

Mineralogy and Thermodynamics in Refractories

A. Buhr

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Mineralogical approaches including the work with phase diagrams can be very useful tools for the assessment of hot temperature properties and reactions occurring during wear of refractories. It does not require sophisticated computer programs to work with the diagram but only a ruler and a calculator. The paper describes the benefit of phase diagram work in the assessment of high alumina refractories by selected examples from high alumina castables for steel applications. The investigation of wear mechanism from Andalusite based castable as tundish permanent lining is another example provided.

1 Introduction

The basics of thermodynamics are included in the curriculum of almost all material sciences. This includes the principles and function of phase diagrams. However, the lectures often focus only on the theoretical background, which includes rather complicated formulas, but the practical work with the diagrams often falls short. Consequently, many engineers remember the theoretical formula challenges with bad feelings when considering thermodynamic, but never apply practical working with phase diagrams.

For the practical work with the diagrams it requires only the knowledge of the phase rule and some basic principles but no complicated mathematics. This shall be briefly discussed using the ternary (three component) phase diagram $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ as an example [1]. The tools are simple as shown in Fig. 1.

2 Basic principles

The phase rule defines the number of phases and degrees of freedom which apply for a system in equilibrium. It says: $P + F = C + 2$, where P is the number of phases, F is the degrees of freedom (chemical composition, temperature, pressure), and C is the number of components (e.g. $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$). The pressure is relevant for geological systems (kbar range) but for

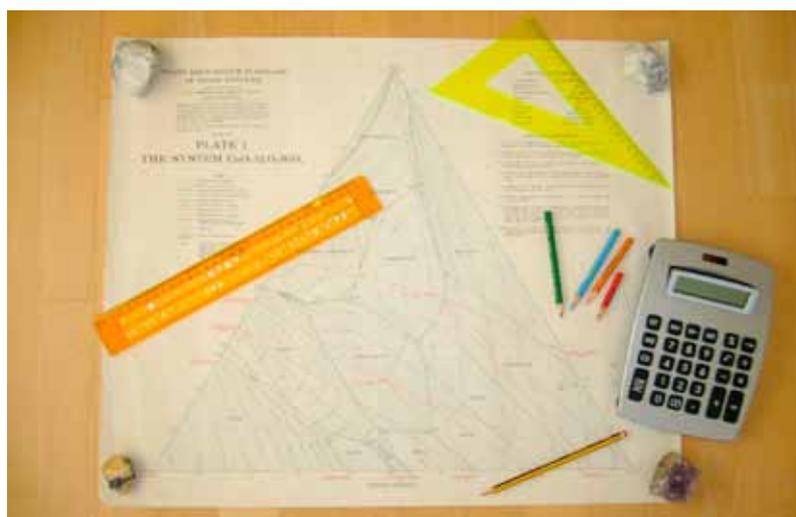


Fig. 1 Tools for the classical work with phase diagrams

most refractory applications it does not vary in relevant ranges and can be considered as constant. The phase rule changes accordingly to $P + F = C + 1$.

In a ternary system ($C = 3$), three phases can occur when the temperature is variable ($F = 1$), for example three solid phases or two solid and one liquid phase ($P = 3$). Four phases, e.g. three solid and one liquid, can only occur in equilibrium, when the temperature is fixed ($F = 0$). These points in a diagram are called "invariant points" and are marked with the specific temperature in the diagram. If more phases occur in a given sample, the

system is not in equilibrium and reactions will occur to achieve the equilibrium stage.

Andus Buhr
Almatis GmbH
60528 Frankfurt
Germany

E-mail: Andus.Buhr@almatis.com
www.almatis.com

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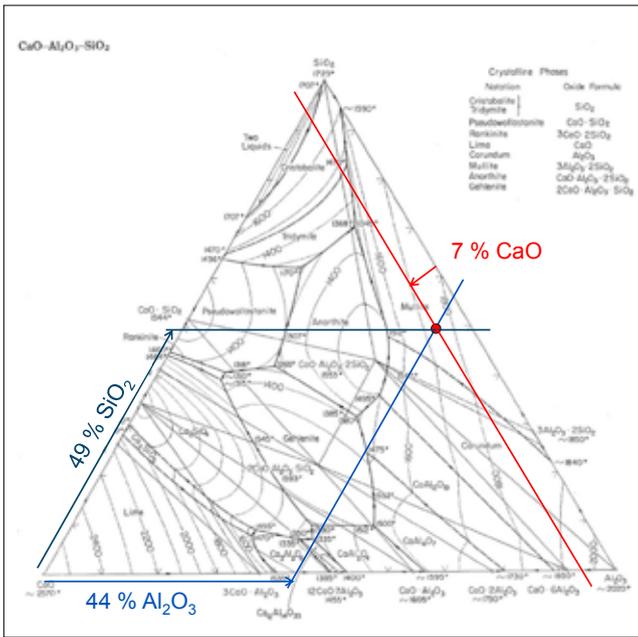


Fig. 2 Position of a given composition in the phase diagram [1] (7 % CaO, 44 % Al₂O₃, 49 % SiO₂)

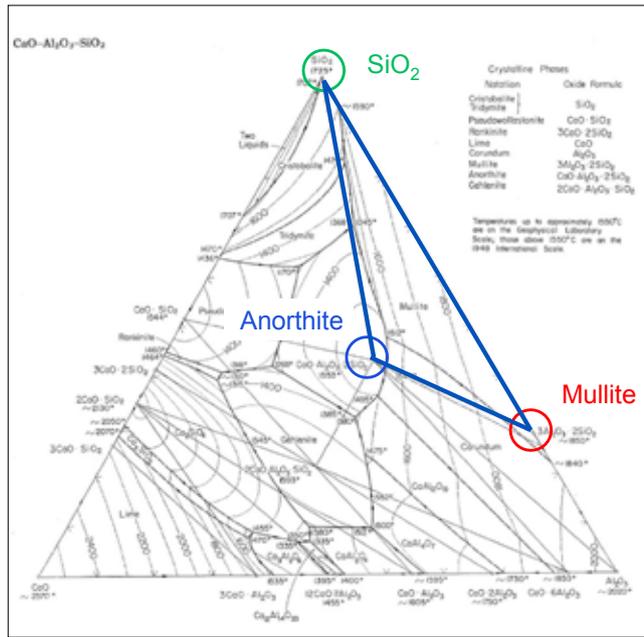


Fig. 3 Single, binary, and ternary compounds and conodes connecting co-existing phases

A few basics for the work with the diagrams will be discussed. Fig. 2 shows how to place a given position in the diagram. The points on straight lines are either single compounds at the edges (e.g. SiO₂), or binary compounds (e.g. mullite 3Al₂O₃ · 2SiO₂), or ternary compounds (e.g. anorthite CaO · Al₂O₃ · 2SiO₂). Straight lines (conodes) show the phase relations in the subsolidus which means all phases are solid, nothing is molten. They connect phases (resp. compounds) which

can co-exist in equilibrium, e.g. SiO₂ – mullite. Triangles connect co-existing phases in a ternary system, e.g. SiO₂ – mullite – anorthite. Only triangles are possible in a ternary system (Fig. 3). The curved lines in the diagram show the primary crystallisation fields of all phases (compounds) in the diagram (Fig. 4). These fields indicate which phase will crystallise first when a liquid of a given composition is cooled down and at which temperature

this will happen. This level of the diagram is therefore named the liquidus. The name of the primary phase is given in each primary crystallisation field. The points where three primary crystallisation fields meet are the solidus. At this temperature, the melting of all compositions inside the according subsolidus will start. If this solidus point lies inside the triangle, it is eutectic melting behaviour (e.g. at 1345 °C for the triangle SiO₂ – mullite

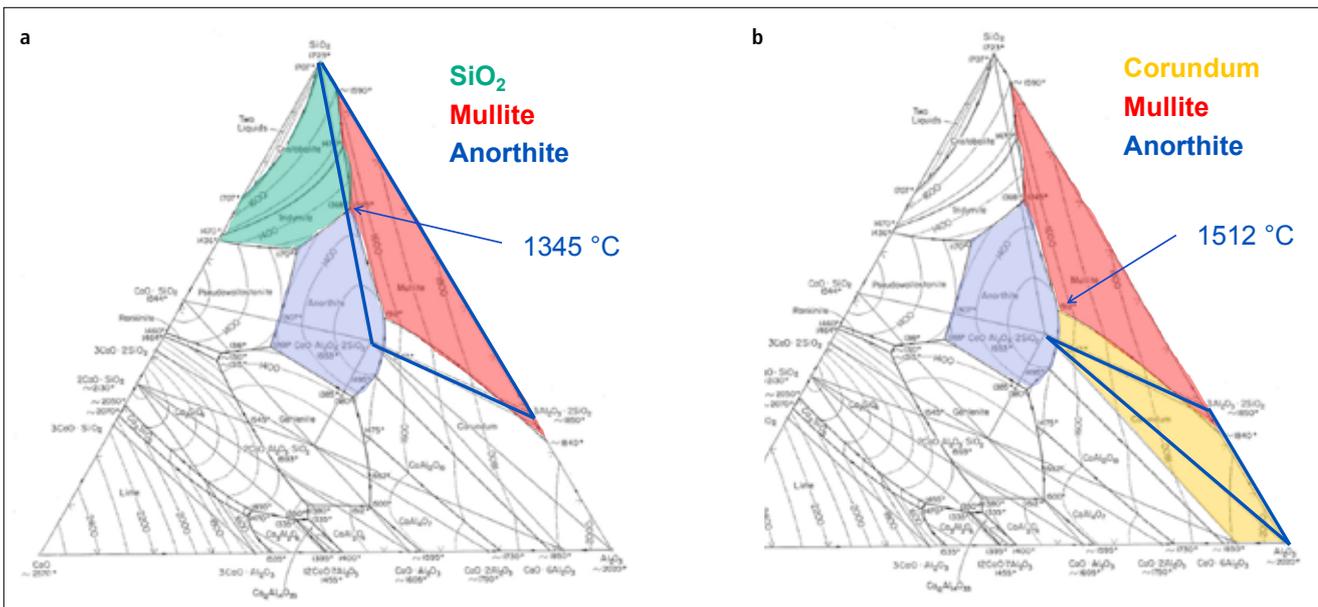


Fig. 4 a–b Primary crystallisation fields and eutectic and peritectic melting behaviour – a) triangle anorthite – SiO₂ – mullite, b) triangle anorthite – mullite – corundum

– anorthite), if it lies outside, it is peritectic melting behaviour (Fig. 4). In case of peritectic melting behaviour compounds do not simply melt but transform into a higher melting compound of this triangle and a liquid phase, e.g. mullite + anorthite = corundum + liquid at 1512 °C (Fig. 4).

3 Hot properties of high alumina castables

Fig. 5 shows the constituents of high alumina castables, and Fig. 6 shows the compositions of 48 high alumina castables in the phase diagram. The melting behaviour from phase diagram evaluation of these castables was compared with the hot properties such as creep resistance and hot crushing strength [2].

Here, two corundum and two andalusite castables are used as examples. Their composition is given in Tab. 1.

The theoretical solidus temperature is derived from the phase diagram and gives the onset of melting. The presence of even small amounts of liquid phase has a significant effect on the thermomechanical properties of the castables, because it works as a lubricant in the microstructure and has an immediate effect on the strength at high temperatures. This shows in the hot crushing strength and the creep resistance at high temperature.

The cement phases in high alumina castables react with the other components in the temperature range from 1100–1500 °C to form higher alumina calcium-aluminates such as CA₂ and CA_v, or anorthite if SiO₂ is present. These sintering reactions also show in refractoriness under load testing unless the samples are pre-fired at high temperature as can be seen in Fig. 7. At 1000 °C pre-firing, the corundum low cement castable shows an intermediate softening before the cement sintering reactions have taken place. Afterwards, the creep rate at 1500 °C is identical when compared to 1500 °C pre-firing.

The samples in this study [2] were normally pre-fired for 12 h at 1000 °C in order to simulate the conditions in steel ladles and tundishes which are typically pre-heated in this temperature range.

The castable corundum 1 has a solidus temperature of 1875 °C, whereas the solidus of corundum 2 is considerably lower at 1512 °C due to the addition of silica fume (about 3,5 %) in the formulation (Fig. 8).

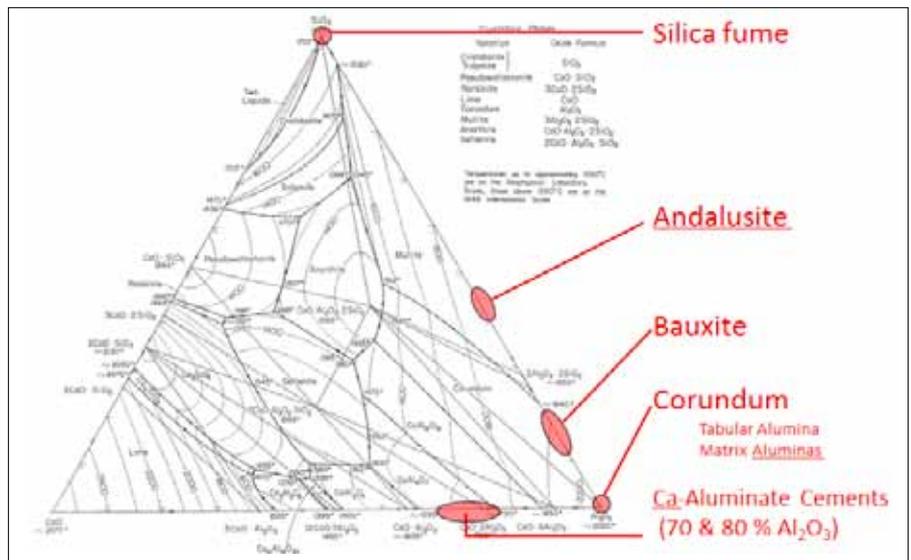


Fig. 5 Constituents of high alumina castables

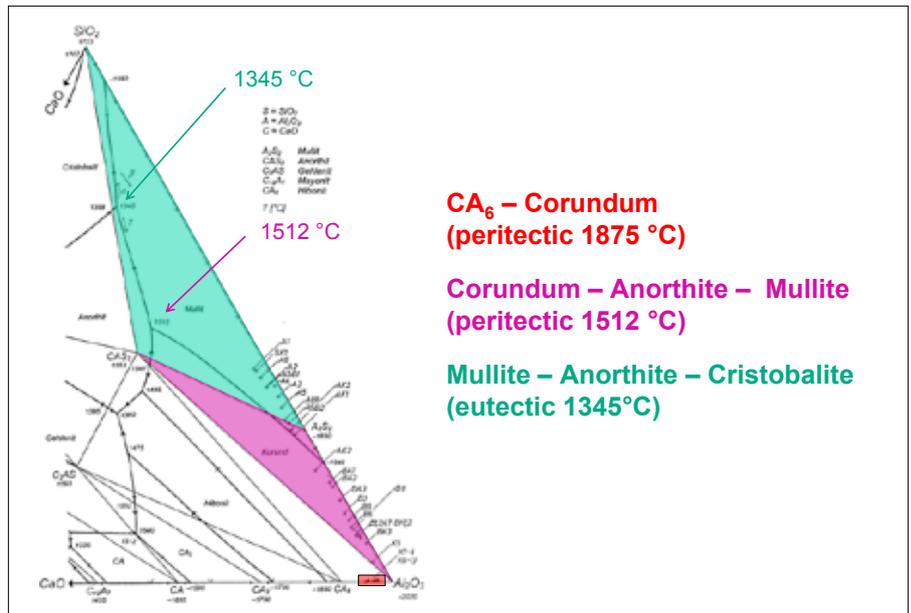


Fig. 6 Position of high alumina castables and according equilibrium phase assembly

Tab. 1 Composition and hot strength of high alumina castables

	Andalusite		Corundum	
	1	2	1	2
SiO ₂ [mass-%]	38	36		3,6
Al ₂ O ₃ [mass-%]	58	61	97	93
TiO ₂ [mass-%]				0,7
CaO [mass-%]	2,3	1	2,5	1,5
Alkalies [mass-%]	0,3	0,3	0,3	0,2
Theoretical solidus temperature [°C]	1345	1345	1875	1512
Hot Crushing Strength @ 1500 °C [MPa]	1	11	48	0
Silica fume	+	+		+
Matrix aluminas		+	+	
Theory vs. practice	OK	? → OK	OK	OK

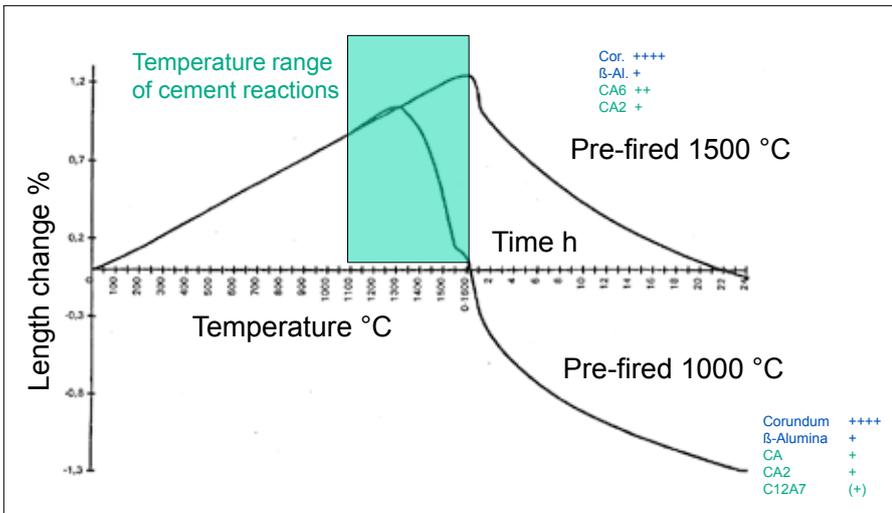


Fig. 7 Impact of pre-firing temperature on creep under compression of a corundum low cement castable (0,2 MPa, 1500 °C)

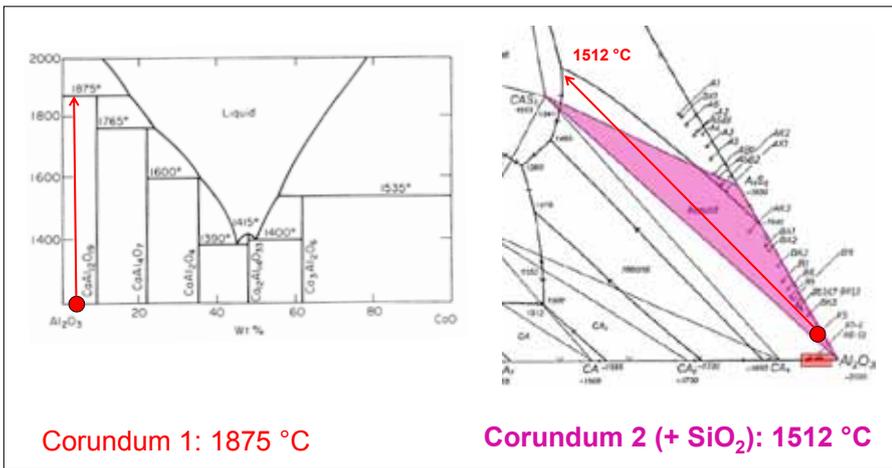


Fig. 8 Solidus temperatures for corundum low cement castables 1 and 2

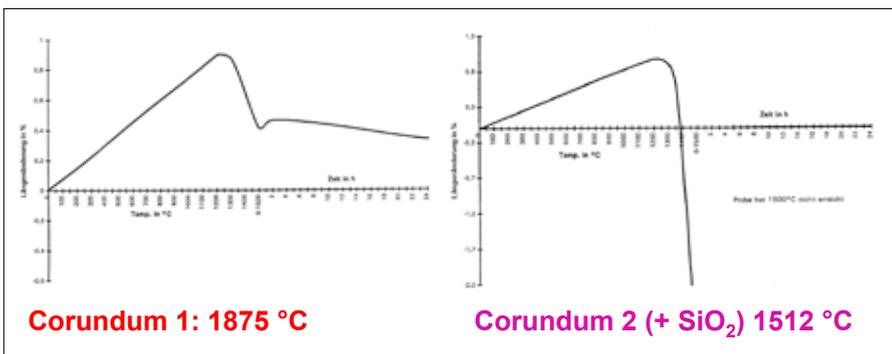


Fig. 9 Creep under compression of corundum low cement castables (0,2 MPa, 1500 °C, 24 h)

The creep under compression at 1500 °C of corundum 1 shows a stable behaviour whereas corundum 2 has no creep resistance at that temperature due to liquid phase formation (Fig. 9). This is in line with the theory especially when the small amounts of additional contaminants such as alkali-

lies and the 0,7 % TiO₂ for corundum 2 are taken into account. TiO₂ plus Na₂O form a liquid already at 1300–1350 °C [3, 4]. Andalusite is a metamorphous mineral formed under pressure at elevated temperature in the earth crust. It is not stable under atmospheric pressure and transforms

into mullite and SiO₂ when fired at temperatures above 1200 °C. Therefore, mullite is the phase to be considered for the phase diagram evaluations in this paper.

Both andalusite low cement castables 1 and 2, should show a solidus at 1345 °C due to their composition in the triangle SiO₂–mullite–anorthite (Fig. 10). However, the thermomechanical testing shows a different picture (Fig. 11). The behaviour of andalusite 1 is in line with the theory as it shows no creep resistance at 1500 °C. In contrast, andalusite 2 shows an unexpected creep resistance after the cement reactions have taken place. This seems to be in conflict with the theory from the phase diagram, because the onset of melting should be at 1345 °C. The obvious discrepancy between the theoretical and practical behaviour of andalusite 2 can be explained when the matrix composition of the castables is taken into account instead of focussing only on the bulk composition of the castables. The matrix composition is of special importance because some constituents of the castables only occur in the matrix fines, such as the cement and the fine fillers silica fume and matrix aluminas.

Andalusite 1 and 2 are quite different in the matrix composition, because andalusite 2 has an addition of matrix aluminas including reactive alumina. The matrix has been defined as the particle size fraction

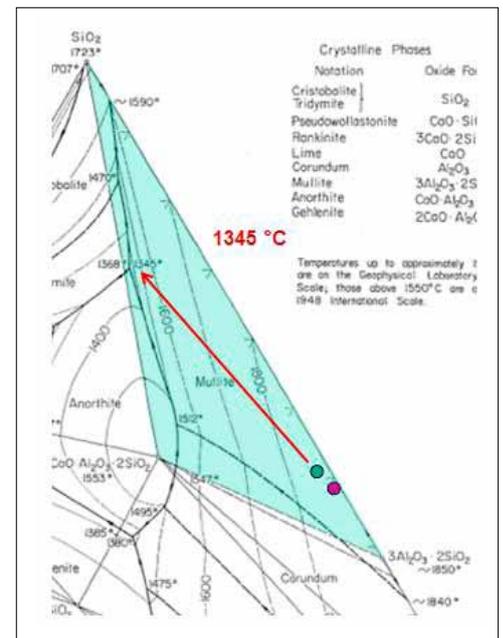


Fig. 10 Position of andalusite low cement castables 1 and 2, solidus temperature for both at 1345 °C

below 0,12 mm, because it enabled an easy screening for analytical purposes.

Fig. 12 shows the position of the matrix composition of castables andalusite 1 and 2. Whereas the matrix composition of andalusite 1 remains in the triangle SiO₂ – mullite – anorthite (solidus at 1345 °C), the matrix composition of andalusite 2 shifts into the triangle corundum – mullite – anorthite (solidus at 1512 °C).

The addition of matrix aluminas leads to a higher solidus temperature for the matrix when compared to the bulk composition of andalusite castable 2. Poirier et al. [5] have shown that the silica released during the mullitisation of andalusite forms a highly viscous molten phase inside the previous andalusite crystals at elevated temperatures. This liquid phase does not interfere with the matrix around the previous andalusite crystals, especially when this matrix itself has a high refractoriness due to the addition of reactive matrix aluminas. This explains the unexpected high creep resistance and hot crushing strength at 1500 °C (Tab. 1) of andalusite castable 2.

4 Wear mechanism of andalusite tundish castable

The wear mechanism of tundish castable was investigated at the Dortmund steelworks [2]. The size of the tundish was about 40 t. Fig. 13 shows the lining with

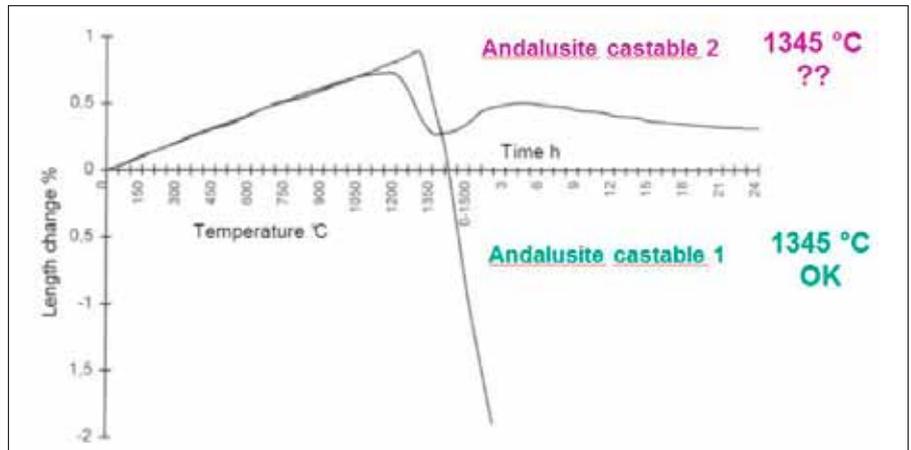


Fig. 11 Creep under compression of andalusite low cement castables 1 and 2 (0,2 MPa, 1500 °C, 24 h)

160–170 mm andalusite low cement castable as permanent lining and 30–50 mm wet sprayed, water glass bonded magnesia-olivine wear lining. The wear lining was removed through tilting the tundish upside down after each casting campaign of typically 4 heats, sometimes up to 15 heats. Afterwards, the tundish cooled down to below 100 °C before a new wear lining was applied.

Once per year after about 1200 heats, the tundish castable was replaced. The remaining thickness was typically between 100–150 mm but in higher challenged areas such as in the impact zone and around the well blocks it could be down to 80–90 mm.

Samples from four different tundishes were taken for investigation of the wear mechanism. The residual cold crushing strength was between 50–70 MPa, comparable to the new castable pre-fired for 12 h at 1000 °C in the laboratory. The mechanical stresses due to tilting the tundish and thermal cycling between each campaign are an important challenge to the tundish castable. However, mechanical and thermal spalling could be excluded as major wear mechanism due to the high thermal shock resistance and sufficient mechanical strength of the low cement andalusite castable. This investigation focuses on the chemical-mineralogical reactions at the hot face of the

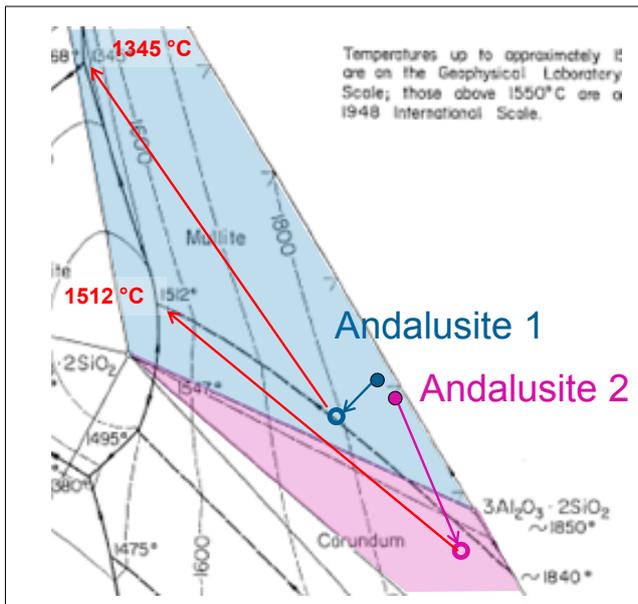


Fig. 12 Composition of andalusite castables 1 and 2, solid points are bulk composition, circles are matrix composition as size fraction below 0,12 mm

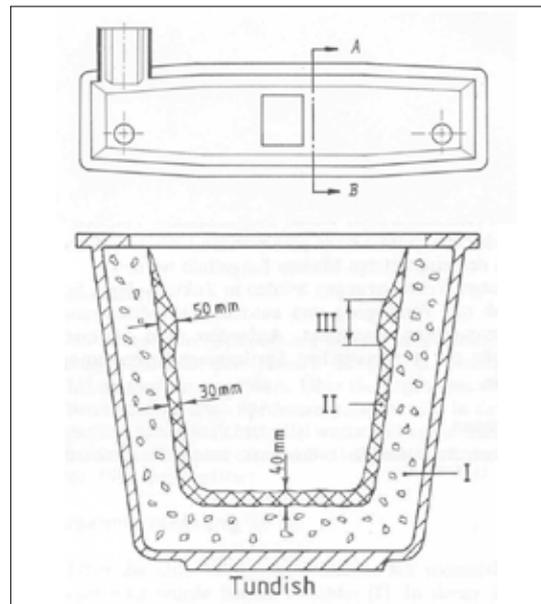


Fig. 13 Tundish with andalusite castable permanent lining (I), and wet sprayed basic wear lining (II-III)

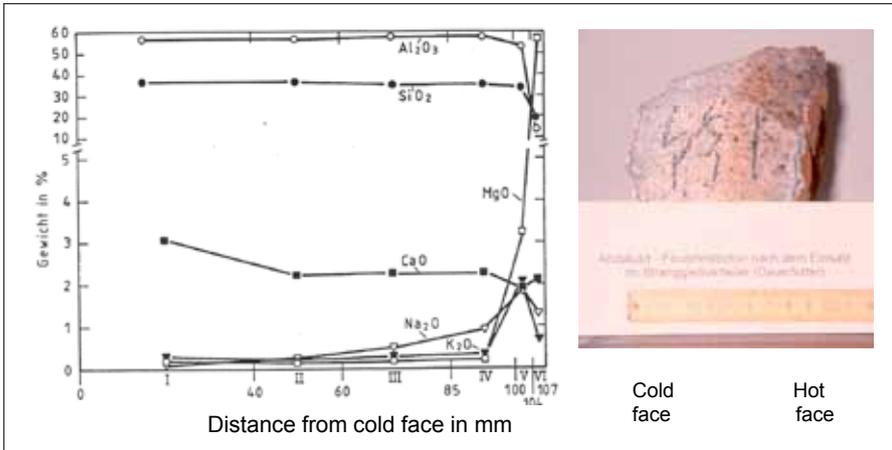


Fig. 14 Tundish andalusite castable after use (1172 heats) with adhering wear lining layer; chemical composition of different layers

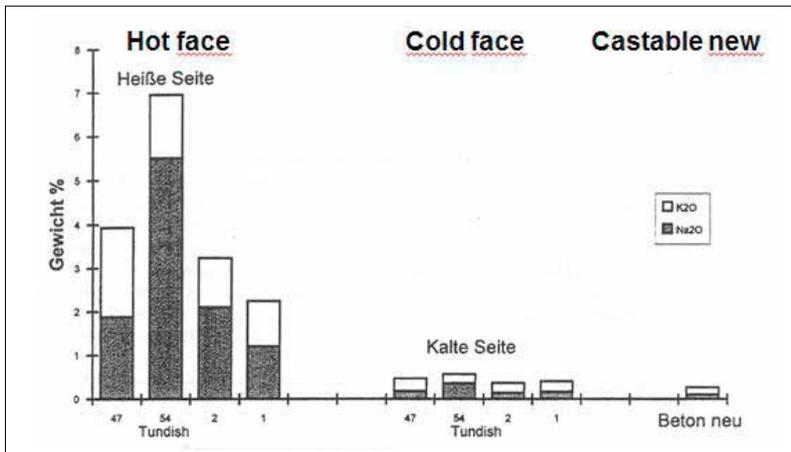


Fig. 15 Alkali enrichment at hot face of andalusite tundish castables after use

tundish castable, which eventually lead to a reduction of lining thickness. Fig. 14 shows a sample from tundish castable after use with an adhering layer of sintered magnesia-olivine wear lining. Normal-

ly such sintering between the basic wear lining and the tundish castable shall not occur and it indicates too high temperature in the contact zone due to insufficient lining thickness of the spray mix or extended cast-

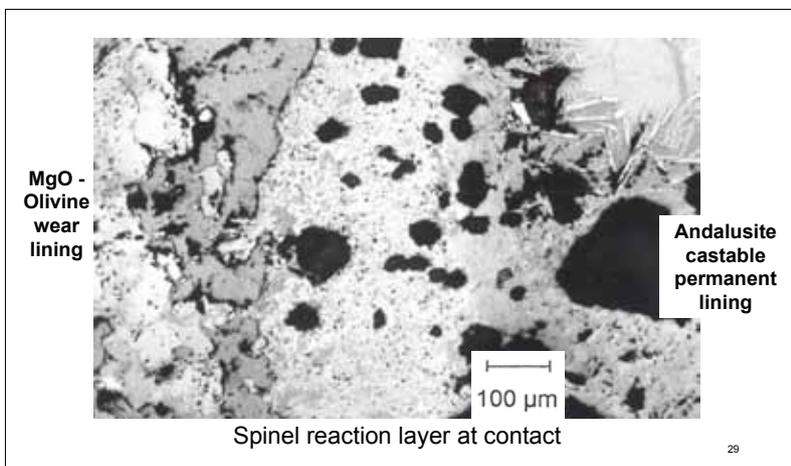


Fig. 16 Spinel formation on andalusite castable

ing times due to an abnormally long tundish sequence without adjusting the spray mix thickness in advance. The chemical-mineralogical composition was measured for different layers. At the hot face of the tundish castable the andalusite was transformed to mullite which indicates temperatures in the range of 1300–1400 °C in that area. In general higher alkali contents in the range of 2–7 % were found in a 3–7 mm thick layer at the hot face of the castable samples (Fig. 15). This is much more than originally contained in the tundish castable (0,2–0,3 % K₂O and Na₂O) and the water glass bonded spray mix (around 0,4 % Na₂O and K₂O). X-ray diffraction (XRD) showed spinel (MgAl₂O₄) in the reaction layer between castable and spray mix, and nepheline ([Na, K]AlSiO₄) in the alkali enriched hot face layer of the castables.

The spinel reaction layer formed during sintering between spray mix and castable is about 300 µm thick (Fig. 16). As shown in the ternary system MgO–Al₂O₃–SiO₂ [1], mullite and periclase (MgO) are not compatible and react to spinel and cordierite (Fig. 17) respectively MgO-containing alkali-aluminium-silicate glassy phase due to the high alkali contents present in the current case and measured by electron microprobe analysis.

Independent from the spinel formation, which only occurs in cases of sintering taking place between the castable and the spray mix, the mullite in the hot face layer is decomposed by the alkalis enriched in this zone. It reacts to corundum (bright ledges in Fig. 18), and nepheline as detected by XRD and electron microprobe analysis respectively a glassy phase of similar composition at elevated temperature during service. Fig. 19 shows the reaction in the ternary system Na₂O–Al₂O₃–SiO₂ [1]. The sample containing 7 % alkalis in the hot face layer of the castable shows complete decomposition of the mullite and just corundum ledges in a matrix of nepheline composition (Fig. 20). In the next layers towards the cold face of the castable, alkali contents are quickly decreasing and at the cold face the alkali contents are the same as for the new castable. At lower alkali contents, the matrix besides mullite (or andalusite transforming into mullite) consists of anorthite respectively a glassy phase with similar composition.

The chemical-mineralogical wear mechanism of the tundish castable can be summarized as alkali diffusion from alkalies in the spray mix at temperatures around 1500 °C towards the cold side into a thin layer of less than 10 mm at the hot face of the castable. Here, the alkalies accumulate, first due to solid solution formation with the anorthite in the matrix and then through reaction with the mullite to corundum and nepheline at higher alkali contents. This reaction is accompanied with a volume expansion of about 20 %, which could lead to spalling (alkali-bursting).

However, no evidence for such spalling was found in the samples from the tundish castables, even for alkali contents as high as 7 % in the hot face, where mullite was completely decomposed. At service temperatures in the tundish the nepheline forms a glassy phase which releases the stresses necessary for the occurrence of alkali-bursting.

A second wear mechanism is the spinel formation through intense sintering with the basic spray mix, which only occurs occasionally when temperature in the contact between castable and spray mix becomes too high. When removing the wear lining after use, this strongly sintered and densified layer will often be removed as well, leading to reduction of castable thickness. The sample shown in Fig. 14 with adhering spinel reaction layer and residual sintered spray mix can be considered an exceptional case here as the layer sticks to the castable.

Calculations have shown that such strong sintering and spinel formation cannot occur during every casting sequence of the tundish. Otherwise long lining life of one year or about 1200 heats, respectively 300 casting sequences would not be possible. Nevertheless, when comparing the effect of both wear mechanisms it is the strong sintering accompanied with spinel formation between the layers which finally leads to wear of the tundish castable requiring a renewal each year.

5 Conclusion

For the practical work with phase diagrams no sophisticated calculations and theory are required. The understanding of a few basic principles and sufficient training during the scientific education provides the

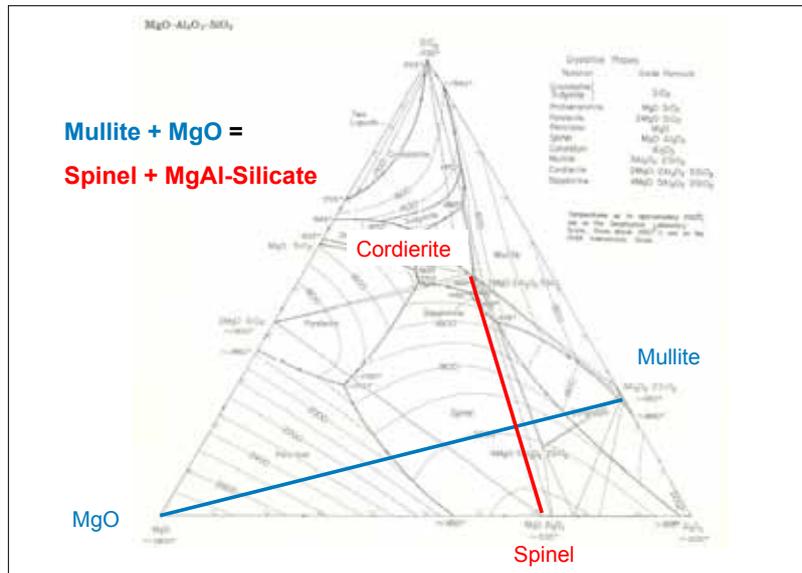


Fig. 17 Mullite decomposition through MgO

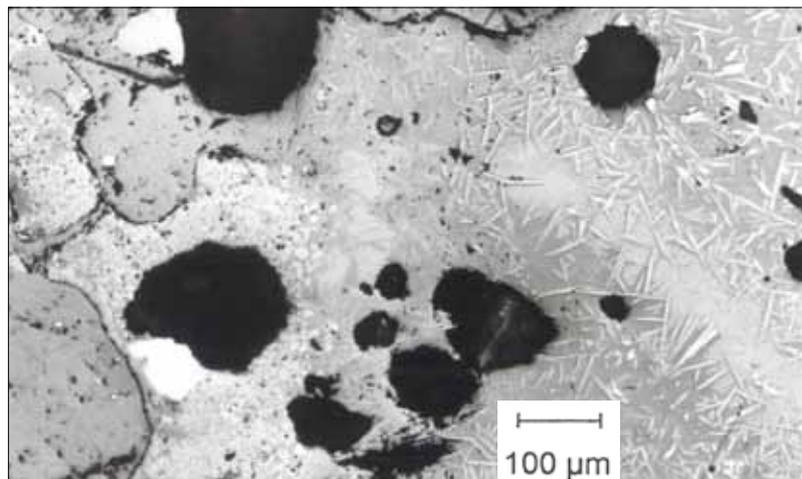


Fig. 18 Mullite decomposition through alkali attack at hot face from tundish castable

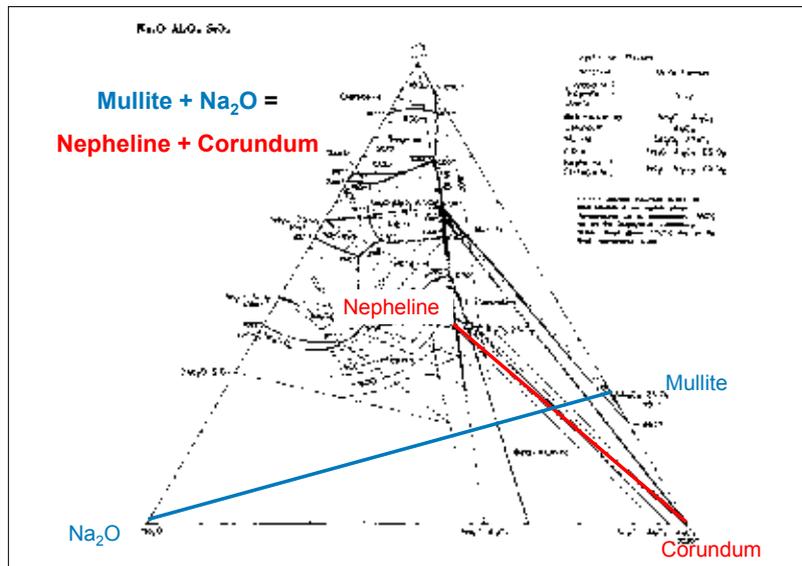


Fig. 19 Mullite decomposition by alkalies (here Na₂O)

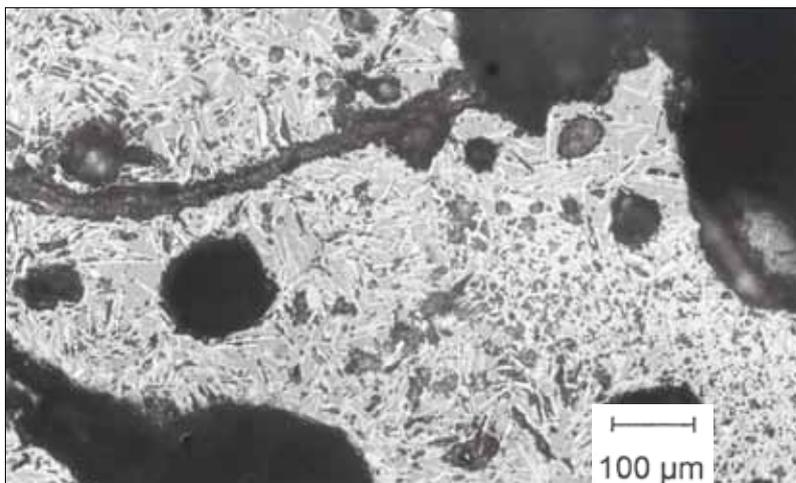


Fig. 20 Mullite completely transformed, corundum ledges in matrix of nepheline composition

necessary skill set for refractory engineers to apply work with phase diagrams in their daily work. Phase diagram evaluations can be very helpful to assess the behaviour of refractories at high temperatures. This includes also their stability in contact with other materials e.g. slags or reactions between different layers in a lining, which has been briefly discussed for a tundish lining in this paper.

Each refractory engineer and metallurgist should be able to do work with phase diagrams. The use of modern computer pro-

grams such as FactSage® [6] is convenient and, given a reliable data base, extends the thermodynamic work in more complex systems or areas, where no phase diagrams are available for the practical approach briefly described in this paper. However, they should not simply replace the basic understanding of the work with phase diagrams. Without any plausibility check, the results of such modern tools can be misleading.

The matrix composition of refractories is often defining the thermomechanical behaviour, because the matrix contains all the

relevant chemical components. Therefore a special focus should always be given on the matrix composition.

The addition of matrix aluminas, especially high performance reactive aluminas improves the thermo-mechanical properties of high alumina refractories and enhances their overall performance in application.

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