Synthesis of Mg-α SiAlON powders from talc and halloysite clay minerals

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Abstract

Carbothermal reduction and nitridation (CRN) of SiO_2 is an attractive method to manufacture Si_3N_4 powders with controlled grain morphology. Some inexpensive raw materials were previously used to synthesize β-sialon powder, resulting in cheaper products to be useful for some engineering applications. In this work, Mg-α sialon ($Mg_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}$) powders were achieved by CRN of mixtures of talc ($Mg_3(Si_2O_5)_2(OH)_2$) and NZ halloysite clay ($Al_2Si_2O_5(OH)_4$) minerals. The final products consisted mainly of α-sialon and β-sialon phases. Small amounts of 15R AlN-polytypoid and SiC were also identified in the synthesized powder. By adding a small amount of α-Si_3N_4 powder as seeds to the starting composition, the conversion rate of α-sialon phase was significantly enhanced and powders with up to 90 wt% of α-sialon were produced. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Sialon ceramics (α′ and β′ mainly) have attracted intensive attentions for more than 30 years because of their excellent mechanical properties for engineering applications especially at high temperatures. Sialons are usually prepared by firing powder compacts of Si_3N_4, AelN, Al_2O_3 and some oxide sintering additives at high temperatures via a liquid phase sintering mechanism.[1] Because of the expensive starting materials and manufacturing process, the prices of final sialon products are usually much higher than those of most oxide based ceramics, limiting the practical use of sialon ceramics in small scales even until recent years.

Carbothermal reduction and nitridation (CRN) of SiO_2 is one of the most worthy methods in manufacturing Si_3N_4 powders currently used: it proceeds following the overall reaction (1) at a typical temperature range of 1400–1500°C in flowing nitrogen gas and a few hours are required to complete the synthesis:[2]

$$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO \qquad (1)$$

Based on this principle, Lee and Cutler[3] first synthesized β′ ($Si_{6-z}Al_zO_zN_{8-z}$) powders by substituting SiO_2 with natural clay ($Al_2Si_2O_5(OH)_4$) mineral as a starting material. The general reaction for synthesizing β-sialon powders was given as:

$$3(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) + 15C + 5N_2 \rightarrow 2Si_3Al_3O_3N_5 + 15CO + 6H_2O \qquad (2)$$
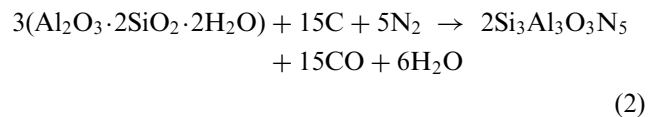
This led to an alternative way to fabricate sialons economically because of the low cost of raw materials and the relatively simple technique. Since then, many attempts have been made to optimize the experiment parameters for the powder synthesizing process and for the subsequent densification of such sialon powders.[4–9] Results showed that fully densified β-sialon materials could be achieved using the clay-derived powders at a relatively low temperature and with no sintering additive.[9] Most of the previous research was concentrated in synthesis of β′ powders from clay mineral because the Si/Al ratio in clay equals 1, which could give a controllable composition of β-sialon solid solution.

Like β', α' is one of the most important members in the sialon family. The structure of α' is based on the α-$Si_{12}N_{16}$ unit cell, stacking of Si–Al layers in ABCD sequence and presenting two large isolated interstices in which some metal cations could be accommodated.[10] Therefore α sialon is generally formulated as $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ with $x \leqslant 2$, where M is metal cation and x is related to the valence of the cation according to the relationship of $x = m/v$. The cations M which have been reported to stabilize α' are Li, Ca, Mg, Y and most lanthanide elements.[11–13]

In the process of synthesizing β' using clay, some liquid phase must have formed at a lower temperature before the main reaction takes place because of inevitable existence of impurities in raw minerals. Such a liquid phase would in turn facilitate the synthesis reactions through some liquid–solid–gas interaction mechanisms. On the other hand, based on the knowledge of phase diagram, the eutectic temperature of a system will further decrease by adding extra elements. Nevertheless, impurities remaining in the powders through CRN must have particular impact on the final properties of sintered ceramics if such powders are used as precursor materials. Therefore, it is necessary to find an effective way to eliminate the impurities after the synthesizing reaction. On the other hand, the formation of α' provides the advantage of holding some cations into its structure hence suggesting that if α' powder is synthesized from minerals in the same way as β' was, some impurity elements could be incorporated into α' lattices as well as remain in the final product as grain boundary phases.

There have been only a few works on preparing α' powders by CRN so far. Mitomo et al. reported that Ca-α' and Y-α' powders were formed by CRN of powder mixtures of SiO_2–Al_2O_3 with metal compounds (alkaline earth or rare earth oxides).[14] Rutten et al. also obtained Ca-α' powders by heating carbon-containing powder mixtures of SiO_2–Al_2O_3–$CaSiO_3$.[15] By adding Y_2O_3 to the starting clay/SiO_2 or clay/Si, Y-α' powder was synthesized by CRN by Ekstrom et al.[16] However, there was no report in any open literature about synthesis of α' using only minerals as raw materials.

MgO was used as one of the first sintering additives to effectively densify Si_3N_4 ceramics.[17] Meanwhile, Mg has been identified as a stabilization additive for the α' lattice. But the formability of Mg-α' is much lower than that of Ca, Y and heavy rare earth α-sialons as the single phase Mg-α' has never been obtained by any sintering means.[18,19] Partly for this reason, the exploration for Mg-α' has been insufficient compared with other counterparts. On the other hand, magnesium is plentiful in nature and exists in many minerals as either a main component or an impurity. Some Mg containing crude minerals, for example talc ($Mg_3(Si_2O_5)_2(OH)_2$), are easy to obtain at a quite low price.

Based on the above considerations, the present research was carried out to explore the possibility of synthesizing Mg-α' powder from inexpensive raw materials. Two minerals, talc and halloysite clay, in addition to carbon powder were used as starting compositions.

2. Experimental

The starting minerals used were talc (Haicheng, China) and New Zealand halloysite clay (NZ, China Clays Ltd) whose characteristics are given in Table 1. The powders were weighed and mixed with carbon black (650B, Mitsubishi Chemical Co.) in a fixed ratio according to preliminary results. One to 5 wt% of α-Si_3N_4 was added to starting compositions in some cases. The mixture was then placed in a plastic pot and ball milled for 24 h with ethanol and sialon balls as media. The dried powder batch was ground and passed through a sieve with 300 μm holes. The well-mixed batch was then put in a graphite crucible. CRN was performed in an electrical furnace in high purity nitrogen gas (99.9995% N_2, $0_2 < 0.5$ ppm $CO < 1.0$ppm $CO_2 < 1.0$ ppm $CH_4 < 1.0$ ppm) with a flow rate of 0.5 el/min. The heating rate was about 11°C/min, and the cooling rate 20°C/min. The remaining carbon was finally removed by burning the synthesized powder at 700°C for 2 h. The crystalline phases of the reaction product were identified by X-ray diffraction technique (XRD, Rigaku, RAD-2R). The semi-quantitative estimation of α'/β' ratio was based on a calibration curve by using the intensities of diffraction lines of (210) for both α' and β' phases. To determine the cell dimension of α' lattice, silicon powder was used as the internal standard, mixed with some synthesized powder for XRD scanning. The particle morphology of samples was characterized by scanning electron microscopy (SEM, Jeol JSM-5200). An energy dispersive spectrometer (EDS,

Table 1
Chemical compositions of the talc and halloysite clay used

Component	Talc (wt%)	Clay (wt%)
MgO	32.02	< 0.04
Al_2O_3	0.01	34.41
SiO_2	60.63	51.89
Fe_2O_3	–	0.3
TiO_2	0.01	0.09
CaO	0.97	< 0.01
K_2O	0.01	0.05
N_2O	0.01	< 0.09
P_2O_5	–	0.11
C	–	0.3
LOI[a]	6.18	12.34
Total	99.86	99.63

[a] Loss on ignition.

Link, QX2000J) was used to determine the element distribution in synthesized particles.

3. Results and discussion

A series of starting compositions with various ratios of talc to halloysite were attempted to give products of highest sialon proportion. The results showed that a weight ratio of talc: halloysite = 1.5: 1, i.e. 4.5MgO:8-SiO$_2$:Al$_2$O$_3$ in the starting composition, if the crystal water and impurities in the minerals were ignored, was optimum. From the XRD patterns of resultant powders synthesized at 1450°C for 6 h [Fig. 1(a)], it was concluded that α′ together with β′ account for the main phases and a small amount of AlN 15R polytypoid as well as SiC as remainders. Although α′ was not the major phase in the final product, by adding a very small amount of α-Si$_3$N$_4$ powder into the starting composition, the yield of α′ phase in the synthesized powder increased significantly. Up to 90 wt% of α′ was observed in a 3 wt% α-Si$_3$N$_4$ additive sample after firing at 1450°C for 6 h [Fig. 1(b)].

Fig. 2 shows the SEM morphology of the synthesized powders for the composition containing 3 wt% α-Si$_3$N$_4$ additive. It was found that the synthesized α′ particles had a regular and uniform feature, with an average diameter of about 1 μm. The chemical compositions of such synthesized particles were revealed by EDS analysis, showing Si, Al, Mg, O and N contents in them. The typical one of EDS patterns is presented in Fig. 3. Combing with the XRD result, it could be ascertained

that the synthesized powders were composed mainly of Mg-α′.

Due to the substitution of Si–N (1.74 Å) by Al–N (1.87 Å), the cell dimensions of α′ lattice expand with increasing m and n values in composition. On this basis, the composition of Mg-α′ powder was determined by measuring the cell dimensions of the α′ phase from the XRD data (a_o = 7.7934 Å, c_o = 5.6638 Å). The calculation was conducted according to the equations revised by Sun et al.[20] as follows:

$$a_o\left(\overset{\circ}{A}\right) = 7.752 + 0.045m + 0.009n \qquad (3)$$

$$c_o\left(\overset{\circ}{A}\right) = 5.620 + 0.048m + 0.009n \qquad (4)$$

From Eqs. 3 and 4 the m- and n-values were estimated to be 0.8 and 0.6, respectively. Therefore, the overall composition of Mg-α′ powder might be determined as
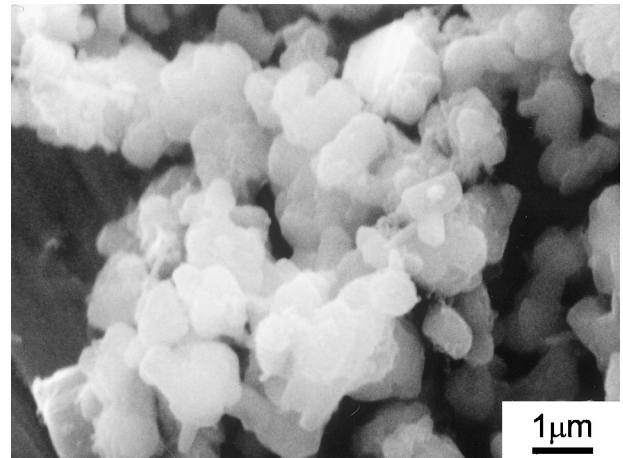

Fig. 2. SEM photograph of sialon powders synthesized from talc and halloysite clay minerals fired at 1450°C for 6 h (90% α′).
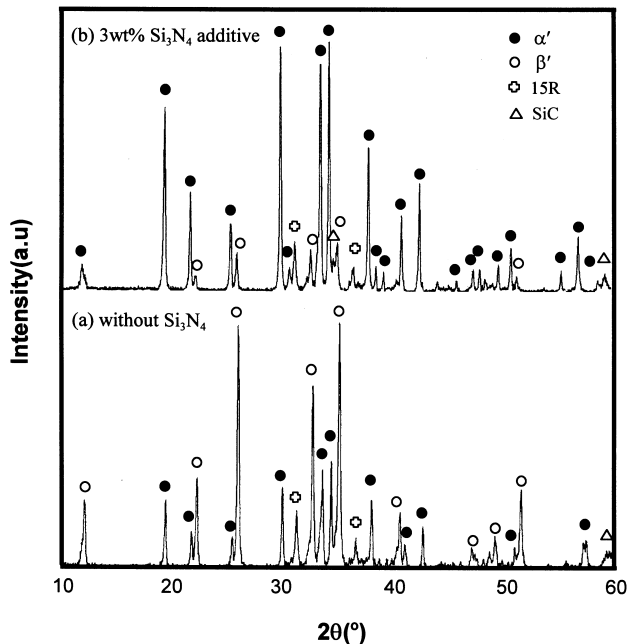

Fig. 3. Typical EDS spectra of Mg-α′ particle synthesized from talc and halloysite clay minerals with 3 wt% Si$_3$N$_4$ additive by CRN at 1450°C for 6 h.

Fig. 1. XRD profiles of synthesized products from talc and halloysite clay minerals fired at 1450°C for 6 h with and without Si$_3$N$_4$ additive.
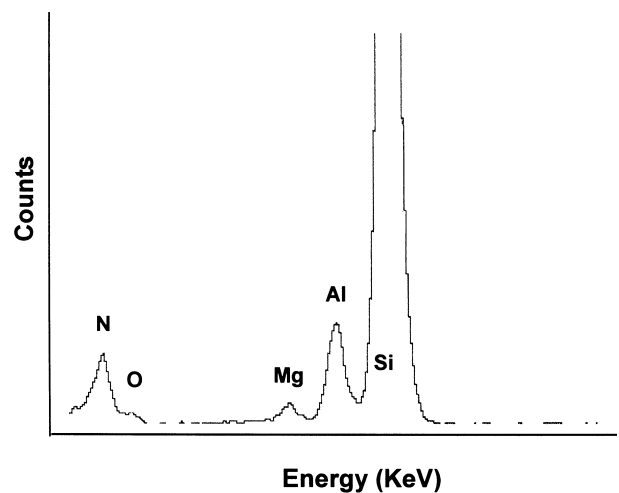
$Mg_{0.4}Si_{10.6}Al_{1.4}O_{0.6}N_{15.4}$. Actually, the extent of lattice expansion for an α' is also dependent on the species of the stabilizing cation and some similar equations like Eqs. 3 and 4 have been revised specially for Y–, Ln– and Ca-α sialons by many researchers.[20–23] But until now, no cell dimension data of Mg-α' was reported. The calculation in this work was made according to equations for Y-α'. The estimated m- and n-values are, therefore, considered to be slightly smaller than the actual ones because the ionic radius of Mg^{2+} (0.66 Å) is less than that of Y^{3+} (0.89 Å).

In order to find out the reaction mechanism behind the Mg-α' formation during the CRN of talc and halloysite clay minerals, the mixtures without Si_3N_4 additive were heated to 1300, 1400 and 1450°C and kept for 30 min. The crystalline phases appearing in powders fired at different temperatures were determined as shown in Fig. 4. At lower temperature of 1300°C, $MgSiO_3$, mullite and SiO_2 were found as main crystalline phases in the fired sample [Fig. 4(a)]. This indicates that during early stage of firing, two minerals, talc and clay, gave out crystal water and decomposed to silicates and silica, namely,

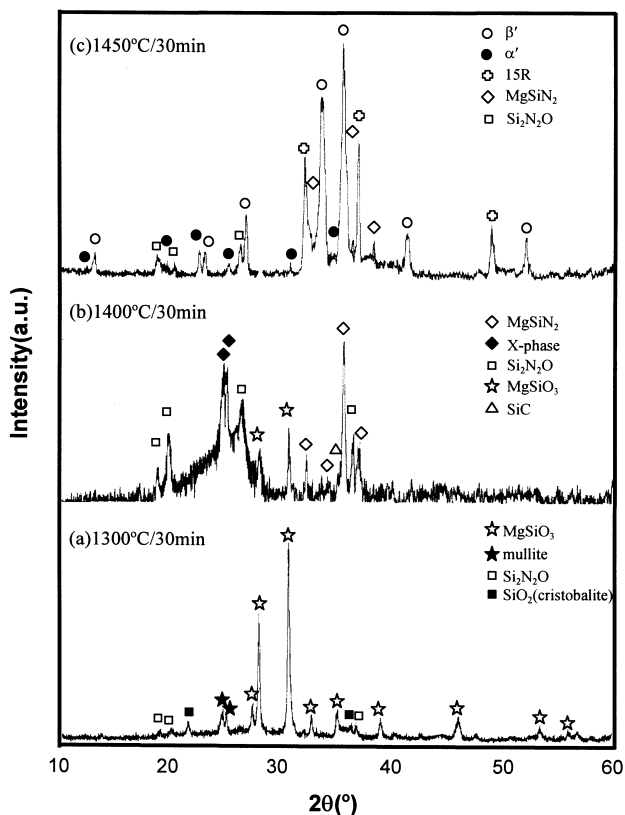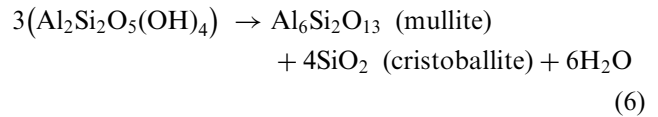$$Mg_3(Si_2O_5)_2(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O \quad (5)$$

Fig. 4. XRD patterns of powders synthesized from talc and halloysite clay minerals fired at different temperatures for 30 min.

$$3(Al_2Si_2O_5(OH)_4) \rightarrow Al_6Si_2O_{13} \text{ (mullite)}$$
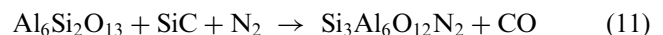$$+ 4SiO_2 \text{ (cristoballite)} + 6H_2O \quad (6)$$

Besides silicates, a small amount of Si_2N_2O phase was detected, suggesting that the initial reactions at 1300°C also involved the conversion from SiO_2 to Si_2N_2O through reaction 7
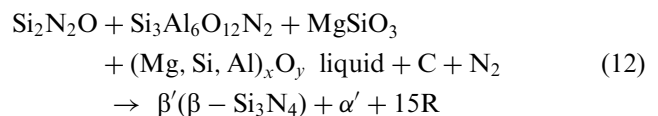
$$SiO_2 + C + N_2 \rightarrow Si_2N_2O + CO \quad (7)$$
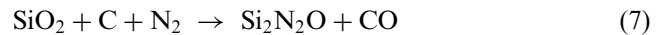
When temperature increased to 1400°C, a large quantity of amorphous phase appeared in the sample as indicated by the big hump at the low 2θ angle of XRD spectrum [Fig. 4(b)]. This was a result of liquid formed in the sample as the eutectic temperature for the Mg–Si–Al–O system is about 1355°C.[24]

$$MgSiO_3 + Al_6Si_2O_{13} + SiO_2 \rightarrow (Mg, Si, Al)_xO_y \text{ liquid} \quad (8)$$
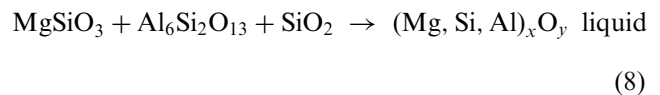
Meanwhile, CRN reactions occurred at this stage, resulting in the formation of $MgSiN_2$ and X-phase ($Si_3Al_6O_{12}N_2$) from $MgSiO_3$ and mullite, respectively. In addition, SiC, which was a common intermediate phase or byproduct observed in the final β' and α' powders synthesised by CRN of clay or SiO_2–Al_2O_3–M_xO_y mixture[3–8] appeared also at this temperature. The suggested reactions to form these phases are given as following:

$$SiO_2 + 2C \rightarrow SiC + 2CO \quad (9)$$

$$MgSiO_3 + 3C + N_2 \rightarrow MgSiN_2 + 3CO \quad (10)$$

$$Al_6Si_2O_{13} + SiC + N_2 \rightarrow Si_3Al_6O_{12}N_2 + CO \quad (11)$$

CRN reactions were accelerated by elevating the temperature to 1450°C. At this stage, β' or β-Si_3N_4, α' and 15R polytypoid appeared at the expense of the amorphous phase. The reaction at this stage may be estimated as (note: no balance was made for every element in the following equation):

$$Si_2N_2O + Si_3Al_6O_{12}N_2 + MgSiO_3$$
$$+ (Mg, Si, Al)_xO_y \text{ liquid} + C + N_2 \quad (12)$$
$$\rightarrow \beta'(\beta - Si_3N_4) + \alpha' + 15R$$

Prolonged firing times obviously fulfilled the above reaction. After 6 h at 1450°C, all intermediate phases, Si_2N_2O, X-phase, $MgSiO_3$ and $MgSiN_2$, disappeared and the final products were mainly composed of β' and α' phases [Fig. 1(a)].

The magnesium content in the starting composition (Mg/Si = 0.56) was more than the stoichiometric value required and far greater than the measured value in the

final product (Mg/Si = 0.04). In spite that some Mg existed in a Mg-containing glass and the unidentified phase in the final product, it is still not possible to reach a balance of magnesium content between the starting and resulting compositions. Thus, it is assumed that part of Mg may have lost during the reaction. This may be due to the decomposition of $MgSiN_2$ which was present in the sample fired at $1400°C$, but decreased markedly when temperature increased [Fig. 4(c)] and completely disappeared at $1450°C$ after 6 h [Fig. 1(a)]. It was possible that $MgSiN_2$ could decompose into Si_3N_4, Mg and N_2 according to the following reaction:

$$3MgSiN_2(s) \rightarrow Si_3N_4(s) + 3Mg(g) + N_2(g) \qquad (13)$$
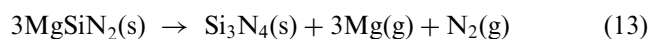
Because magnesium has a low melting point $(650°C)$ and boiling point $(1107°C)$,[25] it could evaporate after decomposition of $MgSiN_2$ and be blown out by flowing nitrogen gas.

In the previous work on synthesis of Si_3N_4 from SiO_2, Inoue et al. and Kang et al. discovered that a small amount of Si_3N_4 addition in the starting silica and carbon mixture could produce a rapid increase of α-Si_3N_4 content in the final product.[26,27] An explanation proposed for the result suggested the Si_3N_4 particles acted as seeds for the formation and growth of Si_3N_4 from the CRN of SiO_2. The same effect was also found in the present study. Fig. 5 plots the relationship between the amount of α-Si_3N_4 added in the starting mix and the α' content in the final synthesized product. It is clear that the amount of α' phase increases with the increase of α-Si_3N_4 additive, and exceeds 90 wt% when the additive is more than 3 wt%. Both α' and α-Si_3N_4 have the same crystal structure except that the α' phase contains some Al and O, as well as stabilizing metal cations. It has been observed by several researchers that α sialon developed from α-Si_3N_4 nuclei in sintering.[28,29] Therefore, it is believed that the α-Si_3N_4 added in the starting

mix enhanced the nucleation and growth of Mg-α' grains in the CRN reaction.

4. Conclusions

Mg-α' powders ($Mg_{0.4}Si_{10.6}Al_{1.4}O_{0.6}N_{15.4}$) were successfully achieved by CRN of mixture of talc and halloysite clay minerals. The final product consisted mainly of α' and β' phases. Small amounts of 15R AlN-polytypoid and SiC were also identified in the synthesized powder. By adding α-Si_3N_4 powders to the starting mixture, the α'-phase conversion rate was significantly enhanced, up to 90 wt% after firing. An extra amount of magnesium was necessary in the starting composition to compensate the evaporation loss of Mg due to the decomposition of an intermediate phase $MgSiN_2$ during CRN reaction. The synthesized powder exhibited a regular and uniform morphology, with an average grain size about 1 μm. Densified Mg-α' is expected to be manufactured by using the Mg-α' powders as the starting material.

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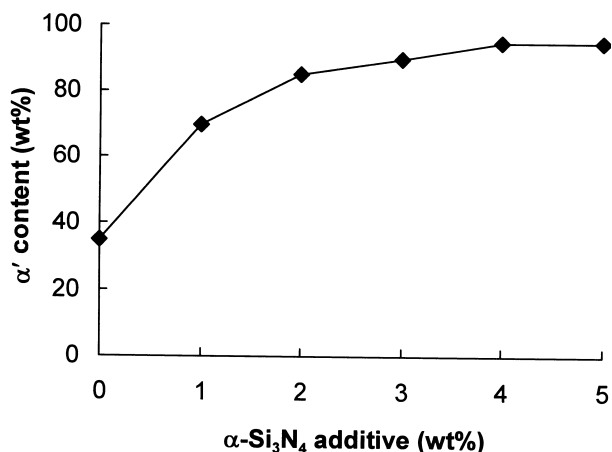

Fig. 5. The content of α' phase increases with the increase of α-Si_3N_4 additive.

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