accuracy.
7. In subsequent work involving cold pressed and sintered samples, ceramic powders should be separately milled prior to mixing. Large initial size differences, if combined, will prevent the achievement of a uniform powder size during milling, as demonstrated by the current work. A uniform (or controlled) distribution of very fine particles will maximize densification upon sintering. It will also minimize the segregation of co-dopants at grain boundaries.
8. Perform thermal conductivity measurements on this work's prepared samples to establish the effects of co-dopants. Through-volume (lattice) thermal conductivity is expected to reduce with the addition of large and heavy dopant cations [81]. Since the ionic radii of cations utilized here are in the order of Nb^{5+} (0.74 Å) < Ce^{4+} (0.97 Å) < Yb^{3+} (0.985 Å) < Y^{3+} (1.019 Å), expected thermal conductivities of co-doped compositions are $\text{Nb:7YSZ} > \text{Ce:7YSZ} > \text{Yb:7YSZ}$. However, this assumes equal (and uniformly distributed) co-dopant cation concentrations in each composition.

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APPENDIX A: MIXTURE CALCULATIONS

The following shows the calculation of oxide molar amounts in each of the mixtures used in the presented experiments (Yb:7YSZ, Ce:7YSZ and Nb:7YSZ).

For Yb:7YSZ and Ce:7YSZ

- Mixture: $x \cdot (\text{YbO}_{1.5} \text{ or } \text{CeO}_2) + y \cdot \text{Y}_2\text{O}_3 + z \cdot \text{ZrO}_2$ (1)

- Knowns: $x + y + z = 1$ (2)

$$x = 0.0500 \text{ (chosen to be this)} \quad (3)$$

$$\frac{y}{y+z} = 0.0395 \text{ (standard 7 wt\% } \text{Y}_2\text{O}_3 \text{ in } \text{ZrO}_2\text{)} \quad (4)$$

- (2) + (3): $z = 0.9500 - y$ (5)

- (4) + (5): $z = \frac{y}{0.0395} - y = 0.9500 - y$

$$y = 0.9500 \cdot (0.0395) = 0.0375 \quad (6)$$

- (5) + (6): $z = 0.9125$ (7)

- (1) + (3) + (6) + (7), in mol%:

$$5 \cdot (\text{YbO}_{1.5} \text{ or } \text{CeO}_2) + 3.75 \cdot \text{Y}_2\text{O}_3 + 91.25 \cdot \text{ZrO}_2$$

For Nb:7YSZ

- Mixture: $x \cdot \text{Nb}_2\text{O}_5 + y \cdot \text{Y}_2\text{O}_3 + z \cdot \text{ZrO}_2$ (1)

- Knowns: $x + y + z = 1$ (2)

$$x = y \text{ (chosen to be this)} \quad (3)$$

$$\frac{y}{y + z} = 0.0395 \text{ (standard 7 wt\% Y}_2\text{O}_3 \text{ in ZrO}_2\text{)} \quad (4)$$

- (2) + (3): $z = 1 - 2x$ (5)

- (4) + (5): $z = 1 - 2x = \frac{y}{0.0395} - y$ (6)

- (3) + (6): $x = \frac{0.0395}{1.0395} = 0.0380$ (7)

- (5) + (7): $z = 0.9241$ (8)

- (1) + (3) + (7) + (8), in mol%:

APPENDIX B: DETAILED COMPOSITIONS

7YSZ		Molar Concentrations			Concentrations by Weight		
Element	Molar	mol	mol%	mol%	g/mol	g	wt%
Zr	0.9605	0.9605	31.20%	92.41%	91.2240	87.6243	68.85%
O		1.9211	62.39%	-	15.9994	30.7361	24.15%
Y	0.0395	0.0789	2.56%	7.59%	88.9059	7.0164	5.51%
O		0.1184	3.84%	-	15.9994	1.8940	1.49%
Total (all)		3.0789	100.00%	100.00%		127.2709	100.00%
Total (cation)		1.0395				94.6408	100.00%

5CeO ₂ + 7YSZ		Absolute mol%'s			Absolute wt%'s		
Element	Molar	mol	Element mol%	Compound mol%	At. Wt. g/mol	Weight g	Element wt%
Ce	0.0500	0.0500	1.63%	5.00%	140.1160	7.0058	5.41%
O		0.1000	3.25%	-	15.9994	1.5999	1.24%
Zr	0.9125	0.9125	29.68%	91.25%	91.2240	83.2431	64.27%
O		1.8250	59.35%	-	15.9994	29.1993	22.55%
Y	0.0375	0.0750	2.44%	3.75%	88.9059	6.6556	5.15%
O		0.1125	3.66%	-	15.9994	1.7993	1.39%
Total (all)		3.0750	100.00%	100.00%		129.5131	100.00%
Total (cation)		1.0375				96.9145	100.00%

5YbO _{1.5} + 7YSZ									
Element	Molar Mixture	Stoich- iometry	Absolute mol%'s			At. Wt. g/mol	Weight g	Absolute wt%'s	
			mol	Element mol%	Compound mol%	Cation mol%		Element wt%	Compound wt%
Yb	0.0500	1	0.0500	1.64%	5.00%	4.82%	173.0400	6.62%	7.53%
O		1.5	0.0750	2.46%		-	15.9994	0.92%	
Zr	0.9125	1	0.9125	29.92%	91.25%	87.95%	91.2240	63.66%	84.46%
O		2	1.8250	59.84%		-	15.9994	22.33%	
Y	0.0375	2	0.0750	2.46%	3.75%	7.23%	88.9059	5.10%	6.47%
O		3	0.1125	3.69%		-	15.9994	1.38%	
Total (all)			3.0500	100.00%	100.00%		130.7593	100.00%	100.00%
Total (cation)			1.0375			100.00%	98.5607		100.00%

3.8Nb ₂ O ₅ + 7YSZ									
Element	Molar Mixture	Stoich- iometry	Absolute mol%'s			At. Wt. g/mol	Weight g	Absolute wt%'s	
			mol	Element mol%	Compound mol%	Cation mol%		Element wt%	Compound wt%
Nb	0.0380	2	0.0759	2.35%	3.80%	7.06%	92.9064	5.32%	7.61%
O		5	0.1898	5.88%		-	15.9994	2.29%	
Zr	0.9241	1	0.9241	28.63%	92.41%	85.89%	91.2240	63.61%	85.93%
O		2	1.8482	57.26%		-	15.9994	22.31%	
Y	0.0380	2	0.0759	2.35%	3.80%	7.06%	88.9059	5.09%	6.88%
O		3	0.1139	3.53%		-	15.9994	1.37%	
Total (all)			3.2278	100.00%	100.00%		132.5301	100.00%	100.00%
Total (cation)			1.0759			100.00%	98.1018		100.00%

APPENDIX C: DIE SET DRAWINGS

UNITS: MM	
SCALE: 2:1	PG 1 OF 1
DATE: APRIL 28, 2009	
TITLE: INSERT	
MATERIAL: 17-4 PH SS	DRAWN BY: J. PETITJEAN