

Spinel: In situ versus Preformed – Clearing the Myth

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The paper discusses the difference in the formulation concepts of alumina-spinel (spinel containing) and alumina-magnesia (spinel forming) castables and the influence on their physical properties. The individual property profile will be discussed with regard to the requirements on refractory lining materials for the different zones of a steel ladle.

1 Introduction

Since beginning of the 1990s alumina-spinel castables are widely used as steel ladle lining below the slag line and as pre-cast shapes like purging plugs and well blocks. A great deal of studies has been conducted on the effect of spinel-types, spinel grain size and amount of spinel on the chemical and mechanical resistance of alumina-spinel castables [1–5]. In the past ten years the castables used for the ladle side wall have progressively changed from alumina-spinel castables to alumina-magnesia types. One driver for this change was the consideration that a finer spinel, like the in situ formed spinel in alumina-magnesia castables would bring better corrosion and penetration resistance than a pre-reacted spinel. Cost pressure and the idea to use cheaper raw materials like alumina and magnesia that form spinel during use instead of pre-reacted spinel was another reason in favour of spinel forming castables. Today, both concepts are success-

Tab. 1 Requirements on refractories in different zones of a steel ladle

	Ladle side wall	Ladle bottom	Impact area (pad)	Purging plug/well block
Thermal stability	++	++	++	+++
Thermo-mechanical stability	+	+++	+++	+++
Erosion resistance	+	++	+++	+++
Corrosion resistance	++	++	+++	++
Potential for stress relaxation (thermal shock resistance)	+++	+++	+++	+++

fully in use. The purpose of this paper is to discuss castables designed with pre-reacted spinel and those with alumina-magnesia and to link their individual property profile to the requirements for refractories in a steel ladle.

2 Requirements on refractories for steel ladle linings

The impact of secondary metallurgy on refractory linings and the different wear mechanisms of a monolithic ladle lining are described by Buhr [6] and Alasaarela/Eitel [7]. The requirements on refractory materials used for ladle linings can be summarized as follows:

High thermal stability

- increased tapping temperature into ladle
- exothermic reactions by thermal heating and alloying
- hot spots from electrodes in ladle furnace operation
- oxygen cleaning of well blocks and purging plugs

High thermo-mechanical stability

- increased steel residence time in the ladle
- ladle movements like tilting and hard placing down
- elastic deformation of the steel shell during ladle transport

High erosion resistance

- intense stirring in the ladle
- vacuum (tank) degassing
- tapping conditions (height/temperature)

High corrosion and penetration resistance

- various aggressive slag compositions
- vacuum degassing

- metal bath infiltration in cracks
- Potential for stress relaxation/“Elasticity”
- elastic deformation of the steel shell caused by charging of liquid steel
- deformation of the ladle during transport
- heat shock when charging the ladle
- thermal shock when cold stirring gas passes the purging plug
- Thermodynamic stability

- stability of refractory oxides against reduction by alloying or desoxidation compounds.

Depending on the steel ladle zone the predominant wear mechanisms vary. Tab. 1 gives an overview of the wear mechanisms per ladle zone and their importance for the selection of the best suited refractory product. The sidewall for example has usually less mechanical stress due to erosion (except when there is heavy stirring) whereas the bottom, especially the impact area and the area around the purging plug, suffer strong erosion due to the steel movement. Volume- and thermal stability are the main requirements for the bottom to avoid cracking and accelerated wear due to spalling whereas a controlled volume expansion of the sidewall lining is favourable because it will brace the lining and thus reduce the opening of cracks. For the formulation of a refractory castable some of the requirements described are hard to achieve in one product. As a consequence, several optimized refractory materials are in use today that responds to the different wear pattern. High alumina castables with spinel and/or magnesia addition are the most common monolithic lining today and their differ-

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Tab. 2 Properties of spinel, periclase and corundum [9]

	Spinel MgAl ₂ O ₄	Periclase MgO	Corundum Al ₂ O ₃
Density [g/cm ³]	3,58	3,58	3,99
Thermal conductivity [W/m·K]	5,9	7,1	6,3
Thermal expansion coefficient [Δl/l · K·10 ⁻⁶]	7,6	13,5	8,8

ent properties with regard to the requirements described before will be discussed in the following.

3 Why spinel?

The general formula of the spinel group is AB₂O₄, where A represents a divalent metal ion such as magnesium, iron, nickel, manganese and/or zinc, and B represents trivalent metal ions such as aluminium, iron, chromium or manganese. The most common spinel and the only compound in the binary system MgO–Al₂O₃ is Magnesium-aluminate spinel (MgAl₂O₄) with a stoichiometric ratio of 71,8 % Al₂O₃/28,2 % MgO. Magnesium-aluminate spinel is a highly refractory material, with a melting point of 2135 °C. A strong feature of all spinels is the tendency to substitutional solid-solutioning, where large percentages of one or both of the spinel components may be substituted by others of

the group. For the Magnesium-aluminate spinel both magnesium and aluminium cations can be replaced by others with similar size. Additionally, the MgAl₂O₄-structure shows an increasing phase region with increasing temperature, especially towards higher alumina contents. The electrochemical balance is achieved by vacancies at metal cation and oxygen-anion sites in the structure. This allows the production of alumina-rich spinels like AR 78 and AR 90. When produced at high production temperatures up to 1900 °C the alumina-rich spinel phase can be maintained by rapid cooling. Due to these vacancies in the crystal structure, pre-reacted, alumina-rich spinel has the capability to absorb FeO and consequently retard the infiltration of slag. This is an important feature and a major factor in the advantage of spinel containing mixes for resistance to steelmaking slag [8].

Tab. 2 shows a comparison of properties of spinel and its compounds, MgO and Al₂O₃. The decrease in density, respectively the volume increase of 7,9 % as result of the spinel formation from the compounds is a characteristic that needs consideration when formulating castables with in-situ spinel formation.

4 In-situ versus preformed spinel

The formulation of castables containing pre-reacted spinel and that of spinel forming, alumina-magnesia castables require in general different approaches whereby the formulation of alumina-magnesia-castables is in general more challenging. The use of magnesia, as one of the reactants for the spinel-formation in castables, often causes difficulties like poor flow or quick setting because of the hydration of the magnesia. Furthermore the volume expansion due to the hydration may lead to cracking during the drying of the castable which is especially critical when producing pre-cast shapes. The in situ formation of spinel is also linked with a strong volume expansion that needs to be controlled. A too high expansion would lead to mechanical stresses and thus spalling of the lining. Extensive work was done in the frame of the FIRE project [10–14] to develop methods to

Tab. 3 Spinel containing and spinel forming test castables and mixtures thereof

	SP	SF	SP-SF	SP-SF-NC
	Spinel	Spinel forming	Spinel + spinel forming	Spinel + spinel forming
Mix	LCC	ULCC	ULCC	NCC
Components [%]				
Coarse 0,5 - 6 mm				
Tabular Alumina T60/T64	50	60	50	55
Matrix <0,5 mm				
Tabular Alumina T60/T64	–	15	–	–
Spinel AR 78	25	–	20	10
Alumina	20	16,5	25	30
Dead burnt magnesia <90 μm	–	5	1,95	2,5
Microsilica Elkem 971 U	–	0,5	0,5	0,5
Cement CA-14 M	5	3	2,5	–
Alphabond 300	–	–	–	3
MgO content total	5,5	5,0	6,3	4,5
H ₂ O	5,0	5,5	5,0	5,3
Open Porosity [vol.-%]				
After drying at 110 °C	13,0	14,5	14,5	14,8
After firing at 1000 °C	13,6	15,9	16,1	17,9
After firing at 1500 °C	17,7	17,5	15,3	16,2

control the expansion behaviour of alumina-magnesia castables. Beside the right fineness for the reactive components alumina and magnesia, the addition of fumed silica in a range of 0,5-1 % is commonly applied to counterbalance the expansion and to achieve good workability of the castables. Most of the commercially available spinel-forming products follow this route. Castables containing pre-reacted spinel do neither have this expanding behaviour nor any unwanted hydration and can thus be formulated without fumed silica addition. The influence of these different formulation concepts on the properties of the castables are described based on four different kinds of spinel castables (Tab. 3). The castables chosen for comparison test are:

- spinel containing low cement castable (SP),
- spinel forming ultra low cement castable (SF),
- spinel containing plus spinel forming ultra low cement castable (SP-SF),
- spinel containing plus spinel forming no cement castable (SP-SF NCC).

Castable SP (Spinel containing) was formulated with an addition of 25 % pre-reacted spinel type AR 78 in the matrix (<0,5 mm). The spinel forming castable contains 5 % dead burnt magnesia $\leq 90 \mu\text{m}$ thus leading to a theoretical spinel formation of 22 %. In practical applications, a combination of spinel formation with pre-reacted spinel is also widely used. The two remaining castables belong to this group of products, one with an ultra low cement bond (SP-SF) and the other with Alphasbond as binder (SP-SF-NC). A MgO-content of 4,5–6,3 % respectively spinel content in the range of 16–25 % provides the best balance between corrosion and penetration resistance according to literature [1]. Practical experiences over the past 20 years have also proved this. An addition of 0,5 % of fumed silica was made for the castables with in situ spinel formation (SF, SP-SF, SP-SF-NC) to control the expansion whereas the castable with only pre-reacted spinel (SP) was formulated without fumed silica. The water addition was kept in the same range for all castables to achieve a comparable porosity level. The castables were fired at 1000 °C and 1500 °C to measure their permanent linear change (PLC), open porosity and cold mechanical strength (CCS, MOR). The samples for the measure-

Tab. 4 Expansion reactions of cement bonded, spinel forming castables [10, 15, 16]

Temperature [°C]	Reaction	Permanent Dimensional change after 5 h hold [%]	
		Volume	Linear
1100–1400	$\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4$	+7,9	+1,99
1100–1300	$\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 2\text{Al}_2\text{O}_3$	+13,6	+4,76
1400–1650	$\text{CaO} \cdot 2\text{Al}_2\text{O}_3 + 4\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 6\text{Al}_2\text{O}_3$	+3,01	+1,01

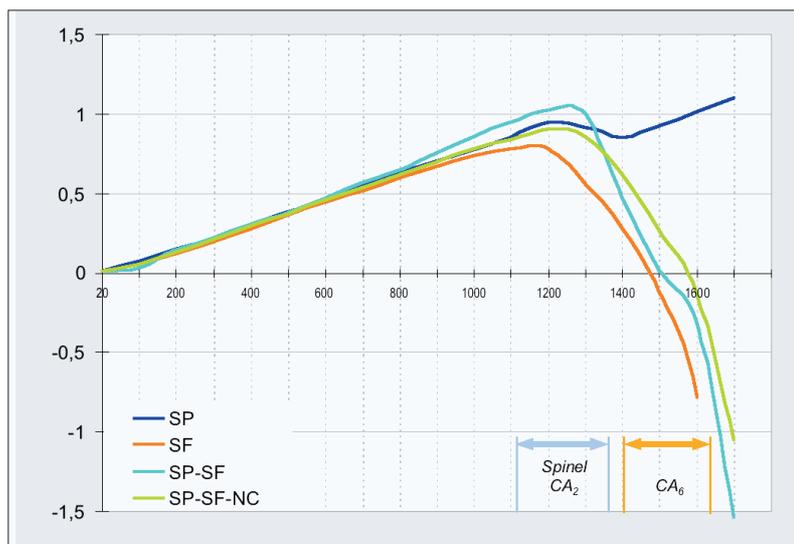


Fig. 1 Refractoriness under load (RUL) of spinel containing and spinel forming castables and mixtures thereof. Samples prefired at 1000 °C/5 h respectively 1200 °C/5 h for SP-SF-NC

ment of refractoriness under load (RUL) and hot modulus of rupture (HMOR) and for the corrosion test were prefired at 1000 °C except for the castable with Alphasbond-bonding which required prefiring at 1200 °C to achieve sufficient strength for sample preparation.

4.1 Thermo-mechanical behaviour

Cement bonded alumina-magnesia-castables show three expansive reactions related to new mineral formations (Tab. 4). The expansion of the spinel reaction is counterbalanced by a liquid phase formation due to the addition of fumed silica. But even a small amount of fumed silica has a considerable impact on the refractoriness under load (RUL). As shown in Fig. 1 all castables with silica addition show a beginning of softening at a temperature of around 1200 °C. The silica-free formulation with pre-reacted spinel in contrary has no softening effect. The slight drop in the RUL-curve in the temperature range from 1250 to 1400 °C is not a softening due to liquid phase formation but can be

explained by a not completely developed (cement) matrix. The sample prefired at 1000 °C has not sufficient time during heat-up in the RUL test (heating rate 5 K/min) to form a strong CA₂-structure. The same test with samples prefired at higher temperature does not show this slight deformation in the temperature range from 1250 to 1400 °C. The expansion at temperatures >1400 °C is caused by the CA₆-formation and can be influenced by the cement amount in the mix. The spinel forming, spinel containing castable (SP-SF) reaches its d_{max} at 1250 °C whereas the spinel forming castable (SP) shows the lowest d_{max} at 1150 °C. This is in line with the theory. The CaO-MgO-Al₂O₃-SiO₂ phase diagram shows that the temperature of onset of melting for the castable compositions concerned would decrease from above 1820 °C for SiO₂-free formulations to below 1400 °C for SiO₂-containing formulations [16]. The degree of softening depends on the composition of the matrix fines, their reactivity and the position in the phase diagram. The softening of the cement free mix

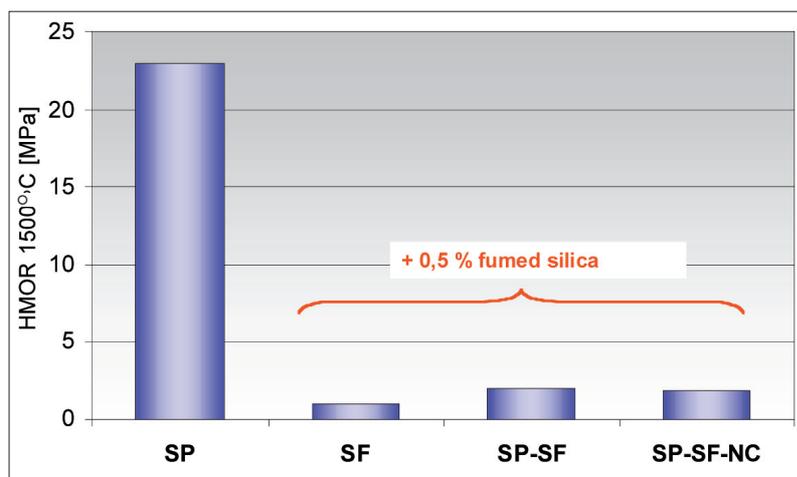


Fig. 2 Hot Modulus of Rupture (HMOR) at 1500 °C of spinel containing and spinel forming castables and mixtures thereof. Samples prepared at 1000 °C/5 h respectively 1200 °C/5 h for SP-SF-NCa

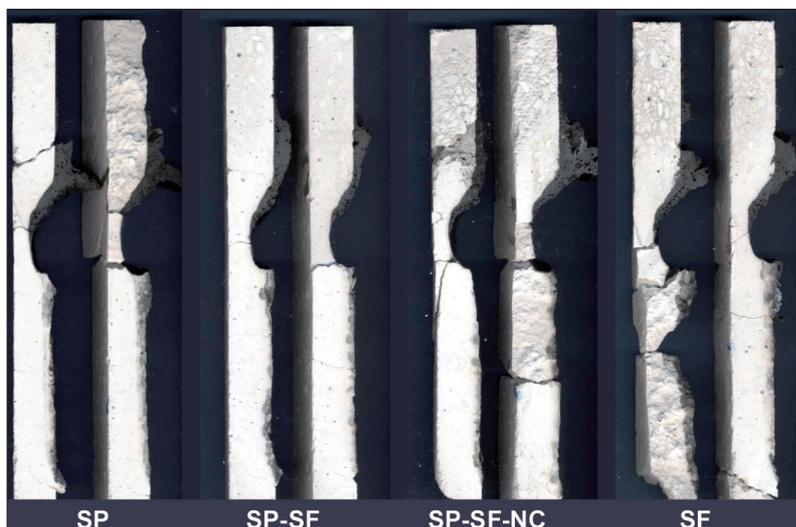


Fig. 3 Test bars of spinel containing and spinel forming castables and mixtures thereof after induction furnace corrosion test 1650 °C/2h; C/A ratio 1,08

Tab. 5 Test conditions for induction furnace test at DIFK, Bonn, Germany

Test conditions							
Temperature [°C]	Duration [h]	Steel [kg]	Slag [kg]				
1650	2	15/St 52	0,75				
Slag composition [mass %]							
CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	MnO	CaF ₂	C/A ratio
40	37	5	5	3	4	6	1,08

with Alphabond (SP-SF-NC) starts at slightly higher temperatures and the drop is less dramatic corresponding to a higher maximum application temperature for this castable. It is important to mention that there will be a softening effect even so no fumed silica is added when impure aggregates like brown fused alumina or bauxite are used together with pre-reacted high-alumina spinel. The

same effect can be seen using Bauxite based spinels due to their high impurity level (SiO₂, TiO₂, Fe₂O₃, alkalis). This type of formulations can not be compared with mixes using high purity spinels and Tabular alumina.

4.2 Erosion resistance

The hot modulus of rupture (HMOR) gives an indication about the behaviour of the mater-

ials when used in erosive conditions. A low HMOR is an indication for the presence of liquid phase in the matrix. Under erosive conditions the matrix can not withstand and the grains get washed out. For cement bonded mixes the development of the hot strength is mainly associated with the formation of CA₆. In mixes with pre-reacted spinel and high purity alumina the CA₆ is formed by a solid state reaction creating a strong bridging effect between the particles. When silica fume is present like in alumina-magnesia castables the formation is a liquid phase reaction leading to small CA₆-crystals in the matrix, embedded in a glassy phase [11]. This effect can be clearly seen in Fig. 2. The spinel containing mix (SP) reaches a HMOR of 23 MPa whereas none of the silica containing mixes shows a significant hot strength.

4.3 Corrosion- and penetration resistance

The slag resistance of alumina-rich spinels is one of their most important properties, and the primary reason for the use of spinel in steel-making refractories. Alumina rich spinels can incorporate low-melting, low-viscosity components such as MnO and FeO of the infiltrated slag into the spinel crystal structure. This leads to an increase of the slag viscosity and reduces further penetration. A reduced penetration is important for two reasons. It hampers the progress of the corrosion front and reduces the risk of spalling. Under thermal cycling the penetrated layers of a refractory lining tend to spall off due to the stresses caused by different densities and expansion coefficients of penetrated layer and original lining material. Such spalling is leading to predominant wear.

In situ formed spinel in a steel ladle castable will show a stoichiometric composition but no alumina rich solid solution. The temperatures of about 1600 °C are too low. Stoichiometric spinel can incorporate FeO or MnO only in substitution for MgO. The corrosion and penetration behaviour of the selected castables was tested in an induction furnace test at the German Refractory Institute (DIFK)/Bonn. The samples were simultaneously subjected to 15 kg of steel ST 52 and calcium aluminate rich slag under oxidizing atmosphere (air). The slag compositions is typical for aluminium-killed steel.

Calcium fluoride (CaF₂) was added to the slag to give more severe test conditions. The detailed test conditions are given in Tab. 5. The test specimens were cut in longitudinal direction and the wear profile was measured at the slag level. Furthermore the discolouration of the sample, slag penetration and the formation of cracks were investigated. Fig. 3 illustrates the result of the corrosion test on the cut samples and Fig. 4 gives detailed data on penetration depth and wear rate.

Although visually the samples show no major difference, the penetration depth varies in the range of 5,9–11,4 mm and is the highest for the alumina-magnesia castable (SF). The cement bonded castables containing pre-reacted spinel show a slightly lower penetration but still higher than the Alphabond bonded castable. Since the open porosity of the castables is in the same range (Tab. 3) the different penetration behaviour can either be caused by a different pore size or the distribution of spinel in the matrix. As described by Buhr et al. [18] the addition of fumed silica to a calcium aluminate matrix leads to a significant growth of the pore size in the temperature range above 1000 °C. Fig. 5 shows the evolution of the pore size distribution for the silica-free castable SP (5a) and the spinel forming castable SF with addition of 0,5 % fumed silica (5b). The presence of the liquid phase in the silica containing mixes leads to a significant pore size growth reaching an average pore size of 2–3 µm after firing at 1500 °C. In comparison the silica free castable containing pre-reacted spinel has an average pore size of about 0,8 µm when fired at 1500° C. The Alphabond bonded castable with the smallest average pore size diameter of ~0,3 µm at 1000 °C consequently shows the lowest penetration depth. Some literature describes that the volume expansion caused by the spinel formation leads to a densification of the microstructure of the castable. This would reduce the open porosity and have a beneficial effect on the penetration resistance of castables with in situ spinel formation. However, Soudier et al. [17] could not find a direct proof for this. They found no correlation between the permanent linear change (PLC) and the densification of the structure when firing the castables under constrained conditions. This was also confirmed by the corrosion test done

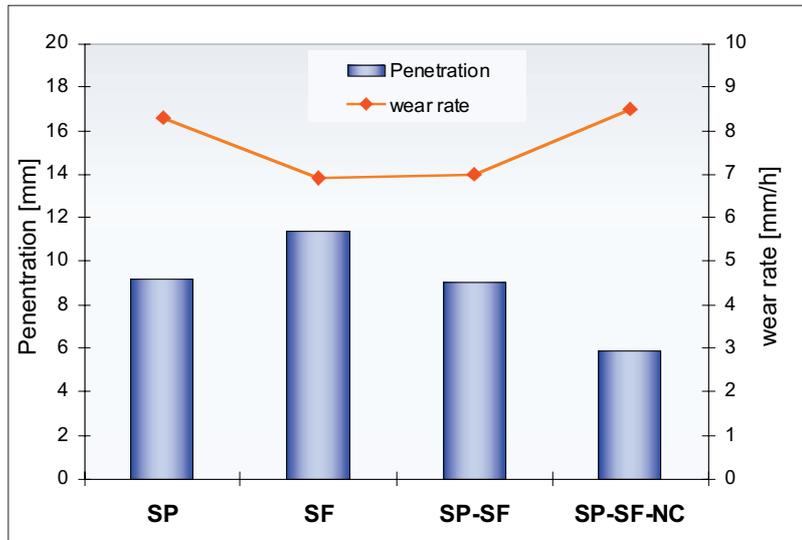


Fig. 4 Penetration depth and wear rate of spinel containing and spinel forming castables and mixtures thereof after induction furnace test 1650 °C/2 h; C/A ratio 1,08

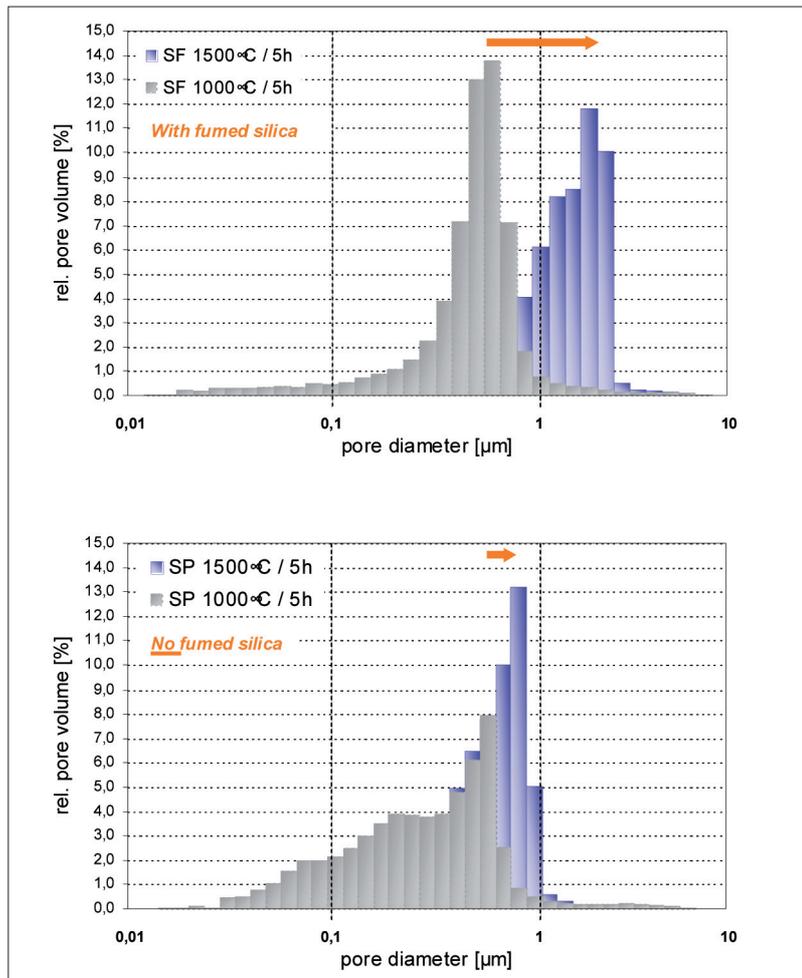


Fig. 5 Pore size distribution of a) spinel containing (SP) and b) spinel forming (SF) castables after pre-firing at 1000 °C/5 h and 1500 °C/5 h

with the selected castables, where the spinel forming castables did not show a higher penetration resistance. Although the lower penetration rate is achieved with mixes con-

Tab. 6 Properties of spinel castables by formulation concept

	Spinel	Alumina-magnesia	Alumina-magnesia + Spinel	Alumina-magnesia + Spinel/NC
Thermal stability	+++	+	+	++
Thermo-mechanical stability	+++	+	+	++
Erosion resistance	+++	+	+	+
Corrosion resistance	++	++	+++	++
Potential for stress relaxation (thermal shock resistance)	+	+++	+++	++

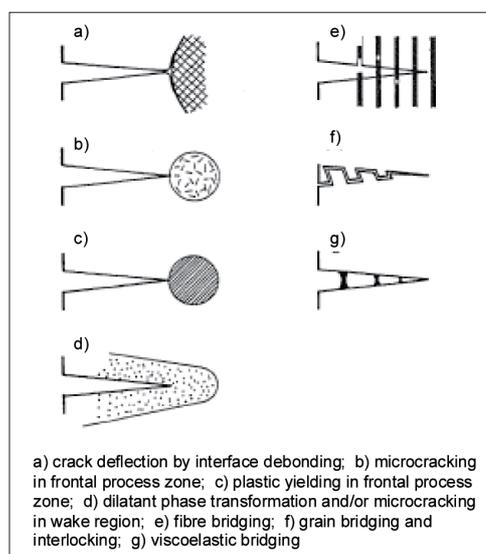


Fig. 6 Various stress shielding processes according to Sakai, Bradt [22]

taining pre-reacted spinel and conclusions in the direction of higher corrosion resistance of pre-reacted, alumina-rich spinel in comparison to in situ formed spinel would be tempting, there is not sufficient data proving that this is actually the case.

The wear rates of the castables are very close and in the range of 7 to 8,5 mm/h. This is comparable to the wear rate of AMC bricks with 5–6 % MgO tested under the same conditions [19].

The cement bonded castables with in situ spinel formation (SF and SP-SF) have the highest corrosion resistance whereas the Alfabond bonded mix (SP-SF-NC) and the spinel containing (SP) corrode at a slightly higher speed. According to Reisinger et al. [20] a spinel containing matrix improves the corrosion behaviour of a castable independently whether the spinel has been added as such to the matrix, whether it developed due to the reaction of alumina with added fine magnesia or whether it is newly formed “in

situ” together with the MgO of the infiltrating slag. The two important facts for an improved corrosion resistance are the total amount of spinel and its distribution/finesse. The amount of spinel in the test castables ranges from 16 to 25 %. The spinel containing castable has the highest amount of 25 %, followed by the spinel forming castable (SF) with ~22 % and the spinel containing, spinel forming castable (SP-SF) with ~20 %. The spinel forming NCC mix has a total spinel content of only 16 % which explains the slightly inferior corrosion resistance of the castable in the test.

As described by Braulio et al. [14] the spinel formation is controlled by the finesse of the magnesia. The spinel forming castables contain fine, dead burnt magnesia of <90 µm size and reactive alumina as partner for the spinel formation. The in situ formed spinel is finely distributed in the matrix whereas the pre-reacted spinel was added as coarser 0–0,5 mm fraction. For the same amount by weight of spinel after firing the pre-reacted spinel is not as well dispersed as the in situ formed. Consequently the spinel-containing mix was less efficient than the castables with spinel formation. Overall the spinel containing, spinel forming castable (SP-SF) shows the best results when considering both penetration depth and wear rate. With the addition of extremely fine ground spinel in the sizing of <45 µm or <20 µm and the co-ground reactive alumina E-SY 2000 in the matrix the slag resistance of the latter mix could be further improved.

4.4 Potential for stress relaxation “Elasticity”

Thermal shock during tapping and cooling down and the deformation of the ladle shell create thermo mechanical stress that can cause severe damage to the refractory lining.

Developing materials with extremely high strength to avoid crack formation will not lead to the desired results since the occurring stress is far above the mechanical resistance of even the best known refractory material. The maximum thermal stress under uniaxial load in an alumina ceramic exposed to a thermal shock of 1000 K will be in the range of 3000 MPa [21]. The only way to improve the resistance of refractory materials under these conditions is to improve their resistance to crack propagation by increasing their potential for stress relaxation. Seven different mechanisms for stress release are described in the literature.

Castables with pre-reacted spinel have proven their good thermal shock behaviour in practical applications, for example in purging plugs when cold stirring gas is blown through the hot ceramic. This behaviour is mainly due to differences in thermal expansion between alumina and spinel (Tab. 2). The different expansion leads to microcracks in the matrix that act as crack arresters (mechanism b in Fig. 6) when the material is thermally stressed. For spinel forming castables the situation is different. Magnesia has the highest thermal expansion of all refractory oxides (Tab. 2). Therefore it reduces the thermal shock resistance of spinel forming castables unless the spinel has been formed. However, spinel forming castables show an elastic behaviour at elevated temperatures (mechanism c in Fig. 6). The liquid phase formation by the addition of fumed silica leads to a softening of the castable (steep drop in RUL curve) so that thermal stresses can be released.

5 Material selection for steel ladle lining

The final properties that will be achieved with spinel forming or spinel containing castables are quite different (Tab. 6). Castables formulated with high quality pre-reacted spinel exhibit high thermomechanical stability, high mechanical strength and erosion resistance as well as an improved penetration resistance. Spinel additions in the fine fraction of the formulation show the highest benefit. Spinel forming mixes proof a good corrosion resistance but have a low hot strength and consequently low erosion resistance. The softening of the castable is a drawback when high thermo-mechanical stability is required but is advantageous

when stress relaxation (elastic behaviour) is important.

However, which concept is the best depends upon the application. As shown in Tab. 1, in steel ladle bottoms the volumetric stability under high temperature and pressure is most important. High erosion resistance is also important. Castables containing pre-reacted spinel are the material of choice for these applications. The reduced erosion resistance of in-situ spinel formulations would reduce the life and increase operating cost.

The requirements in steel ladle side walls are different. Since every steel ladle shell shows some deformation when manipulated, the ability for stress relaxation is of high importance to avoid stress peaks which may lead to cracking. Therefore castables with spinel formation provide advantages in ladle side walls. A remaining expansion level in the range of 1–2 % permanent linear change will be beneficial when open cracks in the lining can be closed due to spinel formation. Ladle sidewalls are less subject to erosion when compared to the bottom. The lower hot strength of the in-situ castable is therefore less of a factor. However, poor tapping practices or extensive stirring can cause significant higher sidewall erosion, and spinel-forming refractories with high silica contents will then exhibit higher erosion rates. The combination of spinel containing and spinel forming can be considered the best solution here.

Pre-cast shapes like impact pads, purging plugs and well blocks are exposed to high erosion thus demanding a material with high hot strength. Furthermore a high thermal stability is required. Spinel containing castables are mainly used in this application, although impact pads made of spinel-forming castables can be found. But the production of pre-cast shapes with spinel-forming formulations is more difficult and requires special attention. The use of magnesia additive may lead to short workability and the drying curves need to be adapted to reduce the critical time in warm, humid atmosphere to avoid cracking by the hydration of magnesia.

6 Conclusion

The influence of the formulation concepts of alumina-spinel (spinel containing) and alumina-magnesia (spinel forming) castables on their physical properties was shown. Although the achieved property profiles are

significantly different, both types of castables have their advantages in the lining of steel ladles. In order to achieve a long service life it is necessary to select the right material, taking into consideration the different requirements on refractory lining materials for the different zones of a steel ladle. But whatever the formulation concept, the installation of the castables has an important influence on their final performance. Segregation and vibrating holes, especially in the ladle bottom often lead to a predominant wear of the lining. The use of self flowing castables reduces this risk of inhomogeneities leading to a reduced and predictable even wear of the lining.

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