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The Effect of Precursor Composition and Sintering Additives on the Formation of β -Sialon from Al, Si and Al_2O_3 Powders

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Abstract

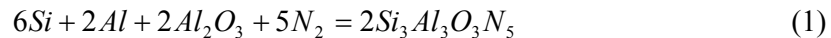
A study was performed to investigate the effect of increasing the Al or Al_2O_3 precursor content, above the stoichiometric amount, on the formation of β -sialon by pressureless sintering of Al, Si and Al_2O_3 powders in flowing nitrogen gas. The effect of adding Y_2O_3 or Fe to the precursor mixture, on the β -sialon formation, was also studied. The phase morphology and yield produced by the various compositions were examined using X-ray diffraction (XRD). Additional Al_2O_3 decreases the β -sialon phase yield and results in a greater amount of Al_2O_3 in the final sintered material. Additional Al improved the conversion to β -sialon up to a maximum of 4 wt% Al beyond which the β -sialon : 15R sialon ratio in the sintered material decreases. 1 wt% Y_2O_3 was determined to be the optimum sintering additive content, as yttrium aluminium garnet (YAG) was found to be present in materials formed from higher Y_2O_3 containing precursors. The presence of Fe in the precursor powder retards the formation of β -sialon by preferentially forming Fe silicides at low temperatures, thus depleting the reaction system of elemental Si, favouring the formation of 15R sialon.

Keywords: A. Sintering; C. Ceramics; D. Sialon; E. Refractories

1. Introduction

The effect of sintering parameters on the formation of β -sialon by pressureless sintering of Al, Si and Al_2O_3 powders in a nitriding atmosphere was previously examined by the present authors [1]. A combination of nitrated pressureless sintering and direct nitridation of metallic Si and Al was found to be capable of producing low-cost sialon products, benefiting from ease of forming and green machining due to the presence of Al and Si particles. However, the materials formed were found to exhibit low density $\sim 70\%$ and full conversion to β -sialon was not achieved even after sintering at 1600°C [1]. The aim of the present work is to examine the effect, on β -sialon formation and density of the final materials, of increasing the amount of Al or Al_2O_3 reactants and including Y_2O_3 or Fe sintering additives in the precursor powder.

An advantage of the reaction sintering process is that with the inclusion of additional reactants the reaction tends towards the formation of β -sialon, as illustrated in Eq. 1.



Simultaneous reaction and sintering control is a key factor in the production of β -sialon and is sensitive to starting material composition, understanding the effects of additional reactants and additives will allow the microstructure and properties of the final β -sialon to be controlled.

It is well known that pressureless sintering of dense Si_3N_4 -based ceramics requires the use of a sintering additive [2-12]. However, the introduction of such an additive gives rise to residual glassy and/or crystalline intergranular phases [2-4] as a result of the formation of a liquid phase during sintering. As a rule, the presence of such secondary

phases has a detrimental effect on the high temperature properties of the ceramic [5]. The most frequently used sintering aids are MgO and Y₂O₃ but other additives such as CaO, Sc₂O₃, CeO₂, BeO and Li₂O have also been investigated [6-8]. Additives have been shown to influence nitridation by interacting with silicon particles and the surface silica layer. Specifically, iron has been shown to help initialise nitridation, either by reacting directly with the silicon to form iron silicides [9], by causing devitrification or the removal of the silicon's silica surface layer [10]. The addition of sintering aids such as yttria have been shown by transmission electron microscopy (TEM) analysis to aid the early stages of nitridation by reacting with the silica surface layer and promoting its removal [11]. The inclusion of these additives generally results in increased rates of nitridation when compared to that of pure silicon, which requires a long sintering time (e.g. ≥72 h at 1400°C) for successful nitridation due to the highly exothermic nature of the reactions between silicon and nitrogen [12].

In the present work, the effect of yttria and iron sintering additives on β-sialon formation from Al, Si and Al₂O₃ powders is examined. The effect of increasing the amount of alumina and aluminium beyond the stoichiometric amount, obtained from Eq.1 and given in Table 1, is also investigated.

2. Experimental

2.1 Powder processing and compact nitriding

β-sialon (Si_{6-z}Al_zO_zN_{8-z}, z = 3) was selected as the target material in the present investigations. The precursor compositions investigated are detailed in Table 1. Each series is based on previous experiments with the inclusion of subsequent compositional variations. The basic composition of the samples, i.e., stoichiometric amount obtained

from Eq. 1, is also detailed in Table 1. The following starting powders were used: Si (98.17%, $d_{50} = 15.83 \mu\text{m}$, Aldrich Chemicals Ltd.), Al (99%, $d_{50} = 36.35 \mu\text{m}$, Aldrich Chemicals Ltd.), Al_2O_3 (99.87%, $d_{50} = 4.65 \mu\text{m}$, Alfa Aesar, UK), Y_2O_3 (99.99%, $d_{50} = 74 \mu\text{m}$, PI-KEM, UK) and N_2 gas (99.998%, white spot grade, BOC, UK).

The starting material mixtures were dry milled for 1 h using zirconia milling media, to produce homogeneous batches. The powder mixtures were weighed then mixed in an alumina mortar, using a few drops of a 5 wt% aqueous solution of polyvinyl alcohol (PVA) as a temporary binder. The powders were then pressed in a cylindrical steel die with an inner diameter of 14 mm using a pressure of 100 MPa. After pressing, green compacts were dried at 150°C overnight and then held at 500°C for 3 h to remove the binders. The dried specimens were then weighed and sintered in a horizontal tube furnace under flowing N_2 introduced at a rate of 6 l/min under 10^5 N/m^2 pressure at 1500°C.

The sintering schedule was kept constant and all sialon precursor mixtures were heated to 1350°C at $5 \text{ }^\circ\text{Cmin}^{-1}$, held for 120 minutes, heated to 1500°C at $2 \text{ }^\circ\text{Cmin}^{-1}$ then held at this temperature for 180 minutes.

2.2 Characterisation

The crystal lattice parameters of β -sialon and the phase composition of the final reaction products were analysed by X-ray diffraction using a Philips PW1120 X-ray diffractometer ($\text{CuK}_{\alpha 1}$, 40 KV, 20 mA). Peak areas were used to estimate semi-quantitatively the evolution of the reaction products.

The bulk density and apparent porosity of each specimen was measured by the Archimedes method. The samples were weighed before and after sintering.

3. Results and discussion

3.1 Effect of additional Al₂O₃

The inclusion of additional Al₂O₃ powder, above the stoichiometric ratio, to the precursor mixture was not found to benefit the nitridation reaction, as the percentage weight gained by the materials during sintering decreased as the Al₂O₃ content in the precursor increased, Fig. 1(a).

This observation was also supported by the XRD results, Fig. 2(a), which shows that increasing amounts of Al₂O₃ in the precursor powder caused the relative amount of β-sialon formed to decrease as the amount of Al₂O₃ in the product material rose.

The bulk density of the product material increased linearly with increasing additional Al₂O₃ included in the precursor, Fig 3(a). This again is consistent with the above observations that more Al₂O₃ in the precursor results in more Al₂O₃ in the product. Al₂O₃ is denser than sialon (3.987 g/cm³ for Al₂O₃ cc 3.077 g/cm³ for β-sialon [13]) and therefore an increase in the Al₂O₃ : β-sialon ratio in the product material would be expected to result in a material with higher bulk density.

The apparent porosity of the sintered materials, also shown in Fig 3(a), shows the reverse behaviour to that of the bulk density, i.e., a linear decrease with increasing Al₂O₃ precursor content. This further supports the observation that more Al₂O₃ in the precursor results in more Al₂O₃ and less sialon in the product material as Al₂O₃ materials densify more easily than sialons. Therefore, a material with more Al₂O₃ present in the starting mixture would be expected to experience greater densification during sintering at 1500°C, resulting in lower porosity.

The nitridation reaction in the present system (Si-Al-Al₂O₃-N₂) depends on species which are able to introduce nitrogen into the structure of the reaction product, such as

[SiN₄] or [AlN₄] allowing sialon materials to form. Silicon and aluminium metal are able to react with nitrogen gas to form [SiN₄] or [AlN₄], however the role of Al₂O₃ in the reaction sequence is to provide Al-O units [1] and additional Al₂O₃ does not result in an increase in the sialon formation.

Therefore, the results clearly indicate that the addition of Al₂O₃, beyond the stoichiometric amount, to the precursor powder mixture, does not improve the nitriding reaction to form sialon and results in an increase in the residual Al₂O₃ phase within the final material.

3.2 Effect of Additional Al

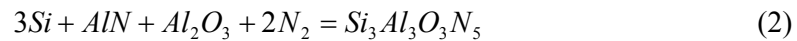
Increasing the amount of aluminium metal within the precursor powder in excess of the stoichiometric amount appeared to benefit the nitridation reaction, as the percentage of weight gained by the materials during sintering increased with increasing aluminium in the precursor powder, up to a maximum of 13.1 wt% total Al (4 wt% above the stoichiometric amount), Fig. 1(b). Above this composition, however, the continued increase in precursor Al content, resulted in a drop in weight gain (approximately 3%) which continued to decrease as the Al precursor content was increased further, suggesting that the nitridation reaction is being retarded by the excess Al.

This change in observed behaviour, when the total Al content exceeds 13.1 wt%, appears to be due to the formation of increasing amounts of 15R polytype sialon at the expense of β -sialon formation, in the product material. The evolution of the crystalline phases detected by XRD plotted in Fig. 2(b), shows that the occurrence of 15R polytype sialon increases with increasing Al precursor content as the amount of β -sialon decreases, when the total Al content exceeds 13.1 wt% (4 wt% above the stoichiometric

amount). The amount of Al_2O_3 in the product material is also observed to increase when the total Al content of the precursor exceeds 13.1 wt%, suggesting that the consumption of Al_2O_3 to form β -sialon, by the reactions shown in equation (1), is inhibited by Al concentrations greater than 4 wt% over the stoichiometric amount.

The Al content is higher in 15R polytype sialon ($SiAl_4O_2N_4$), i.e., Al : Si = 4 : 1, than in β -sialon ($Si_3Al_3O_3N_5$), Al : Si = 1 : 1). Therefore, the increased aluminium content of the starting materials would be expected to favour the formation 15R sialon. It is known from previous study, that Al nitrides to form AlN during the heating stage below $1000^\circ C$, under the current experimental conditions [1]. Therefore, raising the aluminium content in the precursor material will result in an increase in AlN at the reaction temperature, causing the reactant composition to shift towards the AlN edge of the phase diagram promoting the formation of 15R sialon, Fig. 4 [14].

Increasing the AlN : Si ratio will favour the formation of 15R sialon with respect to β -sialon as shown in equations (2) and (3). The stoichiometric ratio of AlN : Si to form 1 mole of β -sialon is 1 : 3 from equation (2), however, the ratio to form 1 mole of 15R sialon from equation (3) is AlN : Si = 1 : 0.38.



The bulk density of the product materials was found to increase linearly with increasing precursor Al content, with a clear shift in behaviour at 13.1 wt% beyond which the bulk density was observed to decrease which is consistent with the previous observations of weight gain behaviour, Fig. 3(b). At compositions of 13.1 wt% and

below the nitrogen increases with precursor Al content as more AlN is present and able to be nitrated further, according to the reactions in equations (2) and (3) to form β -sialon, therefore the bulk density of the product material also increases as more nitrogen is incorporated into the material. At total Al compositions above 13.1 wt% less nitrogen is being incorporated into the material due to the increase in 15R sialon formation and decrease in β -sialon.

The apparent porosity, Fig 3(b), exhibits the inverse behaviour to the bulk density; initially with increasing precursor Al content, there is an increase in matrix phase formation, i.e. β -sialon, as shown in Fig 2(b), which reduces the apparent porosity. However, at Al levels beyond 13.1 wt% there is a decrease in the amount of β -sialon matrix phase formed as 15R sialon becomes increasingly evident in the reaction product.

The results would suggest that 13.1 wt% total Al is the maximum limit to the balanced composition of the sialon precursor as the XRD results, Fig. 2(b), revealed the maximum percentage of β -sialon (83%) in the product material. The reaction product formed from the precursor material with additional 4 wt% Al (13.10 wt% in total) exhibited the highest bulk density (2.195 g/cm³), lowest porosity (28.91%) and highest weight gain (25.35%) over the range of Al compositions examined (additional 2 - 15 wt% Al) suggesting that the inclusion of 4wt% Al in excess of the stoichiometric amount is beneficial to β -sialon formation as well as improving the bulk density and decreasing the apparent porosity.

3.3 Effect of Additional Ytria

The effect of the addition of Y₂O₃ to the precursor material, on β -sialon formation, varied depending on the Y₂O₃ content. Concentrations of 1 wt% Y₂O₃ and below

increased the weight gained by the material during sintering, Fig. 1(c), suggesting that the presence of Y_2O_3 promoted the nitridation reaction. This observation was supported by the XRD results, Fig. 2(c), which indicate that the percentage of β -sialon present within the final material increased with increasing Y_2O_3 content in the precursor up to 1 wt%. An increase in β -sialon in the product material of approximately 4 wt% was observed when comparing the material formed from 1 wt% Y_2O_3 to non Y_2O_3 containing precursors.

As the Y_2O_3 content is increased further however, i.e., Y_2O_3 wt % ≥ 1.5 , the percentage of β -sialon in the sintered material was observed to fall as an additional phase, yttrium aluminium garnet (YAG) ($Y_3Al_5O_{12}$), is found to be present in the material, which increases with increasing Y_2O_3 content.

The most promising results regarding the sialon development with respect to phase evolution (Fig. 2) are the curves obtained when Y_2O_3 is used as a sintering additive. In the presence of Y_2O_3 (Fig. 2(c)), the β -sialon content is clearly higher after sintering than in the case of the other precursors. The β -sialon content has a maximum value (86% in Fig. 2(c)) and the density achieved a maximum of 2.225 g/cm^3 simultaneously at 1 wt% Y_2O_3 content (Fig. 3(c)), suggesting that the addition of 1 wt% Y_2O_3 to the precursor composition is beneficial to promote sintering.

The effectiveness of Y_2O_3 on the sintering behaviour of sialons and agrees with the known role of Y_2O_3 as a sintering aid, i.e., active in removing the silica layer from the silicon powder particles to form a secondary crystalline phase, which participates in the early formation of a liquid phase. The pre-nitridation step (1300°C for 120min) is reported to be accompanied by early reaction of all Y_2O_3 to form yttrium silicate phases [15]. O'Meara [16] reported that the yttrium silicate phases present after the pre-

nitridation step are totally consumed upon full nitridation in favour of a partial Si_3N_4 - SiO_2 - Y_2O_3 - Al_2O_3 liquid phase and YAG formation. Formation of β -Sialon in compositions with lower $\text{Y}_2\text{O}_3 : \text{Al}_2\text{O}_3$ ratios is in agreement with known phase relationships in this system since such compositions are closer to the base of the Jänecke prism and, therefore, to β -sialon [17].

The yttria content, must be balanced to allow maximum nitridation at the lowest temperature to occur but not the formation of too much early liquid, which may tend to close down the pore structure and inhibit nitridation. This is most likely the cause of the decrease in the weight gain (Fig. 1(c)) and the β -sialon content (Fig. 2(c)) with increasing Y_2O_3 content beyond 1 wt% in the precursor powder.

Increasing the Y_2O_3 additive from 0.25 to 1.0 wt% caused the bulk density of the materials to increase, while the apparent porosity decreased, Fig 3(c). 1.0 wt% of Y_2O_3 included in the starting powders produced the highest density (2.225 g/cm^3) and the lowest porosity (25%) of all the Y_2O_3 contents examined (0 – 4 wt%), see Fig.3(c).

The yttrium containing materials possess higher densities (Fig. 3) than all other compositions examined, probably owing to yttrium's role in the formation of a liquid phase at lower temperature as previously discussed.

3.4 Effect of Fe Additions

Adding Fe to the precursor powder reduced the amount of β -sialon and raised the percentage of 15R sialon and residual Al_2O_3 in the product material, Fig. 2(d).

Increasing amounts of Fe exacerbated this effect.

Fig. 3(d) shows that the bulk density passed through a maximum (2.26 g/cm^3) at 0.2 wt% Fe and then decreased, with further increasing Fe content. The apparent porosity

increases from 0.2 to 0.6 wt% Fe and then decreases as greater amounts of Fe are included.

Weight gain during sintering was observed to be less when 0.2 wt% Fe was included in the precursor powder compared with 0 wt% Fe precursors, Fig. 1(d). However, increasing the Fe content further caused the weight gain during nitriding to increase.

Fe is known to facilitate nitridation either by reacting directly with silicon to form iron silicides [15, 16] or by causing devitrification and removal of the silica surface layer on silicon particles [18]. The susceptibility of the silica layer to the effects of iron impurities in the early stages of nitridation have been related to the thickness of the silica layer and iron impurities have been shown to lower the temperature of nitridation [19].

According to the Fe – Si phase diagram [20], a eutectic is formed at 1207°C suggesting that the formation of a liquid phase will occur before the onset of nitriding in the present system, which was found to occur above 1400°C [1]. FeSi₂ is the lowest-melting of the iron silicides and is most likely to form during the reaction-sintering process. This is verified by XRD analyses of samples with ≥ 0.6 wt% Fe, which indicate the presence of trace amounts of silicides (Fig. 5). The small peaks at approximately 17°2 θ and 45°2 θ in Fig. 5 correspond to FeSi₂.

The formation of iron silicides, at temperatures (1207°C) well below the onset of sialon formation reactions at 1400°C, depletes the system of silicon metal which could otherwise be available to participate in sialon formation. This has the effect of altering the chemistry of the system such that the ratio of AlN : Si is increased. Increasing the AlN : Si ratio will favour the formation of 15R sialon with respect to β -sialon as

discussed previously. Therefore, the addition of Fe to the stoichiometric precursor ratio was found to be detrimental to the formation of β -sialon.

4. Conclusion

The present work, to examine the effects of precursor composition and sintering additives on the formation of β -sialon by the pressureless sintering of Al, Si and Al_2O_3 powder in a flowing nitrogen atmosphere at 1500°C , determined that increasing the amount of Al_2O_3 powder in the precursor beyond the stoichiometric amount, did not benefit the formation of β -sialon and resulted in an increase in residual Al_2O_3 in the product material suggesting that additional Al_2O_3 does not participate in the nitridation reaction.

Increasing the amount of Al in the precursor powder beyond the stoichiometric amount promoted the formation of β -sialon in the product material with a maximum occurring when the total Al content was 13.1 wt% (4 wt% above the stoichiometric amount). Beyond this Al concentration the formation of 15R polytype sialon became more pronounced at the expense of β -sialon. This is proposed to be due to the increase in AlN : Si ratio with increasing Al content in the starting material.

The addition of Y_2O_3 to the precursor powder mixture (which included the stoichiometric amounts + 4 wt% additional Al) promotes the formation of β -sialon and improves the density of the product material, by forming liquid phases which promote diffusion, with a maximum occurring with an Y_2O_3 concentration of 1 wt%. Further increases in the Y_2O_3 content resulted in the formation of yttrium aluminium garnet (YAG) within the product material.

The addition of Fe to the precursor mixture (which included the stoichiometric amounts + 4 wt% additional Al) was found to be detrimental to the formation of β -sialon and promoted the formation of 15R polytype sialon, resulting in a reduction of the β -sialon : 15R sialon ratio in the final material. This effect is proposed to be due to the formation of iron silicides at temperatures (1207°C) well below the onset of nitridation (1400°C), which depletes the system of silicon and raises the AlN : Si ratio which favours the formation of 15R sialon.

The reaction to form β -sialon did not reach completion with any of the compositions studied and residual Al₂O₃ and silicon were present in all materials produced. 15R sialon was always found to be present when β -sialon formed.

The lowest apparent porosity (25%) and the highest bulk density (2.225g/cm³) was achieved when 1 wt% Y₂O₃ and an additional 4 wt% Al were included in the precursor powder.

The optimal precursor composition, from the present work, for forming β -sialon by pressurelessly sintering Al, Si and Al₂O₃ powders in a flowing nitrogen atmosphere at 1500°C, based on the β -sialon : 15R sialon ratio in the product material, bulk density and apparent porosity was found to be; the stoichiometric composition (12.66 wt% Al, 39.52 wt % Si, 47.82 wt % Al₂O₃) plus the addition of 1 wt% Y₂O₃ and an additional 4 wt% Al.

Acknowledgements

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[20] V. Raghavan, Phase diagrams of ternary iron alloys. Part 5, Ternary systems containing iron and oxygen. The Indian Institute of Metals, Calcutta. 1989, Fig. 36.1.

Figure Captions

Fig. 1 Weight gain during sintering vs. (a) Al_2O_3 , (b) Al, (c) Y_2O_3 and (d) Fe content

Fig. 2 Phase evolution of sintered samples vs. (a) Al_2O_3 , (b) Al, (c) Y_2O_3 and (d) Fe content

Fig. 3 Density & porosity vs. (a) Al_2O_3 , (b) Al, (c) Y_2O_3 and (d) Fe content

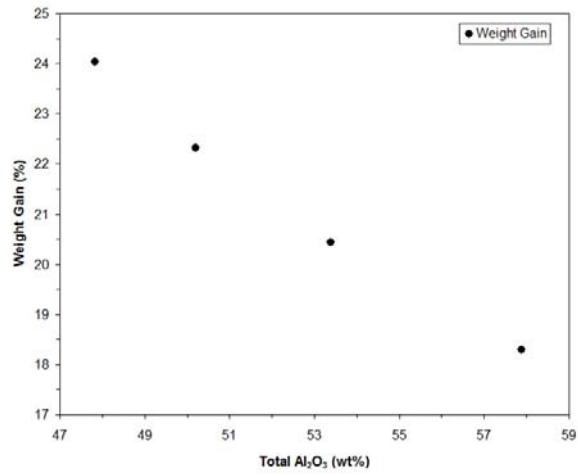
Fig. 4 Si-Al-O-N system phase diagram at 1400°C [14]

Fig. 5 XRD pattern of 1.0 wt% Fe additive sample (Arrows at approx. 17 and $45^\circ 2\theta$ correspond to FeSi_2 , arrow at approx. $53^\circ 2\theta$ corresponds to Fe_3Si)

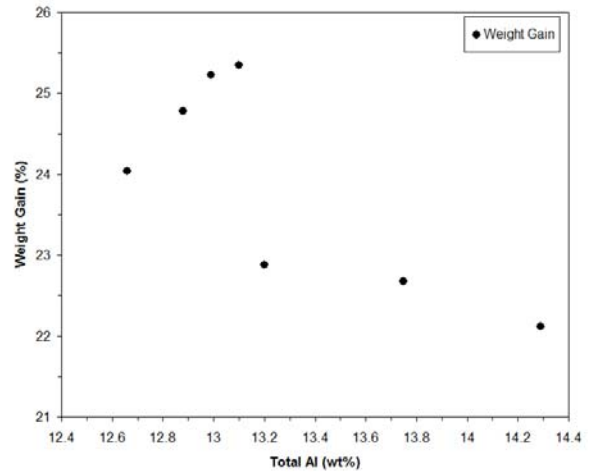
Table 1

Precursor compositions examined

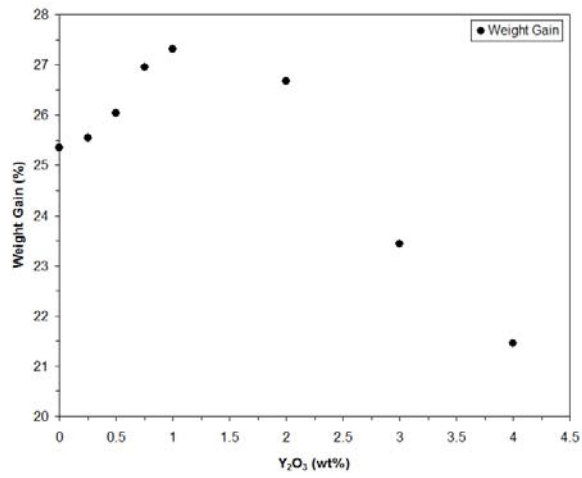
Series		Composition (wt%)				
		Si	Al	Al ₂ O ₃	Y ₂ O ₃	Fe
Basic Composition		39.52	12.66	47.82		
Additional Al ₂ O ₃	10	37.72	12.08	50.20		
	25	35.30	11.31	53.39		
	50	31.89	10.22	57.89		
Additional Al	2	39.42	12.88	47.70		
	3	39.37	12.99	47.64		
	4	39.32	13.10	47.58		
	5	39.27	13.21	47.52		
	10	39.03	13.75	47.22		
	15	38.78	14.29	46.93		
Y ₂ O ₃	0.25	39.22	13.07	47.46	0.25	
	0.50	39.12	13.03	47.34	0.50	
Additive	0.75	39.03	13.00	47.22	0.75	
	1	38.93	12.97	47.10	1.00	
(4 wt% Al Additional)	2	38.53	12.84	46.63	2.00	
	3	38.14	12.71	46.15	3.00	
	4	37.75	12.58	45.68	4.00	
Fe	0.2	39.24	13.07	47.48		0.2
	0.4	39.16	13.05	47.39		0.4
Additive	0.6	39.08	13.02	47.29		0.6
	0.8	39.01	13.00	47.20		0.8
	1.0	38.93	12.97	47.10		1.0



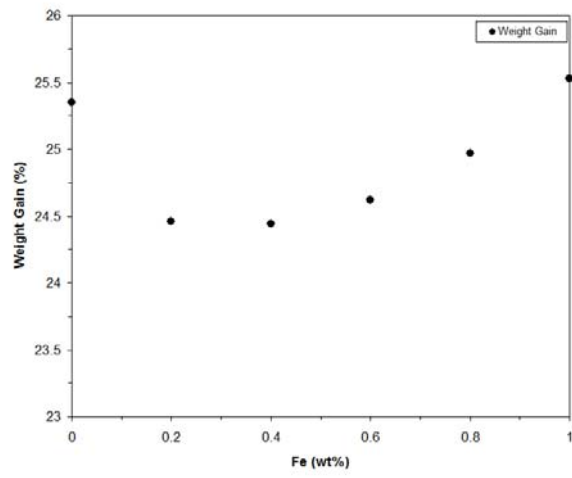
(a)



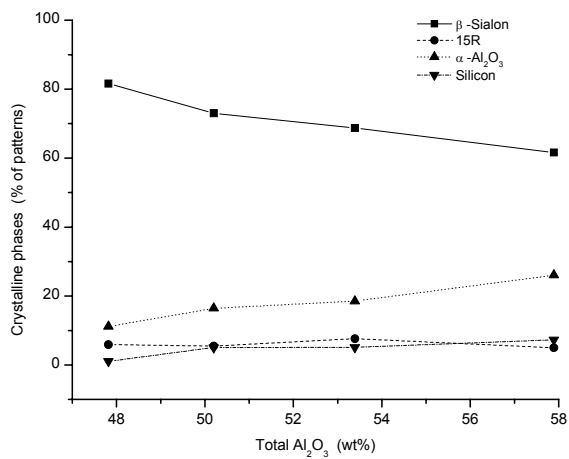
(b)



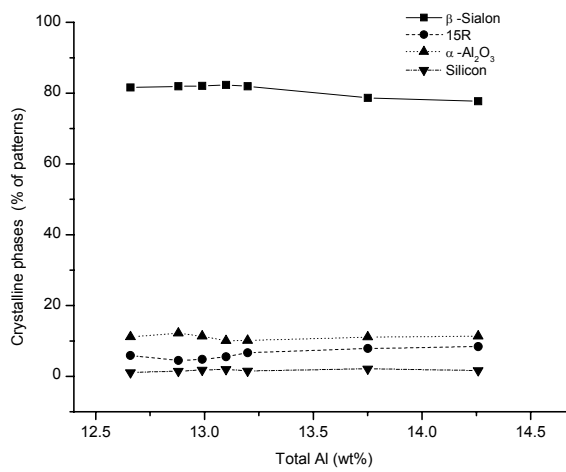
(c)



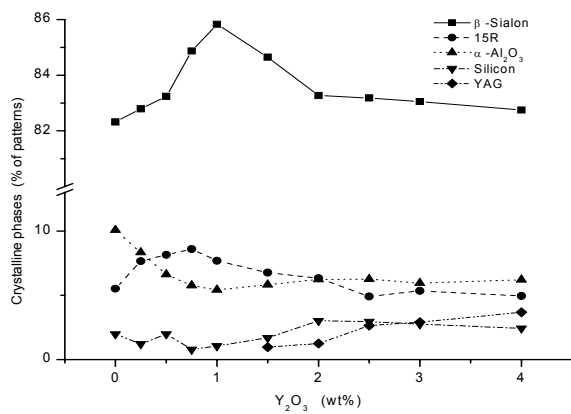
(d)



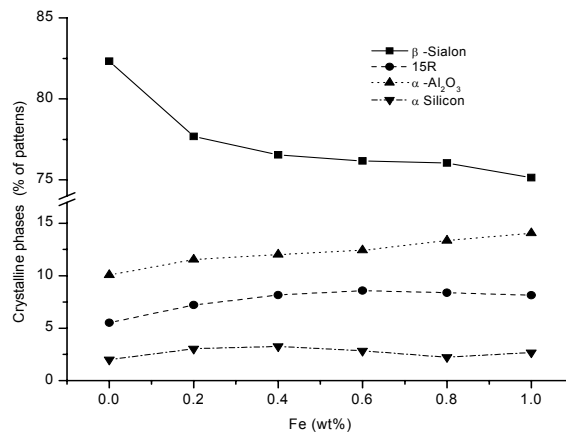
(a)



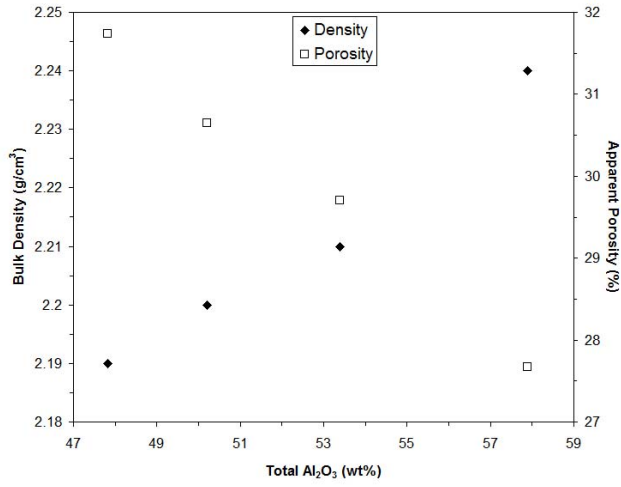
(b)



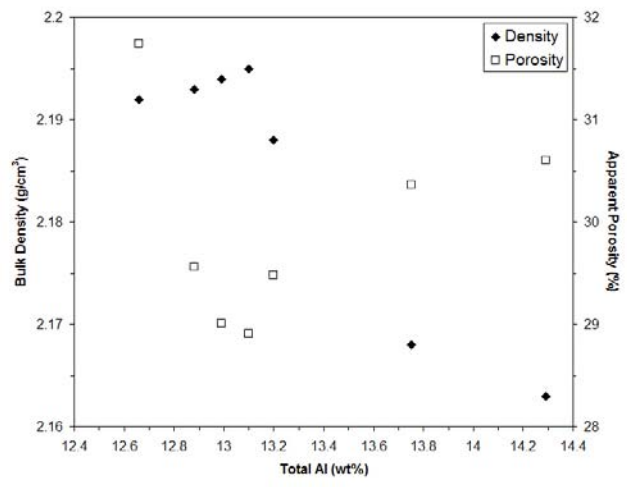
(c)



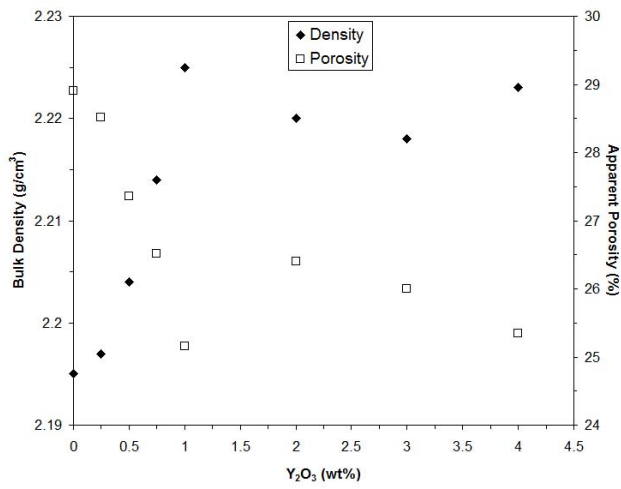
(d)



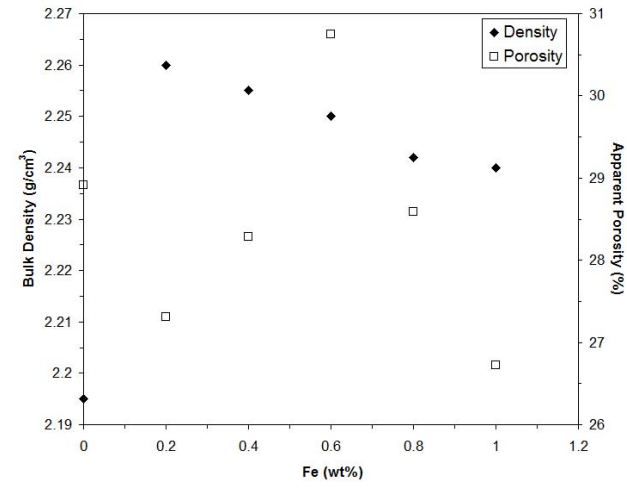
(a)



(b)



(c)



(d)

