Mullitization of Diphasic Aluminosilicate Gels

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Recent studies have shown that the mullitization of diphasic aluminosilicate matrices comprising transitional alumina and amorphous silica occurs via a nucleation and growth process. Nucleation is preceded by a temperature-dependent incubation period. Following this incubation period, rapid nucleation of mullite occurs, producing about 1.8 × 10^{11} nuclei/cm^3, which remains constant throughout the rest of the transformation. Both incubation and mullite growth are thermally activated processes with apparent activation energies of 987 ± 63 and 1070 ± 200 kJ/mol, respectively. The growth rate of mullite grains under isothermal conditions is time dependent. An interpretation of these results is proposed on the basis of the nucleation and growth concepts of LaMer and Dinegar which supports the concept that the growth rate of mullite grains is controlled by the dissolution of transitional alumina into the amorphous matrix. [Key words: mullite, gels, nucleation, processing, aluminosilicates.]

I. Introduction

RECENT activities on the processing of mullite (3Al$_2$O$_3$·2SiO$_2$) have emphasized the utilization of chemically synthesized precursors that convert to mullite in the temperature range of 850° to 1350°C.[1-18] The general observation is that the scale of chemical homogeneity of the precursors plays a key role in the mechanisms of mullite formation and thus determines the temperature range where total mullitization is achieved. The mechanisms that lead to the formation of mullite in these low-temperature systems fall into two general categories: (i) when the scale of homogeneity is at the atomic level (i.e., monophasic precursors), mullite forms as the first crystalline phase by an exothermic reaction at about 980°C,[1,4,5,8,11,12,14-18] or, (ii) when the scale of homogeneity is in the nanometer range (i.e., ~1 to 100 nm (diphasic precursors)), mullite formation can be delayed to temperatures as high as 1350°C, as evidenced by a higher-temperature (>1200°C) exothermic reaction.[2,3,6-9,11-14,16-18]

In the first category there is now a general agreement that, when an amorphous precursor displays atomic-scale arrangement of –Al–O–Si– groupings very similar to that of mullite, the crystallization of mullite occurs by a nucleation-controlled process with an apparent activation energy of 293 to 362 kJ/mol.[1,5,10,15,16] In the second category, although it is conclusively established that the formation of mullite occurs via a

direct reaction of alumina particles and a silica-rich amorphous matrix, a similarly clear understanding of the rate-controlling steps leading to the formation of mullite has not yet been provided.[2,3,6-9,11-18] For instance, at temperatures around 1200° to 1350°C, the reaction leading to the formation of mullite in these diphasic aluminosilicate precursors is expressed as[6,7]

$$3(\delta\text{-Al}_2\text{O}_3) + 2(amorphous\ \text{SiO}_2) \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \quad (1)$$

Based on a detailed study of the reaction kinetics, microstructures, and phase-transformation mechanism, Wei and Halloran[7] were the first to illustrate that mullite formation in this case occurs by a nucleation and growth mechanism in the silica-rich matrix with an apparent activation energy of 1070 ± 200 kJ/mol, which is significantly higher than that of the single-phase precursor systems. Also, unlike the single-phase systems, the transformation is preceded by a temperature-dependent incubation period with a similarly high apparent activation energy of 987 ± 63 kJ/mol.[7] Following this incubation period, nucleation occurs in a very short time producing about 1.8 × 10^{11} nuclei/cm^3, a density which remains constant throughout the rest of the transformation.[7] Based on these data and the microstructural observations, Wei and Halloran concluded that this transformation is either interface controlled or short-range-diffusion controlled near the alumina/mullite/silica interfaces.[7] Wei and Halloran's analysis of the average grain size as a function of time during isothermal sintering revealed that the growth rate manifested a time dependence,

$$\text{growth rate} \approx t_\text{m}^{-0.63} \quad (2)$$

where t_m is the normalized time ($t - t_0$) and t_0 is the incubation period.[7] Since the microstructure of the interface of alumina/mullite/silica revealed little variation during the transformation, Wei and Halloran could not provide a satisfactory explanation for this time-dependent growth rate. Based on their observations and the rate-limiting step proposed, we would expect a constant growth rate rather than a variable one.

Subsequent studies, in principle, support the data of Wei and Halloran. Li and Thomson[11,15] also agree with the diffusion-limited rate model of Wei and Halloran. However, the work of Huling and Messing[14,17] strongly suggests that the rate-limiting step may not be diffusion-controlled but instead be associated with the presence of alumina (spinel-type) in the matrix.

The goal of this work is to rationalize these recent observations on the transformation kinetics in diphasic aluminosilicates by drawing on the concepts of LaMer and Dinegar[19] on nucleation and growth. The model that we present supports the concept that the growth rate of mullite grains is controlled by the dissolution of alumina particles into the amorphous phase and provides a satisfactory explanation for the time-dependent growth rate observed by Wei and Halloran.

II. Phase Transformation Mechanism

When mullite is produced through a reaction of alumina and silica at temperatures above 1650°C, the nucleation and growth of mullite occurs as an interfacial reaction product between alumina and silica. In this case, the growth rate is parabolic and is controlled by the interdiffusion of aluminum and silicon ions through the mullite layer.[20,21]

Extrapolation of the above to the reaction in diphasic mixtures comprising transitional alumina and amorphous silica at 1200° to 1350°C suggests the formation and growth of mullite along the entire surface between the alumina and silica phases. The recent studies discussed in the previous section, however, have conclusively established that this is not the case.[6,7,11,14,17] Instead, mullite forms in these systems by a nucleation and growth mechanism within the amorphous silica-rich matrix rather than at the alumina/silica interfaces.

There is a fundamental difference in mullite growth in high-temperature (>1650°C) and low-temperature (<1350°C) systems of diphasic precursors described above. In the former case, the alumina and silica sources are present on opposite sides of a mullite layer, necessitating interdiffusion through mullite in order to sustain growth. In the latter case, the alumina and silica sources are present on the same side of the growing mullite surface.

In the following discussion, we follow LaMer and Dinegar[19] to explain the mullitization of diphasic mixtures and postulate the following sequence of events. First, within the aluminosilicate gel, there are transitional alumina and pure, amorphous silica phases. As the sample is heated (or held isothermally at typical mullitization temperatures), the alumina particles dissolve into the silica phase. When the concentration of alumina in the silica phase exceeds the critical nucleation concentration (CNC), mullite nuclei form and grow, which decreases the concentration of alumina in the silica phase to a level below the CNC. These mullite nuclei grow at a rate governed by the rate of dissolution of alumina into the silica phase and other processes such as Ostwald ripening. Subsequent formation of new mullite nuclei does not occur simply because the concentration of alumina in the silica phase never exceeds the CNC again.

The scenario described in the preceding paragraph can be illustrated more effectively by using the free-energy diagram shown schematically in Fig. 1(b). The free energies of the amorphous silica and the crystalline alumina phases are denoted by points A and B in Fig. 1(b), respectively. Also shown in Fig. 1(b) is the free energy of mixing for the amorphous aluminosilicate solution for the composition range up to 50 mol% alumina and for the mullite solid solution. It is emphasized that Fig. 1(b) is, in most part, schematic. Although the shape of the curve for the aluminosilicate solution is in agreement with the calculations of Risbud and Pask,[22] the one for mullite is only schematic and the locations of the curves with respect to point B are chosen to comply with the coexistence compositions indicated in the phase diagram of Fig. 1(a) at $T \approx 1300$°C. However, this schematic representation does not alter the conclusions of the following discussion.

As a consequence of entropic effects, the addition of any second component to a pure phase initially always lowers the molar free energy of the solution. Thus, in the diphasic mixtures of transitional alumina and amorphous silica, a thermodynamic driving force exists for the initial diffusion of silica into the alumina phase and the dissolution and mixing of alumina into the amorphous silica phase. However, because both diffusion and dissolution are thermally activated processes, we expect that the sample must be heated to sufficiently high temperatures (i.e., typical mullitization temperatures) for these processes to occur. From structural considerations, the dissolution and mixing of alumina into the amorphous silica is likely to occur more readily than the diffusion of silica into transitional alumina. Hence, in our subsequent discussion, we consider only the dissolution and mixing of alumina into the
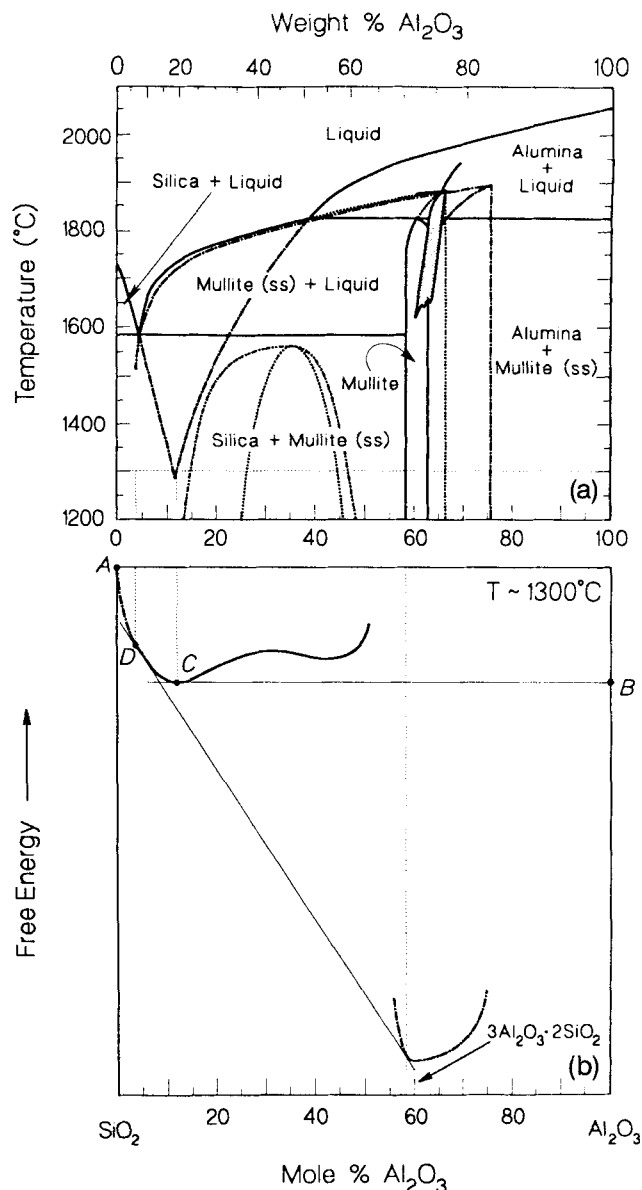

Fig. 1. (a) Stable and metastable phase diagram of the SiO$_2$–Al$_2$O$_3$ system. Immiscibility region is from the calculations of Risbud and Pask[22] and the shaded insert in the mullite solid-solution range is from Klug et al.[23,24] The rest of the diagram is from Aksay and Pask.[20,21] (b) Schematic representation of free-energy versus composition curves for amorphous aluminosilicate and mullite with respect to transitional alumina at 1300°C. Curve for the amorphous aluminosilicate is from Risbud and Pask.[22]

silica phase. As mentioned above, we can expect the molar free energy of the amorphous silica phase to decrease first as the alumina dissolves into it (Fig. 1(b)). If the curve describing the free energy of the amorphous (and molecularly mixed) aluminosilicate matrix is continued, it intersects the pure alumina limit at a point above B, since amorphous alumina is expected to be at a higher free-energy state than that of the crystalline transitional aluminas. This curve is not shown in its entirety, because we neither need it for our discussion nor know the full details of its shape. Irrespective of the details of the shape of this curve, we can draw at least one tangent to this curve that passes through point B, as shown in Fig. 1(b). Thus, if no crystallization occurs, the dissolution of alumina into the amorphous matrix continues until the concentration of alumina in the aluminosilicate matrix reaches an amount corresponding to point C.

Figure 1(b) also shows schematically the free energy corresponding to the crystalline mullite phase. A common tangent

for the curves corresponding to the amorphous alumino-silicate matrix and the crystalline mullite touches the former curve at point *D*. It readily follows from solution thermo-dynamics that nucleation and growth of mullite in an amorphous aluminosilicate matrix is not favorable if the con-centration of alumina in this matrix is below that correspond-ing to point *D*. Because the free energy of stoichiometric mullite is lower than that of the crystalline alumina (point *B*), point *D* must be to the left of point *C*. Furthermore, because we know that crystallization of mullite does indeed occur in these diphasic mixtures, we can also expect that the CNC of alumina in the aluminosilicate matrix must lie between points *D* and *C*.

The sequence of events occurring upon heating the dipha-sic mixture to typical mullitization temperatures can now be stated in terms of Fig. 1(b). The initial concentration of alu-mina in the amorphous (silica) phase corresponds to that of point *A*. The dissolution of transitional alumina into the amorphous phase starts to occur and the alumina concentra-tion in the amorphous phase steadily increases. When the alu-mina concentration exceeds the CNC, mullite nuclei form and grow in the amorphous phase. The initial lag time preceding nucleation and growth of mullite, which has been observed experimentally in such diphasic mixtures,[6,7,11,15,17] is merely the time required for alumina concentration in the amor-phous phase to reach the CNC. After the onset of nucleation and growth of mullite, the alumina concentration in the amorphous phase decreases and stays below the CNC at all future times.

Since Fig. 1(b) is only schematic, it is appropriate to ask how large are the alumina concentrations in the amorphous matrix corresponding to points *D* and CNC. If a substantial amount of transitional alumina were to dissolve into the silica phase before the CNC is attained, a corresponding amount of transitional alumina in the diphasic mixture must decrease appreciably during the initial lag period preceding mullite nucleation. However, Wei and Halloran[7] have clearly demonstrated experimentally that this is not the case. Thus, it follows that the alumina concentration corresponding to points *D* and CNC in Fig. 1(b) must be very small. This con-clusion is also supported by the phase diagram of Fig. 1(a). The approximate locations of points *D* and *C* at 1300°C are at 4 and 12 mol% of alumina, and, thus, the CNC must be <12 mol% alumina.

III. Rate-Limiting Step in Mullite Growth

Three rate processes are involved in mullite grain growth. First, alumina must dissolve into the amorphous phase. Sec-ond, the alumina must diffuse to the growing mullite grain. Third, the alumina must be incorporated (as mullite) on the surface of mullite grains. Let us now examine which of these three rate processes control the growth of mullite. We can immediately rule out the third rate process mentioned above. If this were the rate-limiting process, the concentration of alumina in the amorphous phase would rise, exceed the CNC, and cause a secondary nucleation of mullite, which we know does not happen.[7,11,15,17]

We can also argue that diffusion through the amorphous phase cannot be the rate-limiting step in these diphasic mix-tures for the following reasons. First, if diffusion through the amorphous phase were rate limiting, then the concentration of alumina in the amorphous aluminosilicate matrix in the immediate vicinity of mullite grains would correspond to point *D* in Fig. 1(b), whereas at locations distant from the mullite grain this concentration would be significantly higher, approaching the value corresponding to point *C*. But such a situation should give rise to secondary nucleation in the aluminosilicate matrix, which we know does not happen.[7,11,15,17] Second, if diffusion through the amorphous phase were rate limiting, the alumina/silica interfacial regions would be the

first sites to reach the equilibrium concentration of *C*, which then would result in the nucleation of mullite at the alumina/ silica interfaces. As discussed in Section II, in the tempera-ture range >1650°C, this is indeed the case. However, because of the experimental results summarized in the previ-ous sections, there is now convincing evidence that mullite nucleates directly within the amorphous aluminosilicate ma-trix but not at the alumina interfaces. The work of Huling and Messing[8,14,17] clearly illustrates that the presence of alu-mina can in fact be detrimental to the nucleation and growth of mullite.

We propose that the only possible explanation within the framework of the LaMer and Dinegar[19] model is that the dis-solution of transitional alumina into the amorphous phase is rate limiting and governs the growth of mullite. On the basis of the above discussion, if the nucleation and growth process were to be dissolution limited at low temperatures (*T* < 1350°C) and diffusion limited at high temperatures (*T* < 1650°C), the rate constant for dissolution must increase more rapidly with temperature than the diffusion coefficient for ions in the amorphous phase. Thus, at some point be-tween 1350° and 1650°C, a crossover will occur whereby dif-fusion becomes the rate-limiting step above this crossover temperature. This model would then dictate that the activa-tion energy for diffusion in the amorphous aluminosilicate matrix must be smaller than that for dissolution.

Although—in the low-temperature regime with which we are concerned—the diffusion data in amorphous alumino-silicates are not yet available, an examination of the diffusion data in the temperature range of 1650° to 1870°C (Table I)[25] indicates that the activation energy for diffusion in amor-phous aluminosilicates in the composition range up to 15.5 mol% alumina ranges from 1268 to 698 kJ/mol. Note that, at low alumina contents, the activation energy for diffusion is comparable to the values measured for grain growth in dipha-sic precursors, but the values rapidly fall below as alumina is incorporated into the matrix. Thus, because of these lower values for diffusion, especially in the composition range cor-responding to the points *D* and *C*, it is unlikely that diffusion is the rate-limiting process.

The intermediate temperature range (1350° to 1650°C) where the crossover behavior is expected was studied by de Keyser[26] at 1600°C, by Staley and Brindley[27] at 1500°C, and by Davis and Pask[28] at 1550°C between cristobalite and α-alumina. In all these studies, a liquid-phase formation was observed initially between alumina and cristobalite prior to subsequent nucleation and growth of mullite as an interfacial layer. Because of the dissolution-limited rate model proposed in this paper, these observations would suggest that the crossover point may even be at a higher temperature than 1600°C.

IV. Discussion

The above scenario is consistent with several features that have been observed experimentally by various researchers.

(i) Wei and Halloran[7] reported that primary nucleation of mullite occurred after an initial lag period and that no sec-

Table I. Diffusion Data for SiO_2–Al_2O_3 Melts*

$C_{Al_2O_3}$ (mol%)	< ~1870°C		> ~1870°C	
	D_0 (cm²/s)	Q (kJ/mol)	D_0 (cm²/s)	Q (kJ/mol)
2.53	8.03×10^{22}	1268	7.00×10^{12}	857
5.10	1.55×10^{18}	1070	1.33×10^{12}	821
7.66	5.86×10^{13}	884	2.51×10^{11}	785
10.25	2.07×10^{11}	773	2.07×10^{11}	776
15.51	5.87×10^9	698	5.87×10^9	698

*Interdiffusion coefficients, D_0, and activation energies, Q, are reported for temperature regimes below and above the softening temperature (~1870°C) of amorphous silica.

ondary nucleation could be observed in these diphasic mixtures. They attributed this phenomenon to saturation of the nucleation sites. The scenario suggested in this paper, that the CNC is exceeded only once and only briefly, is another plausible explanation for this observation.

(ii) Huling and Messing[8,14,17] synthesized hybrid gels containing a mixture of polymeric mullite precursor and colloidal gel prepared using boehmite and silica and examined their phase-transformation kinetics and resulting microstructures. A gel containing no polymeric mullite precursor manifested extensive mullitization after 2 h at 1250°C, but not at 1240°C. For hybrid gels containing 10 and 30 wt% polymeric mullite precursor, the temperatures of initial transformation for a 2-h heat treatment were 1230° and 1215°C, respectively. The polymeric mullite precursor crystallizes extensively at temperatures below 1150°C and these crystals serve as seeds for the diphasic aluminosilicate matrix. The observation that seeding results in only a small decrease in the transformation temperature for the diphasic matrix shows that nucleation is not the rate-limiting step for diphasic gels. Our explanation is consistent with the results of Huling and Messing.[8,14,17]

(iii) In the proposed model, both the time lag preceding the appearance of the mullite nuclei and the subsequent growth of these nuclei are governed by a single process, namely, the dissolution of alumina into the amorphous phase. Therefore, within the framework of the model, the temperature dependence of the incubation period and the growth rate of mullite must be the same. Wei and Halloran[7] reported apparent activation energies of 987 ± 63 and 1070 ± 200 kJ/mol for incubation and mullite growth, respectively, which may be considered as roughly equal.

(iv) The growth rate of mullite grains was found by Wei and Halloran[7] to be time dependent. This observation can now be readily explained when we assume that the dissolution of alumina is rate limiting, as described below.

Let us first consider the case where the alumina particles are not trapped by the growing mullite grains. In this case, the number of transitional alumina particles in the diphasic region which has not yet been mullitized remain constant. Furthermore, because the chemical composition of the amorphous aluminosilicate matrix into which the alumina particles dissolve is always at a condition corresponding to point D (Fig. 1(b)) during the growth stage, the dissolution rate of each particle must be approximately time invariant. Therefore, the total amount of alumina dissolving into the amorphous matrix per unit of time should also be time invariant since it is equal to the product of the number of alumina grains and the dissolution rate of each alumina particle, each of which is time invariant. Within the framework of the proposed model, the total rate of alumina dissolution into the amorphous phase is essentially equal to the rate of incorporation of alumina (as mullite) in the growing mullite grains. Because the former is time invariant, it follows that

$$NG^2 \frac{dG}{dt} \approx \text{constant} \tag{3}$$

where N and G are the number and average size of the spherical mullite grains, respectively. An immediate consequence of this relationship is that

$$\frac{dG}{dt} \approx t_m^{-2/3} \tag{4}$$

where t_m is the time elapsed since the appearance of the mullite nuclei. The exponent ($-2/3$) predicted by the model is approximately the experimentally observed value of -0.63.[7] When we consider entrapment of alumina particles by the growing mullite grains,[7] the number of transitional alumina grains remaining in the diphasic region decreases slowly with time. Consequently, the total rate of alumina dissolution into the amorphous phase no longer is constant, but decreases

slowly with time. It then follows that the right-hand side of Eq. (3) decreases slowly with time and that the exponent in Eq. (4) is somewhat less than $-2/3$.

V. Conclusions

The formation and growth of mullite from diphasic aluminosilicate gels occurs via a nucleation and growth mechanism. Wei and Halloran[7] concluded that this transformation is either interface controlled or short-range-diffusion controlled near the interface. They observed a time-dependent growth rate for mullite grains, which could not be explained. We present an interpretation of their results drawing upon the concepts of LaMer and Dinegar[19] on nucleation and growth. We also argue that the growth rate of the mullite grains is controlled by the dissolution of the alumina particles into the amorphous phase. Such a model provides an explanation for the time-dependent growth rate observed experimentally.

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