Journal of the Korean Ceramic Society
Vol. 28, No. 5, PP. 365~372, 1991

Phase Formation and Rheological Characteristics of LAS Derived from the Monophasic Sol-Gel Route

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(Received March 13, 1991)

Sol-Gel 반응으로 유도된 LAS의 상 생성과 점성 특성

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(1991년 3월 13일 접수)

ABSTRACT

LAS (lithium aluminosilicate) sol was synthesized using the hydrolysis-condensation reaction of TEOS, chelated $Al(OBu^s)_3$ and Li-salt with H_2O in alcohol (EtOH+2-Propanol) medium. Effects of important reaction parameters on the properties of sol and gel-derived LAS were examined. The crystallization of the sol-gel derived LAS with β-spodumene composition began at ~600℃, and a series of polymorphic transformations occurred as temperature was increased to 1100℃: amorphous LAS→hexagonal $LiAl(SiO_3)_2$→β-spodumene. Lowering Li content in the gel enhanced densification and retarded the crystallization significantly. Optimum reaction conditions of LAS sol formation for thin coating applications were derived from rheological measurements, and these can be summarized as: H_2O/total alkoxides molar ratio=4, pH=~2.5, and aging time of ~250 h.

요 약

물/알코올 용매내에서 TEOS, chelated $Al(OBu^s)_3$ 및 Li 염을 반응물질로 하고 가수분해-축합반응을 이용하여 LAS(lithium aluminosilicate) sol을 합성하였다. 먼저 반응조건들이 Sol-Gel 방법으로 합성한 LAS의 여러 특성에 미치는 영향에 대해서 검토하였다. β-spodumene의 조성을 가진 합성 LAS gel을 열처리함에 따라 약 600℃에서 결정화가 일어났으며 온도가 증가함에 따라 비정질 LAS→hexagonal $LiAl(SiO_3)_2$→β-spodumene의 단계로 상변태가 진행되었다. Gel의 합성시 Li 함량을 감소시킴으로써 치밀화를 촉진할 수 있었으며, 또한 결정화속도도 상당한 정도로 감소시킬 수 있었다. LAS sol의 코팅 응용에 필요한 sol 합성의 최적 조건들을 sol의 점성 특성을 분석함으로써 도출하였으며 이를 요약하면 다음과 같다: H_2O/총 알콕사이드 몰비=4, pH=2.5 및 숙성시간=약 250 시간.

1. Introduction

Proper control over rheological properties is important in numerous ceramic processing operations, including (i) shape forming, (ii) coating/deposition, and (iii) wet mixing/milling. However, systematic investigations of rheological behavior of ceramic suspensions or sols are relatively limited. In this study, we have prepared

lithium aluminosilicate (abbreviated as LAS hereafter) sol using the hydrolysis-condensation route and have investigated its rheological properties for various reaction conditions of sol formation. The main purposes of this study were to find optimum reaction conditions of LAS sol formation for thin coating applications and to examine phase formation/densification characteristics of the sol-gel derived LAS. More specifically, we tried to find a suitable rheological condition for uniform coating of LAS sol onto SiC fiber as a preliminary study for the fabrication of SiC fiber/LAS glass-ceramic matrix composite with a uniform microstructure by sol-gel process.

Uniform coating of LAS sol derived from the hydrolysis-condensation route and the use of glass-ceramic matrix are very important to a successful fabrication of the composite with a dense, homogeneous microstructure. The coating, in principle, removes problems associated with a direct bonding between SiC fibers during the hot pressing stage and, therefore, maximizes the efficiency of load transfer (in the sintered composite) during the crack propagation, and a glass matrix phase can densify without damage to reinforcing fibers due to its viscous flow characteristics[1]. Since sintering of a glass-ceramic body is driven by the reduction of surface area through a viscous-flow process, it will cease if the viscosity is suddenly increased as a result of crystallization. Because of this, it is essential that crystallization does not commence until sintering is nearly completed. Therefore, we also have examined the effect of composition of the sol-gel derived LAS (especially Li_2O as a network modifier) on the densification and crystallization behaviors.

2. Experimental

LAS sol was synthesized using the hydrolysis-condensation reaction of tetraethylorthosilicate (TEOS), aluminum tri-sec-butoxide [$Al(OBu^S)_3$], and Li-salt($LiNO_3$) with H_2O in alcohol medium. Unless specified elsewhere, the composition of LAS sol used in this study was: $Li_2O:Al_2O_3:SiO_2=1:1:4$, i.e., the composition of β-spodumene. The rate of hydrolysis-condensation reaction of $Al(OBu^S)_3$ was reduced by chemical modification of $Al(OBu^S)_3$ with ethylacetoacetate (β-dicarbonyl compound) which undergoes a rapid keto-enol tautomerism[2]. Lithium acetate as a starting material produced a severe surface segregation problem of acetate salt after the formation of LAS gel in alcohol solvents (for both ethanol+2-propanol and ethylene glycol+2-propanol), while lithium nitrate in alcohol (ethanol+2-propanol) led to a chemically homogeneous gel after the reaction. These conclusions were deduced from the analysis of FT-IR spectra of LAS gels prepared by the hydrolysis-condensation route. The procedure followed for the preparation of LAS sol for the dip coating applications is outlined in Fig. 1.

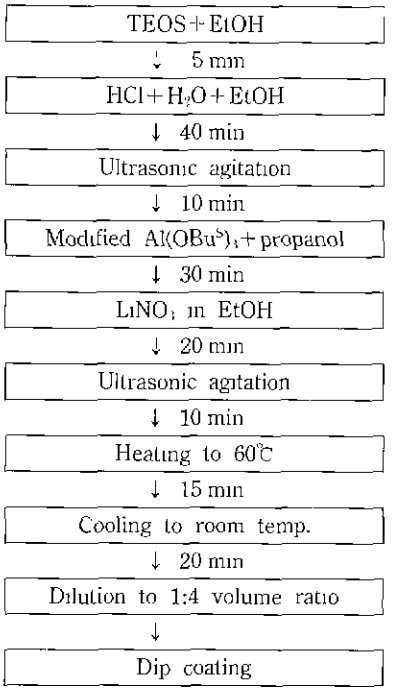

Fig. 1. Experimental procedure used for the preparation of LAS sol for the dip coating.

Effects of important reaction parameters on the properties of sol and gel-derived LAS were examined by laser light scattering analysis (Zeta Sizer III, Malvern), XRD (Rigaku, DMAX-3B), FT-IR (Shimadzu 4300), thermomechanical analysis (TMA 1500, Stanton Redcroft) and DTA/TGA (Perkin Elmer, DTA1700/TGA7). Optimum reaction conditions of LAS sol formation for thin coating applications were deduced from rheological measurements. The parameters examined for this purpose were H_2O/total alkoxides molar ratio, pH, and gelation time. Rheological flow characteristics of LAS

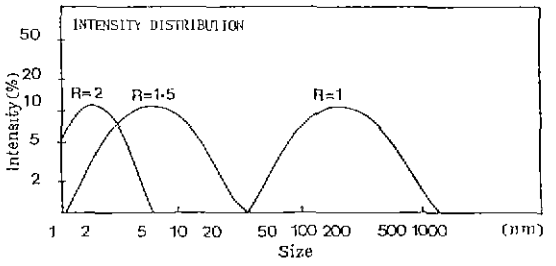

Fig. 2. Size distribution of LAS sol for various values of H_2O/total alkoxides molar ratio in acid catalyzed reaction (*alkoxides:EtOH:HCl=1:3:0.0007*).

sols were determined using a concentric cylinder viscometer (*Model RV-100/CV-100, Haake*). *Steady rotational flow curves* (i.e., shear stress vs. shear rate) were generated by increasing the shear rate from zero to the maximum desired value, in 2 min, immediately followed by decreasing the shear rate back to zero in another 2 min.

3. Results and Discussion

3.1. Characteristics of Sol-Gel Derived LAS

Fig. 2 shows the effect of H_2O/total alkoxides molar ratio (in acid catalyzed reaction) on the size distribution of LAS sol immediately after dilution to a desired *H_2O/alkoxides molar ratio. Throughout the text, R is* defined as (moles of H_2O)/(4×total moles of metal alkoxides). Therefore, R=1 corresponds to 4 moles of H_2O and 1 mole of total alkoxides in the reactant. The result shows that the average size of sol increases rapidly and the size distribution becomes broader as the water content in the medium decreases. According to the study done by Brinker and Mukherjee[3] on the hydrolysis-condensation of multicomponent metal alkoxides, the resulting sol or amorphous gel is less cross-linked when the water content is not high enough for a complete hydrolysis. It seems that this leads to a simple linear chain growth, thereby, increasing the effective scattering cross-section of sol in the initial stage of the hydrolysis-condensation reaction.

DTA study of LAS gel derived from the reaction condition of R=2 (Fig. 3; heating rate, 10℃/min) indicates that the dehydration of physisorbed water and burn-out of the residual organics complete below 330℃ and shows that the exothermic peak associated with crystallization of amorphous gel occurs at ~600℃. The

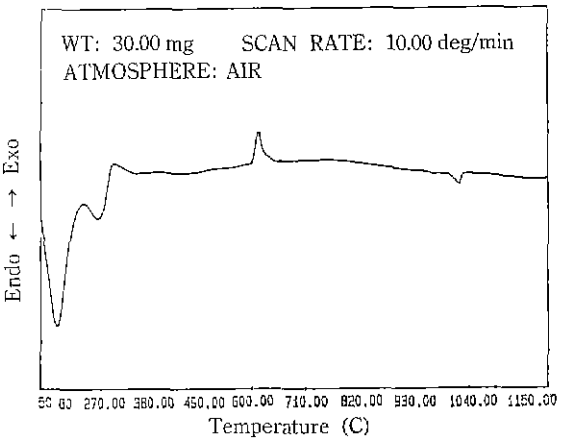

Fig. 3. DTA curve of LAS gel derived from the hydrolysis-condensation reaction.

endothermic peak observed near 1000℃ seems to be associated with a polymorphic phase transformation. Analysis of XRD data showed that this corresponds to the transformation of hexagonal $LiAl(SiO_3)_2$ phase[4] to β-spodumene. Fig.4 shows XRD of LAS gels heat-treated at various temperatures for 1 h. The results indicate that the crystallization begins at ~550℃, and a series of polymorphic transformations occurs as temperature increases, i.e., amorphous LAS→hexagonal $LiAl(SiO_3)_2$→β-spodumene. The hexagonal $LiAl(Si_4O_{10})_2$ *phase*[4], *thus, seems to be quasi-stable intermediate* phase in the formation of β-spodumene from the LAS gel having 1:1:4 composition.

Fig. 5 shows FT-IR spectra of LAS gels heat-treated at various temperatures for 1 h. As temperature increases to 600℃, intensity of the peak at ~1050 cm^{-1} (due to the Si-O stretching vibration in the ~SiO_4 tetrahedron unit[5]) increases significantly, supporting the result of XRD, i.e., the crystallization of amorphous LAS gel to form the hexagonal $LiAl(SiO_3)_2$ phase. As temperature further increases to 900℃, the peak at 1650 cm^{-1} due to the bending mode of molecular water and the broad peak at ~3500 cm^{-1} associated with the O-H *stretching vibration significantly reduce* their intensity. On the other hand, the peak intensity at ~750 cm^{-1} increases sharply as temperature increases from 600℃ to 900℃. This is due to the formation of tetrahedron ~AlO_4 unit in the ~SiO_4 network. Therefore, Al atoms in the octahedral sites incorporate into the tetrahedron unit as the molecularly coordinated water dehydrates above 600℃. As shown in the figure, the

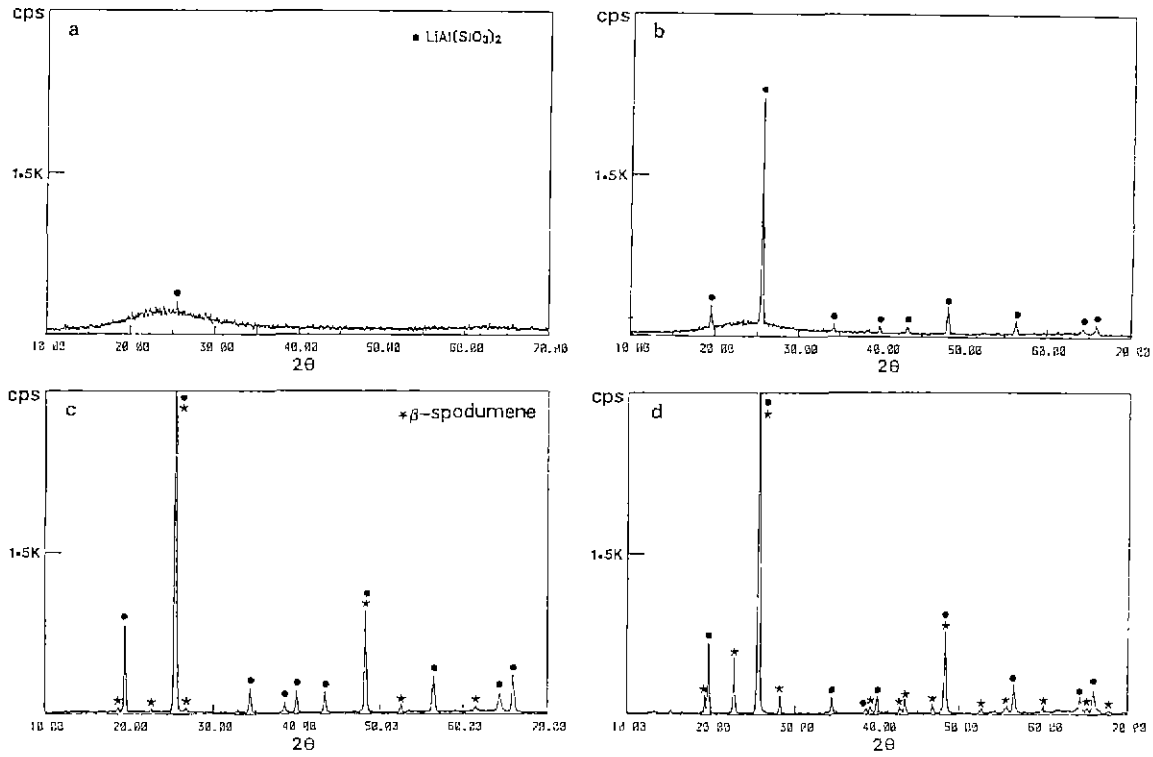

Fig. 4. XRD patterns of LAS gels (1:1:4 composition) heat-treated at various temperatures for 1 h: (a) 550℃; (b) 600℃; (c) 900℃; (d) 1100℃.

peak near 570 cm^{-1} sharply increases in its intensity as temperature increases to 1100℃. This absorption band is associated with the symmetrical vibration motion of the bridged oxygen in the plane bisecting the Si-O-Si bond[5]. Therefore, this indicates a rapid increase in the fraction of β-spodumene in the LAS matrix[5] and does accord with the results of XRD shown in Fig. 4(c) and (d).

Lowering Li content in the glass phase (e.g., 0.44:1:4 composition) usually retards the crystallization of LAS prepared by the conventional melt-quenching process[7]. We have prepared LAS gels with low content of Li (0.44:1:4 composition)[7] to examine whether the above conclusion also holds for the sol-gel derived LAS or not. Fig. 6 shows XRD patterns of the LAS gels (having the above-mentioned composition) heat-treated at (a) 900℃ and (b) 1100℃ for 1 h. A comparison of the result of Fig. 6(a) with that of Fig. 4(c) clearly shows that lowering Li content significantly increases the crystallization temperature. The LAS gel with β-spodumene composition (1:1:4) almost completely undergoes the crystallization to the hexagonal $LiAl(SiO_3)_2$ phase at 900 ℃, while the LAS gel with 0.44:1:4 composition just begins to crystallize at this temperature. As shown in Fig. 6, lowering Li content seems to retard the crystallization up to 1100℃ for 1 h. A complete phase evolution to the β-spodumene phase without the remnant α-cristobalite and hexagonal $LiAl(SiO_3)_2$ was observed after heat-treatment at 1200℃ for 2 h

Fig. 7 shows linear shrinkage of the LAS gel having 0.44:1:4 composition as a function of temperature (heating rate; 10℃/min). A rapid shrinkage occurs between 770℃ and 870℃. On the other hand, the LAS glass specimen (having the above mentioned composition) prepared by the conventional melt-quenching process[7] exhibited a noticeable shrinkage over broad temperature range (800℃~1030℃). A comparison of the result of Fig. 7 with that shown in Fig. 6(a) clearly demonstrates that sintering of the sol-gel derived LAS completes before crystallization initiates. If crystallization occurs before sintering is nearly complete, the viscosity increases to near infinity and sintering stops. There-

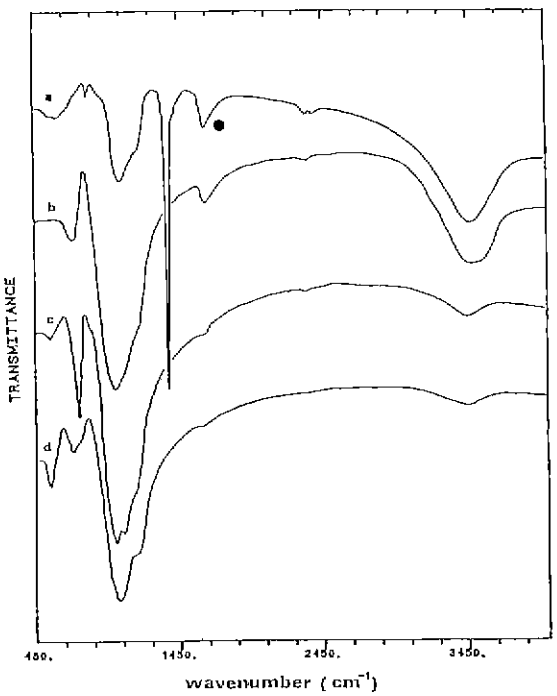

Fig. 5. FT-IR spectra of LAS gels (1:1:4 composition) heat-treated at various temperatures for 1 h: (a) dried gel; (b) 600℃; (c) 900℃; (d) 1100℃.

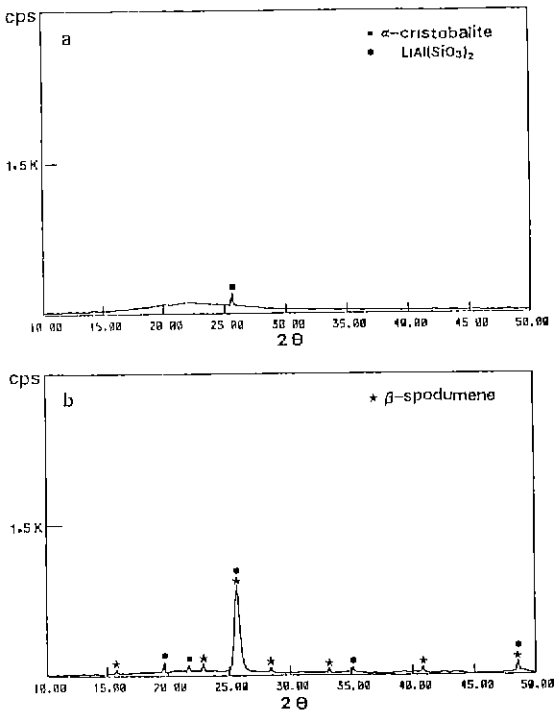

Fig. 6. XRD patterns of LAS gels (0.44:1:4 composition) heat-treated at (a) 900℃ and (b) 1100℃ for 1 h.

fore, the sol-gel derived LAS specimen with low Li content possesses suitable densification characteristics. Density of the sol-gel derived LAS specimen (0.44:1:4 composition) sintered at 1100℃ for 2 h is 2.487 g/cm^3. This value is higher than the theoretical densities of β-spodumene and hexagonal $LiAl(SiO_3)_2$, i.e., 2.377 g/cm^3 and 2.399 g/cm^3, respectively, indicating the presence of Si-rich phases such as α-cristobalite and amorphous silica. As mentioned briefly in "Introduction", the presence of glassy matrix phase is important for densification of fiber/glass-ceramic matrix composite with a minimal damage to reinforcing fibers. Therefore, the above results show a possibility of the fabrication of SiC/LAS matrix composite by suitably varying the Li content during the sol forming stage.

3.2. Rheological Characteristics of LAS Sol

Fig. 8 shows the rheological flow cruves for LAS sols prepared using various conditions of H_2O/total alkoxides molar ratio (R) and pH (about 250-hr aging time). The results show that the sol exhibits a transition in flow characteristics from Newtonian behavior to shear thinning behavior (i.e., the viscosity decreases with increasing shear rate) as the water content or pH in the reaction medium increases. This indicates that the hydrolysis-condensation reaction is practically frozen at low water content (R~0.25) and pH (below, say, 1.5). Since shear thinning (or pseudoplastic) character with relatively low viscosity (~10 mPa·sec) is desirable for thin coating applications, we have examined the aging behavior of LAS sol having shear thinning characteristics. As shown in Fig. 9, the viscosity of the shear thinning sol (at shear rate of 1 sec^{-1}) is essentially independent of reaction conditions (R, pH) below the gelation point.

The hydrolysis-condensation of silicon alkoxide in the acid catalyzed medium with low water content usually produces polysiloxane species which are less branched and more chainlike[8,9]. This linear chain induces extremely slow gelation. As the water content in an acidic medium increases, the hydrolysis/condensation reaction produces highly branched, polymeric poly-

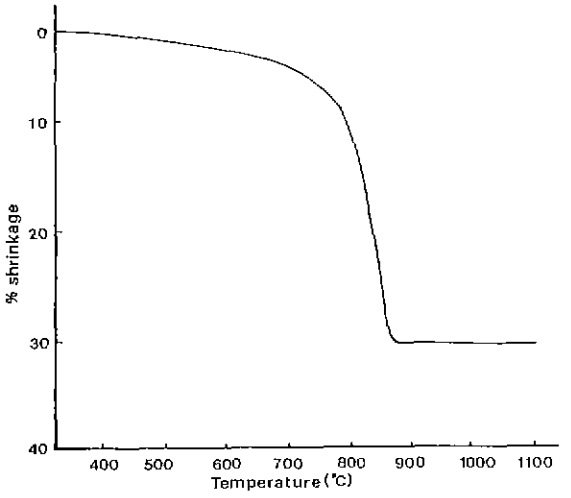

Fig. 7. Linear shrinkage of LAS gel having 0.44:1:4 composition as a function of temperature (heating rate; 10℃/min).

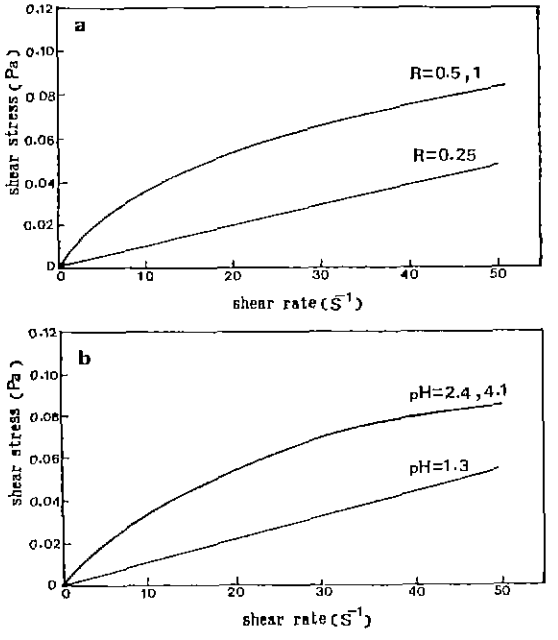

Fig. 8. Plots of shear stress versus shear rate: (a) for various values of R; (b) for various values of pH.

siloxane clusters[9] via the nucleophilic substitution mechanism (S_{N2}). This results in a rapid increase in the gelation rate and effective solids loading since the void space within a cluster agglomerate contains liquid that is unavailable for flow. Therefore, the result shown

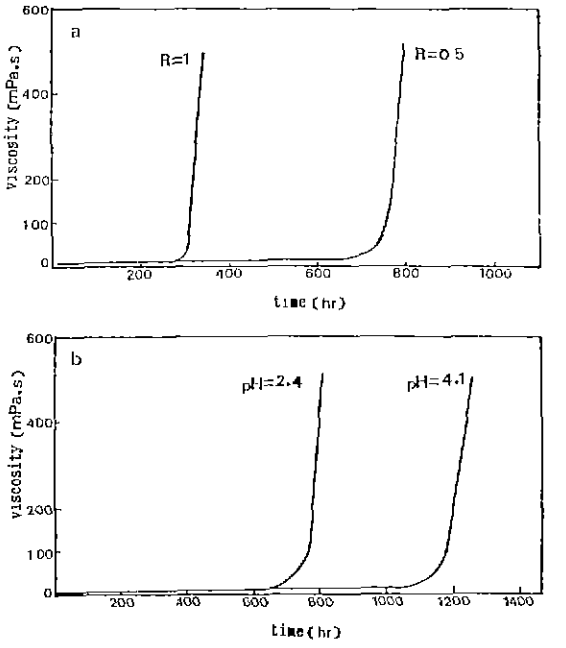

Fig. 9. Plots of viscosity versus aging time for LAS sols prepared using various reaction conditions: (a) for pH=2.5; (b) for R=1.

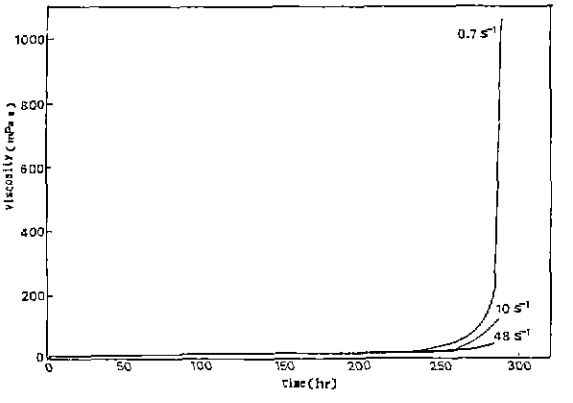

Fig. 10. Plots of viscosity (at indicated shear rate) versus aging time for the sol having R=1 and pH=2.5

in Fig. 9(a) indicates that the above arguments (i.e., effect of water content on gelation time) also apply to the LAS sol derived from the hydrolysis-condensation route. An extremely slow gelation observed for the sol having pH≥4.0 (Fig. 9(b)) presumably indicates that the sol particle obtained in this condition is close to a discrete lyophobic colloid particle rather than a branched lyophilic polymer.

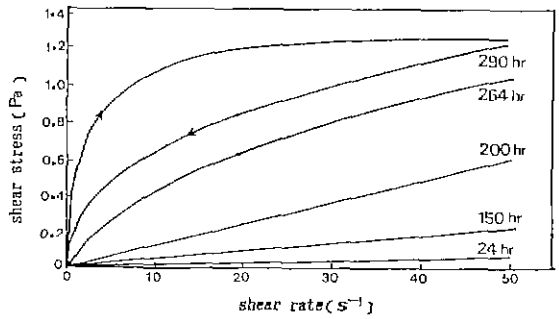

Fig.11. Shear stress versus shear rate for the sol having R=1 and pH=2.5 at indicated aging times.

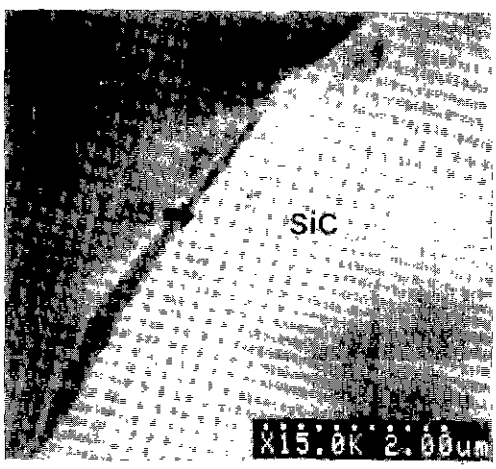

Fig.12. SEM of SiC fiber coated with a thin layer of LAS gel (cross section of fractured fiber).

Fig. 10 is a plot of viscosity versus aging time for the sol (with R=1 and pH 2.5) suitable for thin coating applications. Up to 250-hr aging time, the viscosity is independent of shear rate. For longer aging time, the viscosity becomes increasingly dependent on shear rate. Fig. 11 shows shear stress versus shear rate curves for the above sol at five aging times. With continued aging, condensation growth and agglomeration of polymeric clusters results in the formation of a continuous, 3-D network. The elastic character of the network is characterized by the observation of yield stress at 290-hr aging. Breakdown of the network occurs after the yield stress is exceeded. Therefore, hysteresis is observed in the flow curve above a certain critical aging time, and the sol becomes thixotropic. Since the best spinnability is usually obtained prior to the transition to thixotropic behavior[10], optimum conditions of

Fig. 13. SEM of a bundle of SiC fibers filled with LAS gel matrix (before sintering).

the LAS sol coating can be summarized as: R=1, pH=2.5 and aging time=~250 h.

Fig. 12 shows scanning electron micrograph of the SiC fiber (Nicalon, Nippon Carbon Co., Japan) coated with a uniform, thin layer of LAS gel. The coating was derived from the sol having the above mentioned conditions. A cross-sectional view of the fractured surface for a bundle of SiC fibers is shown in Fig. 13. The LAS gel matrix between the fibers was prepared by a repeated coating (~10 times) of the sol having R=1 and pH 2.5. The solvent used in the thick coating process (Fig. 13) is a mixture of methanol (main component), ethanol, and 2-propanol to rapidly remove the residual solvent from the gel matrix during the drying stage.

4. Conclusions

(1) The crystallization of the sol-gel derived LAS with β-spodumene composition began at ~600℃, and a series of polymorphic transformations occurred as temperature was increased to 1100℃: amorphous LAS →hexagonal $LiAl(SiO_3)_2$→β-spodumene.

(2) Lowering Li content in the gel enhanced densification and retarded the crystallization significantly. Sintering of the sol-gel derived LAS completes before cry-

stallization.

(3) Optimum reaction conditions of LAS sol formation for thin coating applications were derived from rheological measurements, and these can be summarized as: H_2O/total alkoxides molar ratio=4 (R=1), pH=~2.5 and aging time of ~250 h.

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