

## TABLE OF CONTENTS

	Page
TABLE OF CONTENTS.....	i
LIST OF TABLES.....	ii
LIST OF FIGURES.....	iv
LIST OF ABBREVIATION.....	xvi
INTRODUCTION.....	1
LITERATURE REVIEWS.....	4
Spinel.....	4
Spinel preparation.....	14
MATERIALS AND METHODS.....	37
Materials.....	37
Methods.....	39
RESULTS AND DISCUSSION.....	52
CONCLUSION.....	97
LITERATURE CITED.....	99
APPENDICES.....	105

## LIST OF TABLES

Table		Page
1	Important parameters in the various steps of a sol-gel process.....	32
2	The calcined conditions of nickel aluminate precursor.....	41
3	The pH values of solvents on the preparation of NiAl <sub>2</sub> O <sub>4</sub> spinel via sol-gel process.....	46
4	The all conditions studied for sol-gel formation.....	47
5	The color and physical appearances of nickel aluminate precursors...	54
6	<sup>1</sup> H-NMR peak positions and assignments of nickel aluminate spinel precursors.....	57
7	<sup>13</sup> C-NMR peak positions and assignments of nickel aluminate spinel precursors.....	58
8	Percentage weight loss and ceramic yield of the nickel aluminate precursors.....	61
9	FTIR peak positions and assignments of nickel aluminate spinel precursors.....	62
10	X-ray diffraction analysis of product phases calcined at different temperature with a fixed 5 h heating period.....	65
11	X-ray diffraction analysis of product phases calcined at different heating period with a fixed 1000 <sup>o</sup> C calcination temperature.....	66
12	The BET surface areas, pore volume and pore size of NiAl <sub>2</sub> O <sub>4</sub> spinels which directly obtained from nickel aluminate precursor.....	68
13	Gelation time observed at room temperature and 60 °C for SPNO precursor dissolved in ethanol with various concentrations and pH values.....	72

## LIST OF TABLES (continued)

Table		Page
14	Gelation time observed at room temperature and 60 °C for SPNO precursor dissolved in n-propanol with various concentrations and pH values.....	73
15	Gelation time observed at room temperature and 60 °C for SPNO precursor dissolved in i-propanol with various concentrations and pH values.....	74
16	Gelation time observed at room temperature and 60 °C for SPAc precursor dissolved in ethanol with various concentrations and pH values.....	76
17	Gelation time observed at room temperature and 60 °C for SPAc precursor dissolved in n-propanol with various concentrations and pH values.....	77
18	Gelation time observed at room temperature and 60 °C for SPAc precursor dissolved in i-propanol with various concentrations and pH values.....	78
19	The BET surface area, pore volume and pore size of NiAl <sub>2</sub> O <sub>4</sub> spinels obtained by direct calcinations of one pot synthesis product (nickel aluminate precursor) and sol-gel process.....	96

## LIST OF FIGURES

Figure		Page
1	Two octants of the spinel unit cell.....	5
2	Orientations of the B-site cation <i>d</i> orbitals with respect to the spinel structure .....	6
3	Part of the unit cell of the spinel structure showing the occupied lattice sites. Of the eight “cubelets” shown, the upper left front cubelet shows an occupied tetrahedral cation site, whereas the other seven cubelets have some occupied octrahedral cation site.....	9
4	Schematic diagram showing the various steps of a sol-gel process.....	20
5	Schematic diagram showing the variation of hydrolysis and condensation rates of tetraethylorthosilicate with pH, and the effect of relative rate on gel structure.....	23
6	Polymer growth and gel formation in acid-catalyzed systems (polymeric gel).....	24
7	Polymer growth and gel formation in base-catalyzed systems (colloidal gel).....	25
8	Apparatus set up for preparation of nickel aluminate precursor by the One Pot Synthesis.....	39
9	Block diagram of nickel aluminate spinel powders prepared via sol-gel method.....	43
10	Nickel aluminate precursors ( $m/z = 554$ ).....	55
11	The degradation of the nickel aluminate spinel precursor.....	56
12	X-ray diffraction patterns of the powder obtained from 1000 °C (5 h) pyrolysis of gel occurring at room temperature for SPNO precursor in 32.0 % (w/v) ethanolic solution with various pH values; (a) 6.0, (b) 7.0, (c) 8.0, (d) 9.0 and (e) 10.0.....	80

## LIST OF FIGURES (continued)

Figure		Page
13	X-ray diffraction pattern of the powder obtained from 1000 °C (5 h) pyrolysis of gel occurring at room temperature, pH 9.0, in the ethanolic solution of SPNO precursor with different concentrations and gelation times; (a) 24.0 %(w/v), 2.5 h (b) 28.0 %(w/v), 864 h and (c) 32.0 %(w/v), 960 h.....	81
14	X-ray diffraction pattern of the powder obtained from 1000 °C (5 h) pyrolysis of gel occurring at room temperature, pH 7.0, in the i-propanolic solution of SPAc precursor with different concentrations; (a) 20.0 %(w/v), (b) 24.0 %(w/v), (c) 28.0 %(w/v) and (d) 32.0 %(w/v).....	83
15	XRD patterns of NiAl <sub>2</sub> O <sub>4</sub> spinels prepared by different preparation methods and heat at 1000 °C for 5 h in air: (a) coprecipitation, (b) directly calcined SPNO precursor, (c) directly calcined SPAc precursor, (d) SPNO sol-gel and (e) SPAc sol-gel.....	84
16	SEM micrographs of the NiAl <sub>2</sub> O <sub>4</sub> powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 6.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	86
17	SEM micrographs of the NiAl <sub>2</sub> O <sub>4</sub> powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 7.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	87
18	SEM micrographs of the NiAl <sub>2</sub> O <sub>4</sub> powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 8.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	88

## LIST OF FIGURES (continued)

Figure		Page
19	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 9.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	89
20	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 10.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	90
21	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at room temperature in the system of 16.0 % (w/v) in i-propanolic solution of SPAC precursor with pH 8.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	92
22	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at 60 °C in the system of 20.0 % (w/v) in i-propanolic solution of SPAC precursor with pH 8.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	93
23	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at 60 °C in the system of 24.0 % (w/v) in i-propanolic solution of SPAC precursor with pH 8.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	94
 <b>Appendix Figure</b>		
A1	Thermogram of aluminium hydroxide hydrate.....	106
A2	Thermogram of nickel(II) hydroxide.....	107

## LIST OF FIGURES (continued)

Appendix Figure		Page
A3	Thermogram of dried solid SPNO.....	109
A4	Thermogram of dried solid SPCI.....	109
A5	Thermogram of crude SPOH.....	110
A6	Thermogram of crude SPAc.....	111
B1	Mass spectrum of dried solid SPNO.....	112
B2	Mass spectrum of dried solid SPCI.....	112
B3	Mass spectrum of crude SPOH.....	113
B4	Mass spectrum of crude SPAc.....	113
C1	<sup>1</sup> H-NMR spectrum of dried solid SPNO.....	114
C2	<sup>1</sup> H-NMR spectrum of dried solid SPCI.....	114
C3	<sup>1</sup> H-NMR spectrum of crude SPOH.....	115
C4	<sup>1</sup> H-NMR spectrum of crude SPAc.....	115
C5	<sup>13</sup> C-NMR spectrum of dried solid SPNO.....	116
C6	<sup>13</sup> C-NMR spectrum of dried solid SPCI.....	116
C7	<sup>13</sup> C-NMR spectrum of crude SPOH.....	117
C8	<sup>13</sup> C-NMR spectrum of crude SPAc.....	117
C9	DEPT spectrum of dried solid SPNO.....	118
C10	DEPT spectrum of dried solid SPCI.....	118
C11	DEPT spectrum of crude SPOH.....	119
C12	DEPT spectrum of crude SPAc.....	119
D1	FTIR spectrum of dried solid SPNO.....	120
D2	FTIR spectrum of dried solid SPCI.....	120
D3	Representative FTIR spectra of SPNO precursor calcined at different temperatures (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	121

## LIST OF FIGURES (continued)

Appendix Figure	Page
D4	122
Representative FTIR spectra of SPCl precursor calcined at different temperatures (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	
D5	123
Representative FTIR spectra of SPOH precursor calcined at different temperatures (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	
D6	124
Representative FTIR spectra of SPAC precursor calcined at different temperatures (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	
E1	125
Major peak and <i>hkl</i> reflection of reference NiAl <sub>2</sub> O <sub>4</sub> spinel (JCPDS file No. 10-0339).....	
E2	126
XRD patterns of spinel precursor (SPNO) at increasing calcination temperature (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	
E3	127
XRD patterns of spinel precursor (SPCl) at increasing calcination temperature (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	
E4	128
XRD patterns of spinel precursor (SPOH) at increasing calcination temperature (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	
E5	129
XRD patterns of spinel precursor (SPAC) at increasing calcination temperature (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C (f) 1000°C.....	
E6	130
XRD spectra of products calcined (SPNO) at different time (a) 2 h, (b) 3 h, (c) 4 h, (d) 5 h.....	

## LIST OF FIGURES (continued)

Appendix Figure	Page	
E7	XRD spectra of products calcined (SPCl) at different time (a) 2 h, (b) 3 h, (c) 4 h, (d) 5 h.....	130
E8	XRD spectra of products calcined (SPOH) at different time (a) 2 h, (b) 3 h, (c) 4 h, (d) 5 h.....	131
E9	XRD spectra of products calcined (SPAc) at different time (a) 2 h, (b) 3 h, (c) 4 h, (d) 5 h.....	131
E10	(a) Powder diffraction patterns of the SPNO pyrolyzed at 1000°C for 5 h. (b) Powder diffraction patterns of the SPNO pyrolyzed at 500°C for 5 h and held at 1000°C for 5 h.....	132
E11	(a) Powder diffraction patterns of the SPCl pyrolyzed at 1000°C for 5 h. (b) Powder diffraction patterns of the SPCl pyrolyzed at 500°C for 5 h and held at 1000°C for 5 h.....	133
E12	(a) Powder diffraction patterns of the SPOH pyrolyzed at 1000°C for 5 h. (b) Powder diffraction patterns of the SPOH pyrolyzed at 500°C for 5 h and held at 1000°C for 5 h.....	134
E13	(a) Powder diffraction patterns of the SPAc pyrolyzed at 1000°C for 5 h. (b) Powder diffraction patterns of the SPAc pyrolyzed at 500°C for 5 h and held at 1000°C for 5 h.....	135
E14	X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the ethanolic solution of SPNO precursor, pH 6.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....	136

## LIST OF FIGURES (continued)

Appendix Figure	Page
E15	137
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the ethanolic solution of SPNO precursor, pH 7.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E16	138
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the ethanolic solution of SPNO precursor, pH 8.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E17	139
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the ethanolic solution of SPNO precursor, pH 9.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E18	140
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at 60°C in the ethanolic solution of SPNO precursor, pH 9.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E19	141
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the ethanolic solution of SPNO precursor, pH 10.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	

## LIST OF FIGURES (continued)

Appendix Figure	Page
E20	142
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the n-propanolic solution of SPNO precursor, pH 9.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E21	143
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at 60°C in the n-propanolic solution of SPNO precursor, pH 9.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E22	144
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at 60°C in the ethanolic solution of SPAc precursor, pH 7.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E23	145
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the n-propanolic solution of SPAc precursor, pH 7.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E24	146
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at 60°C in the n-propanolic solution of SPAc precursor, pH 7.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	

## LIST OF FIGURES (continued)

Appendix Figure	Page
E25	147
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the i-propanolic solution of SPAc precursor, pH 7.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E26	148
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at room temperature in the i-propanolic solution of SPAc precursor, pH 8.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
E27	149
<p>X-ray diffraction pattern of the powder obtained from pyrolysis of gel occurring at 60°C in the i-propanolic solution of SPAc precursor, pH 8.0 with various calcination conditions: (a) heated at 1000°C for 5 h and (b) heated at 500°C for 5 and held at 1000°C for 5 h.....</p>	
F1	150
<p>SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from SPNO precursor calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	
F2	151
<p>SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from SPCI precursor calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	
F3	152
<p>SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from SPOH precursor calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	

## LIST OF FIGURES (continued)

Appendix Figure	Page	
F4	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from SPAc precursor calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	153
F5	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at room temperature in the system of 20.0 % (w/v) in ethanolic solution of SPNO precursor with pH 10.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	154
F6	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at room temperature in the system of 24.0 % (w/v) in ethanolic solution of SPNO precursor with pH 8.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	155
F7	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at 60°C in the system of 24.0 % (w/v) in ethanolic solution of SPNO precursor with pH 9.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	156
F8	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at room temperature in the system of 24.0 % (w/v) in ethanolic solution of SPNO precursor with pH 10.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	157

## LIST OF FIGURES (continued)

Appendix Figure	Page
<p>F9 SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from gel occurring at room temperature in the system of 28.0 % (w/v) in ethanolic solution of SPNO precursor with pH 7.0 and calcination at different conditions:</p> <p>(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	158
<p>F10 SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from gel occurring at room temperature in the system of 28.0 % (w/v) in ethanolic solution of SPNO precursor with pH 8.0 and calcination at different conditions:</p> <p>(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	159
<p>F11 SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from gel occurring at 60°C in the system of 28.0 % (w/v) in ethanolic solution of SPNO precursor with pH 9.0 and calcination at different conditions:</p> <p>(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	160
<p>F12 SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from gel occurring at room temperature in the system of 28.0 % (w/v) in ethanolic solution of SPNO precursor with pH 10.0 and calcination at different conditions:</p> <p>(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	161
<p>F13 SEM micrographs of the <math>\text{NiAl}_2\text{O}_4</math> powder obtained from gel occurring at room temperature in the system of 28.0 % (w/v) in n-propanolic solution of SPNO precursor with pH 9.0 and calcination at different conditions:</p> <p>(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....</p>	162

## LIST OF FIGURES (continued)

Appendix Figure		Page
F14	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in n-propanolic solution of SPNO precursor with pH 9.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	163
F15	SEM micrographs of the $\text{NiAl}_2\text{O}_4$ powder obtained from gel occurring at 60°C in the system of 32.0 % (w/v) in n-propanolic solution of SPNO precursor with pH 9.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.....	164

## LIST OF ABBREVIATIONS

BET	=	Brunauer-Emmett-Teller
ESI	=	Electrospray Ionization
FTIR	=	Fourier Transform Infrared Spectroscopy
JCPDS	=	Joint Committee on Powder Diffraction Standard
MS	=	Mass Spectrometry
NMR	=	Nuclear Magnetic Resonance Spectroscopy
SEM	=	Scanning Electron Microscopy
TGA	=	Thermogravimetric Analysis
XRD	=	X-Ray Diffraction