
Correlation between mullite formation and mechanical properties of refractory castables at elevated temperatures

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The fine art of



Correlation between mullite formation and mechanical properties of refractory castables at elevated temperatures

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Abstract:

Conditions for mullite formation are discussed in context of the special conditions that exist in alumina based low and ultralow cement castables. The mullite formation has been found to depend on several factors, of which the cement content and the amount of available silica are the most important. Furthermore, the dependence of the hot-strength and mullite formation is demonstrated for the said castables.

Introduction:

Mullite is frequently seen as a component of the bond phase in refractories. Mullite is known to give high refractoriness, moderate thermal expansion and good strength at elevated temperatures resulting in low creep rate and good stability. Although it is a very common mineral phase of fired alumina-silicates, the formation of mullite is known to be strongly influenced by the composition and purity of the bond phase. In this presentation, some results will be presented on this topic:

Background:

Few mineral phases have the same significance in refractories as mullite. The mineral, named after the Scottish Isle of Mull, is rarely found in nature, but is a common mineral in fired alumina-silicate materials. Mullite is the only stable high-temperature phase between alumina and silica and the composition is commonly expressed as A_3S_2 where $A=Al_2O_3$ and $S=SiO_2$. However, it is today widely accepted that mullite has no fixed composition but exhibits a solid solution range. There is some dispute about the solid solution range, but from around 71 wt% to 74 wt% alumina seems to be within most proposals. The largest dispute however has been about the thermochemical nature of the mullite, i.e. the melting behavior. Although a large number of investigations concerning this has been

published, there still exist some uncertainty regarding whether mullite melts congruently or incongruently. Both incongruent and congruent melting have been found by various investigations and an explanation of both was first given by Aksay and Pask.¹ Their binary system was based on the data of many others in combination with their own results. This diagram shows that under stable conditions mullite melts incongruently. According to Risbud and Pask,² congruent melting of mullite is experienced under metastable conditions. Figure 1 shows a revised version of the phase diagram presented by Risbud and Pask.³

For users of refractory castables, the melting behavior of pure mullite is normally of secondary interest. Softening of mullite containing castables is usually caused by ternary impurities, like CaO in cement bonded high-alumina systems. In castables with microsilica and alumina where strengthening is supposed to occur by mullite formation, another aspect of the phase diagram is much more critical than the melting behavior; namely the formation of the mullite.

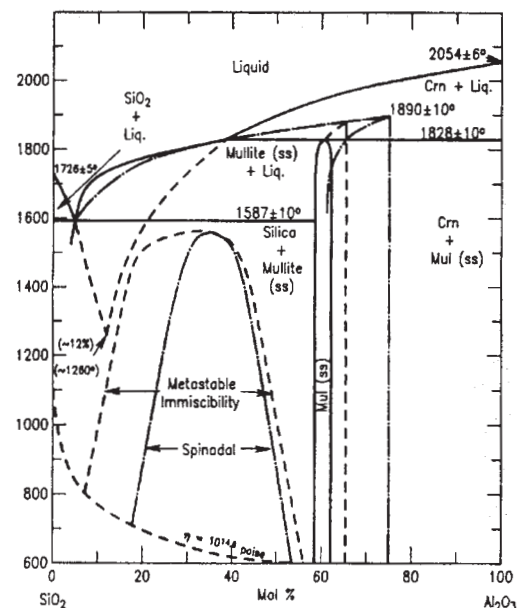


Figure 1: The phase diagram Al_2O_3 - SiO_2 (Risbud and Pask 1978)

The phase diagram of Figure 1 was made by careful studies of contact areas between alumina and silica, and revealed that upon heating, a liquid forms in the contact area before mullite precipitates. This metastable system is indicated as a dotted line in the extension of the liquidus curve in the phase diagram (Fig. 1). Thus a metastable, simple eutectic system with a calculated eutectic at approximately 12 mole% alumina and 1260°C was found.

High-alumina castables containing microsilica and fine alumina in the bond phase, generally softens at temperatures above 1200-1300°C. Depending on the cement (impurity) content and the amount of microsilica present, this softening may be of temporary nature. After prolonged heating, an increase in hot-M.O.R. may be found at temperatures above 1200-1300°C. The temperatures at which the softening commences seem to be depending on the impurity level, primarily in the superfines but also in the bulk. Earlier, the softening has been attributed low melting phases in the system alumina-silica-calcia, but with the evolution of essentially cement free castables it was realized that the softening was still present even without calcia from the cement. Even though this does not rule out the calcium containing liquid, also other explanations had to be found. As the eutectic temperature of the metastable system in the alumina-silica system coincides with the observed softening temperatures, it therefore seems likely that the origin of the softening in the cement free and ultra-low cement systems is the metastable system found in the alumina-silica system depicted in Figure 1.

Absence of mullite formation normally has one main cause; lack of available silica or too much calcia or other fluxing oxides. This is really two sides of the same issue since a certain amount of the silica goes into solution together with the fluxing oxides, sometimes giving other silica containing phases like anorthite.

When a potentially mullite forming castable is heated for the first time, it has been found that the microsilica and the cement reacts almost quantitatively and yields a liquid at temperatures around 1200-1300°C. It is from this liquid that mullite grows. Since all microsilica and all cement reacts to a liquid⁴, the amount of viscous liquid may reach substantial amounts - around 10% of the castable is not uncommon, and the strength of such a castable gets low. With mullite formation this low strength is however of temporary nature as the mullite precipitation both reinforces and reduces the amount substantially. This is seen as a strengthening with time.

Where almost no cement is used, the same mechanisms seem to apply, this time the liquid is supplied by the metastable system referred to above.

When mullite formation has ceased, in the presence of calcia, a certain amount of silica remains in a residual liquid that has been found⁴ to correspond approximately to the composition of the ternary peritectic at 1512°C located close to the composition of anorthite, see Figure 2. This means that since the mullite grows out of this liquid, the liquid is infiltrated with mullite crystals. Mullite crystals within a liquid probably does not add much to strength unless they bridge two neighboring aggregate particles. Thanks to the normally needle-like habit of the mullite crystals this happens relatively easily though. During the mullite precipitation, the amount of liquid also has been reduced so that for some castable compositions, only traces are left. With time also the last traces of liquid may solidify and crystallize. The liquid seems to be quite "persistent" though so the last mentioned step may take excessively long time. Out of the microsilica that is added to the castable, a certain fraction maintain in these liquid residues and does not add much to strength. Since they are infiltrated with mullite crystals, neither this mullite is expected to add significantly to strength unless they bridge adjacent particles. So, all in all, it is the microsilica that is in excess of what goes into the liquid and as non-bridging that adds to strength.

Experimental results and discussion

To investigate the effect of mullite formation further, castables based on white fused alumina (Universal Abrasives) and calcined alumina (ALCOA) with varying amounts of microsilica (Elkem Materials) and cement in the bond phase were prepared. All castables had similar particle size distribution and equal amount of water for casting. The particle size distribution followed the Andreassen distribution with top size 4 mm and q-value approximately 0.25. 13 volume % water was added for casting. In terms of weight 13 vol% equals to 3.8-4.2 wt% depending on microsilica content.

The castable were prepared in such a way that they contained 2, 4, 6 or 8wt% microsilica. Table 1 shows the composition of the bond-phase of the castables if the bond phase is defined as the components with a size below approximately 45 µm.

Table 1: Chemical composition of the bond-phase (fractions < 45 micron).

Sample (microsilica)	Composition of the bond-phases (wt%)		
	Al ₂ O ₃	SiO ₂	CaO
<i>q=0.25,</i>			
<i>0.5 wt% cement</i>			
8	49,4	50,1	0,5
6	65,1	34,4	0,5
4	78,5	21,1	0,4
2	89,6	10,0	0,4
<i>q=0.25,</i>			
<i>6 wt% cement</i>			
8	53,9	38,1	8
6	65,9	26,7	7,5
4	76,3	16,7	7,0
2	85,3	8,0	6,7

Table 2: Samples, time and mullite content after firing at 1400°C.

Sample (microsilica)	time(h)	mullite (wt%)
<i>0.5 wt% cement</i>		
8	0.5	0
8	2	0
8	6	4
8	24	15
6	0.5	0
6	2	1
6	6	10
6	24	14
4	24	7
2	24	0
<i>6 wt% cement</i>		
8	0.5	4
8	6	6
8	24	8
6	24	1
4	24	0

In Figure 2 the phase diagram Al₂O₃-SiO₂-CaO is shown with the approximate composition of the bond phases indicated by an x(LCC) or a circle(ULCC). From the compositions in the phase diagram, we see that all ultralow-cement compositions have a theoretically may yield mullite, since all are located within alkemade triangles where mullite is a coexisting phase. For the low cement compositions, the castable with 2wt% microsilica has a composition that is not coexisting with mullite - hence no, or only small amounts of mullite will be expected. Also the one with 4wt% microsilica(LCC) has a composition that should give only small amounts of mullite.

For the sample preparation, prismatic samples were prepared of the various castables, fired at 1400°C for various duration's, before quantitative XRD analyses with respect to mullite was performed.

Table 2 summarizes the samples, conditions and mullite content that was detected.

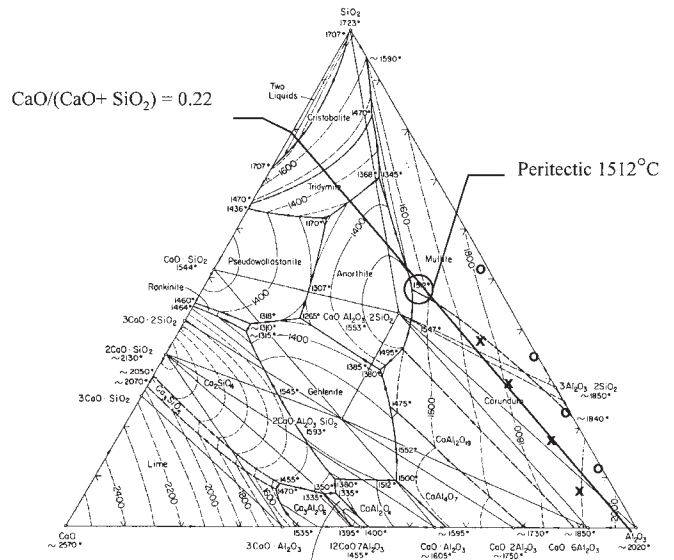


Figure 2: The phase diagram Al₂O₃-SiO₂-CaO after Osborn and Muan.⁵ Approximate compositions of the bond phases are indicated by x(LCC) or o(ULCC). The peritectic at 1512°C and the join from CaO/(CaO+SiO₂)=0.22 towards the alumina corner is also indicated.

The sample with 2 wt% microsilica and 6wt% cement was omitted in the XRD analyses. We see that for a fixed composition, the mullite content is a function of the time at temperature (here 1400°C), the microsilica content and the cement content. Generally, high microsilica and low cement content together with long time at sufficiently high temperature favours formation of mullite. The somewhat quicker mullite formation in the sample with 6wt% microsilica should be attributed to the presence of reactive alumina in the samples with less than 8wt% microsilica. The presence of reactive alumina in castables with less than 8wt% microsilica was in order to maintain a constant particle size distribution also when microsilica is removed from the system.

Like it has been demonstrated earlier, there seems to be a need for a minimum amount of microsilica to get mullite formation. This is dependent on the amount of cement present which is in line with earlier findings. If the low cement castable with 8 and 6 wt% microsilica is considered, one may do simple calculations* of the composition of the remaining glassy phase after 24h. This coincides excellently with the peritectic at 1512°C that is indicated in the phase diagram. The liquid thus contains somewhat less than 6 out of the original 8 (or 6)wt% microsilica, and is another example of mullite formation being hindered by the cement of low cement castables.

* The calculations are performed by calculating the CaO/(CaO+SiO₂) from the cement content and the original microsilica content compensating for the silica in the mullite (24h). Here this fraction equals to 0.22 for both 8 and 6wt% microsilica. If 22% CaO is indicated on the join between CaO and SiO₂ in the phase diagram and a join towards the Al₂O₃ corner is drawn, then this join passes very close to the peritectic at 1512°C. See Figure 2.

For the ultralow cement castables a similar analyses may be made, but here one finds that between 2 and 4wt% of the initial microsilica remains in the residual liquid. Hence, to get mullite formation at all, between 2 and 4wt% microsilica has to be added even to these ultralow cement castables. This result correlates well with earlier findings⁴ where the liquid has been directly analyzed using SEM/EDAX.

Hot strength:

If one starts to measure hot-M.O.R. of such mullite forming alumina-silica castables, a characteristic pattern will appear around 1300°C. Figure 3 shows an example of such hot-M.O.R. measurements, showing the characteristic “dip” that may be seen around 1300°C. At 1300°C the castables are soft giving a plastic fracture, even after 24hours at temperature. Both at 1400 and 1200°C however, fracture is brittle. If strength is monitored as a function of time however, at 1400°C the strengths immediately after heat-up are relatively low, with soft fracture. With time, strength increases and the fracture gets brittle. This behavior is attributed to mullite growing out of a liquid, with simultaneous reduction in the amount of liquid. As these processes are very temperature dependent, involving material transport by diffusion etc., at 1300°C the softness remains even after 24 hours. The softening has traditionally been attributed to liquid formation caused by the cement, but as one found that the same thing happens with 0.5wt% cement, one started wondering whether other factors could contribute. A test sample was then made entirely without cement. And gave the same pattern. Thus the explanation had to be found elsewhere than in the cement alone.

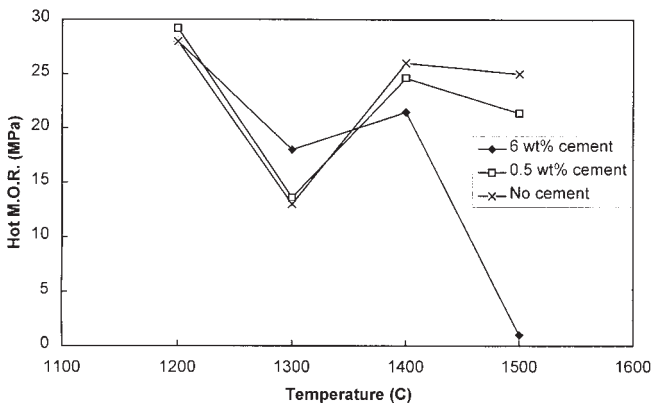


Figure 3: Hot M.O.R. of fused alumina based castables with 8 wt% microsilica as a function of temperature. q=0.25, max. particle size 4mm, 13 vol% water for casting (4.2wt%).

Reverting to Figure 1, the phase diagram Al₂O₃-SiO₂, this tells us that even in very pure systems, the mullite formation goes through some viscous liquid high in silica, and that this metastable system has an indicated eutectic around 1260°C. This coincides well with the

effects we see in Figure 3 with softening i.e. liquid formation between 1200 and 1300°C even for the cement free system. Furthermore as the strengths are reasonably high at 1300°C this implies that the liquid is very viscous - all in line with the expectations from the phase diagram.

This does not exclude that the lime from the cement plays an important role in the mullite formation, it just points out that even without cement, a softening is to be expected in systems consisting of alumina and (micro)silica. If cement is present, the cement is a part of the liquid and gives a liquid with somewhat lower viscosity. The latter effect may speed up the mullite formation as is seen in Table 2. A certain amount of mullite has probably been precipitated in the LCC of Figure 3 at 1300°C which explains why the LCC has higher strength than the other. At higher temperatures, i.e. 1500°C, impurities like CaO will radically lower the hot-strength, cp. Fig 3.

ULCC

Figure 4 shows the hot-M.O.R. of the ultralow-cement castables after 24 hours at temperature, and shows with one exception, 2wt% microsilica, the familiar pattern of softening around 1300°C followed by strengthening around 1400°C. According to the previous discussion, it is unlikely that these castables loose strength at 1300°C by formation of low-melting CaO containing liquids alone. Here the main contributor to the softening probably is in the meta-stable liquid formation in the alumina-silica system. The castable with 2wt% microsilica does not increase in strength because the amount of available silica (2wt%) does not exceed the minimum amount that has been indicated earlier (between 2 and 4wt%). If there is not sufficient silica available, mullite formation will be inadequate or absent. Mullite formation is proportional to the silica content and the hot-strength at 1500°C reflects the amount of mullite that forms.

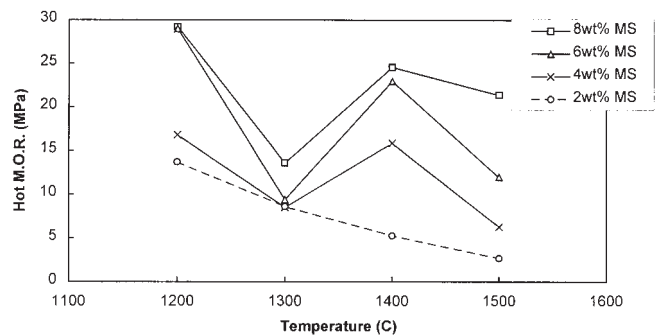


Figure 4: Hot-M.O.R. of ultralow cement (0.5wt% cement), fused alumina based castables as a function of temperature. Castables with different amounts of microsilica. 24hours at temperature. q=0.25, max. particle size 4mm, 13 vol% water for casting (3.8-4.2wt%).

LCC

Figure 5 shows the hot-M.O.R. of the low cement castables as a function of temperature after 24 hours. Here we see that the pattern with softening followed by strengthening at 1400°C seems absent unless 8wt% microsilica is used. With 8wt% microsilica one may get satisfactory hot strength at 1400°C, but because of severe liquid formation in the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ at 1500°C, the strength drops to close to zero. For the other castables, strength at 1400°C is proportional to the microsilica content. None are strong at 1500°C though. For temperatures higher than 1400°C it is advisable to use ultralow cement castables if strength is required.

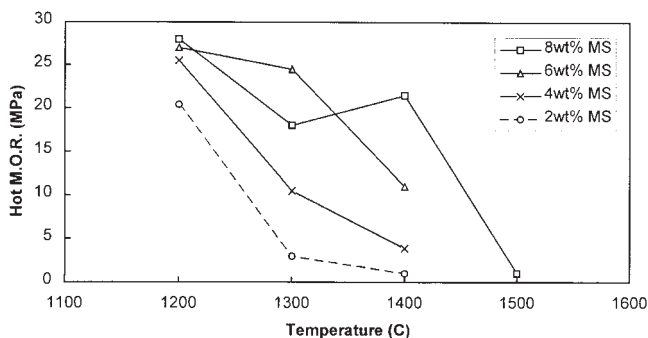


Figure 5: Hot-M.O.R. of low cement (6wt% cement), fused alumina based castables as a function of temperature. Castables with different amounts of microsilica. 24hours at temperature. $q=0.25$, max. particle size 4mm, 13 vol% water for casting (3.8-4.2wt%).

All the results from hot-M.O.R. measurements are in good correlation with the expectations for the earlier discussion, and if we combine strength and mullite formation at 1400°C (Table 2), the following relationship may be drawn (Fig.6).

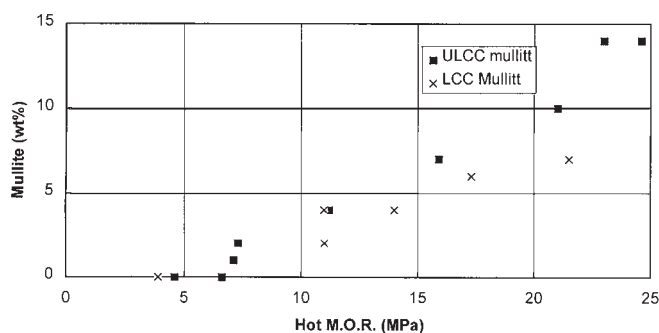


Figure 6: Correlation between strength and mullite content of fused alumina based refractory castables. Temperature 1400°C. Low and ultralow cement compositions. 2-8wt% microsilica, 13 vol% (3.8-4.2wt%) water for casting.

There is a linear relationship between the amount of mullite and strength of the castables investigated here. The low cement castables get somewhat stronger than the ultralow-cement castables for the same mullite content. This may be attributed to the presence of other crystalline components (anorthite) when the cement content is as high as 6wt%. The calcia containing species will not add to strength at 1500°C, actually they are probably responsible for the drastic strength loss that is seen for the LCC's. Figure 6 shows that mullite formation strengthens a castable, which is a desirable property.

Conclusion:

It has been demonstrated that strength at 1400-1500°C of alumina based refractory castables is dependent on the mullite content. The amount of mullite that forms is dependent on the amount of cement but also on the amount of available silica which principally is the amount of microsilica that is added. At 1400°C there is a linear relationship between mullite content and hot strength both for low and ultralow cement castables. Cement does however suppress the mullite formation by making microsilica unavailable. Thus to obtain strong bodies at high temperatures, the following criterion has to be fulfilled; to have as little as possible cement combined with a microsilica content that is sufficiently high.

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