NEW SINTER SPINELS FOR CASTABLES IN STEEL APPLICATIONS

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1. INTRODUCTION

Cement kiln linings of Magnesia Spinel bricks have been used for more than ten years because of their improved performance and their environmental advantages over Magnesia - chromite bricks.
The value of Magnesia Spinel raw materials as a component for refractories used in the steel making process was discovered much later.
In Japan the need for improved refractories for ladle linings, (due to higher temperatures, longer holding times and cleaner steel) generated a new type of castable based on Spinel and Al2O3. These castables have increased in use since first introduced in 1987 and are now common in steel ladles as side walls and bottom, with MgO-C-bricks at the slag line. This lining concept has proven to be the most cost effective and best performing solution to meet the requirements for refractories for modern steel making. A lining life record of 294 heats and a refractory unit consumption as low as 1.06 kg per ton steel has been reported by Kawasaki steel corporation for a 255 t steel ladle [1]. Triggered by the japanese developments the European and USA refractory and steel industries have also started to investigate the value of Spinel containing Alumina castables in steel ladle lining.
The castables developed in Japan were based on a Spinel with a stoichiometric Al2O3/MgO ratio. Recently it has been recognized that spinels with a higher Alumina content are superior in this application to the stoichiometric Spinel [1 - 4].
In order to meet the needs of the refractories industry, Alcoa Industrial Chemicals has developed a process for the production of a range of Spinels of high purity and density, both Magnesia- and Aluminarich. Presently 3 Spinel compositions are commercially available.
This paper discribes the process and properties of Alcoas Spinels.

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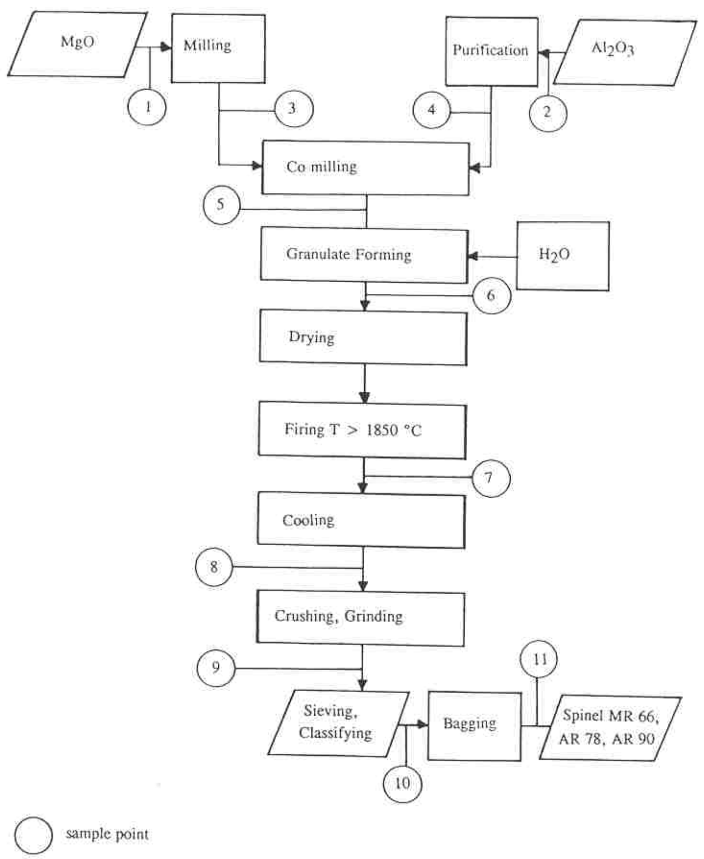
2. THE PRODUCTION PROCESS

Sintered Spinel is produced in a "solidstate reactionsintering" process based on the tabular Alumina production process technology. Fig. 1 gives an overview about the general process flow.

Figure 1

General Process Flow



Great attention is paid to the chemical purity of the raw materials which are carefully homogeneized and sized by a co-milling step. The co-ground Al2O3 - MgO mix is granulated with water and dried. The key step of the process is the sintering of the pre-granulated Spinel mix. During heat treatment one of the most quality influencing characteristics of the Spinel aggregate, the porosity, is controlled. Special attention has therefore been paid during the process development to this step. The tabular sintering technology has proven to be superior to competing firing methods, like rotary kiln firing or tunnel kiln firing.

The sintered ball shaped granulate is cooled and depending on the size-target, crushed or also ground to the final sizes.

The manufacturing process has been designed to produce Spinels with any desired content.

To assure a high and consistent product quality the principles of statistic process control are applied throughout the process. There are 11 sample points within the system with very tight control limits. Fig. 2 - 4 show the BSG control charts for bulk density during a typical production period for all 3 Spinels. This close control of raw materials and manufactoring process yields Spinels with superior properties.

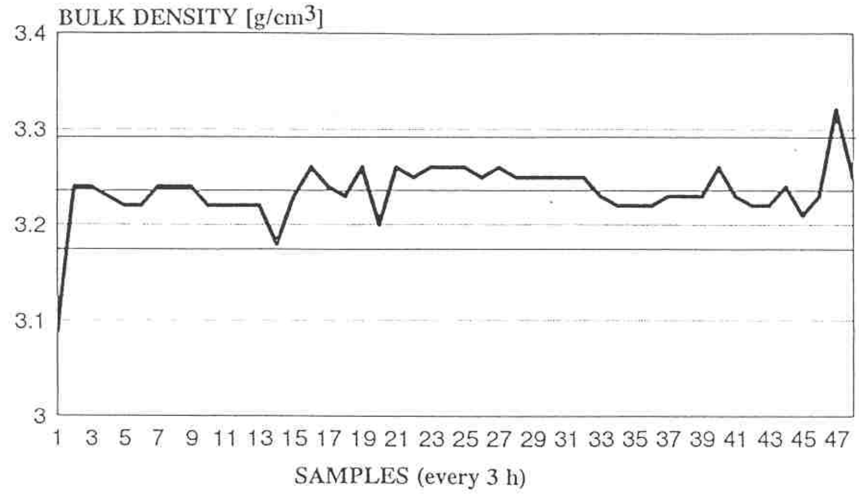


Fig. 2: SPINEL AR 78, 92 PROD.

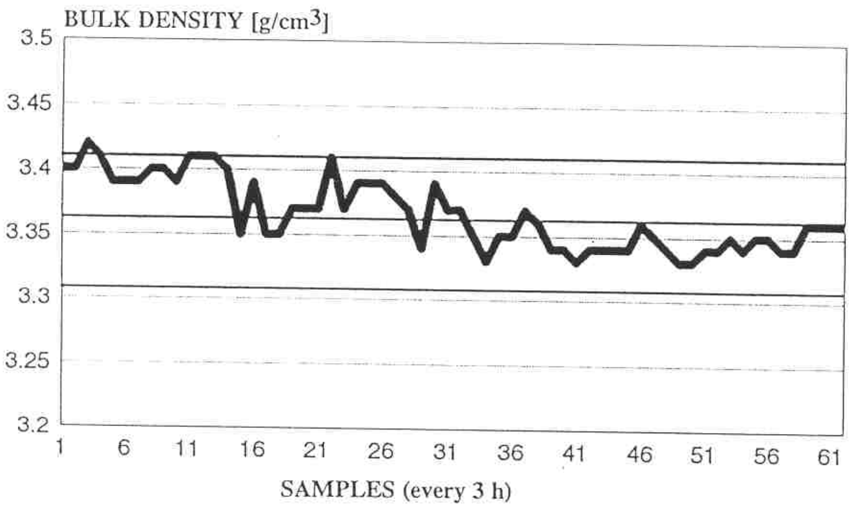


Fig. 3: SPINEL AR 90, 92 PROD.

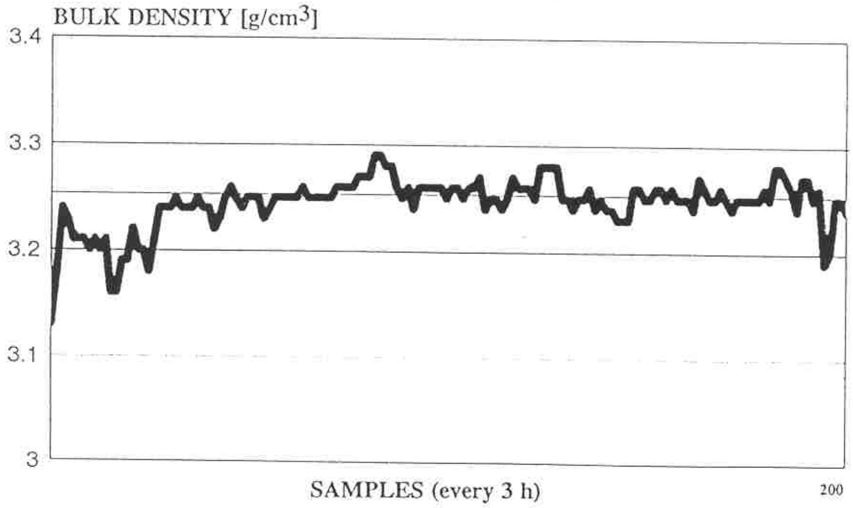


Fig. 4: SPINEL MR 66, 92 PROD.

3. PROPERTIES

3.1 Chemistry

Table 1 gives an overview of the chemical composition of three different Spinel materials which are now produced on a commercial scale, with various Alumina contents. The MR 66 contains 66 % Al_2O_3 and is therefore under-stoichiometric concerning Al_2O_3, that means MgO rich (MR).
The AR 78 and AR 90 contain 76 % and 90 % Al_2O_3 respectively, that means both are Al_2O_3-rich (AR) Spinels. Later, the resulting differences of the phase content of the different materials will be discussed.

	MR 66	AR 78	AR 90
Al_2O_3 [%]	66	76	90
MgO [%]	33	23	9
CaO [%]	< 0.4	< 0.3	< 0.25
SiO_2 [%]	< 0.09	< 0.06	< 0.05
Na_2O [%]	< 0.05	< 0.15	< 0.17
Fe_2O_3 [%]	< 0.1	< 0.1	< 0.1

Tab. 1: Chemical composition of Spinels

The major impurities of the Spinels are CaO, Na_2O, SiO_2 and Fe_2O_3. The total impurity level < 0.8 % is remarkably low and is obtained by the careful selection of raw materials.
Element distribution analysis by EDAX has been done concerning the elements Al, Mg, Ca, Fe and Na. AR 90 as all checked elements evenly distributed. AR 78 shows beside evenly distributed Ca also some Ca concentrations at the grain boundaries. Other elements are evenly distributed. In MR 66 we see clear spots of very high Mg concentration in a size up to 30 μm. Ca is concentrated at the grain boundaries.

3.2 Physical properties

Stoichiometric Mg-Al-Spinel has a theoretical density of 3.58 g/cm3 with Alumina-rich Spinel having a slightly higher density. The bulk density (tab. 2) of the three different Spinels is highest in the AR 90, where it is between 3.30 g/cm3 - 3.40 g/cm3 and about equal in the MR 66 and AR 78 spinel. All densities are approximately 90 % of the theoretical. Important for the material performance concerning corrosion resistance is the amount of open porosity. This is typically about 1 % in the MR 66, in the AR 78 and about 1.5 % in the AR 90.

	MR 66	AR 78	AR 90
Bulk density [g/cm3]	3.24 - 3.30	3.22 - 3.28	3.30 - 3.40
Apparent porosity [%]	0.8 - 1.5	0.8 - 1.5	1.5
Water adsorption [%]	<0.8	<0.8	<1
Crystal size [μm]	20 - 40	60 - 80	60 - 80
Crystal phase			
Spinel	vs [1])	vs	vs
Corundum	-	-	vw
Periclase	w	-	-

[1]) vs = very strong   w = weak   vw = very weak

Tab. 2: Physical properties of Spinels

3.3 Microstructure

The SEM-pictures of the different Spinels (Fig 5 - 8) reveal principle differences between the microstructures of MgO-rich Spinel and Al2O3-rich Spinels. The MR 66 type has a grain size of about 20 - 30 μm, AR 90 and AR 78 with 60 - 80 μm have much bigger grains. All 3 structures are characterized by a high proportion of pores within the grain. The detected inner grain pores have a size up to about 10 μm. This closed pore structure is considered to improve thermal shock stability without having the disadvantages of increased corrosion attack by increased open surface area.

Fig. 5: SEM of the unpolished microstructure of MR 66

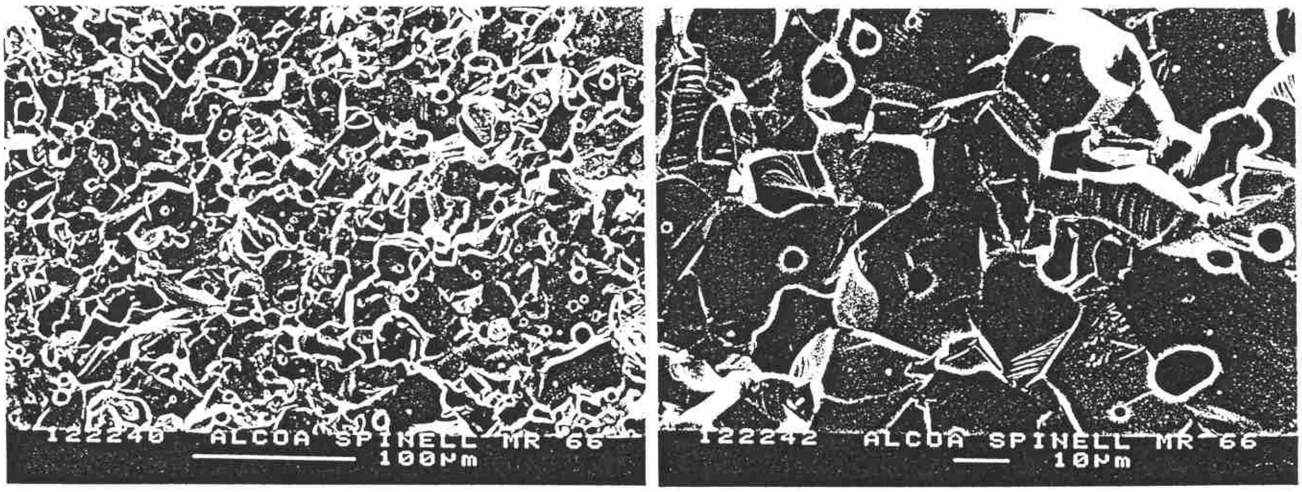


Fig. 6: SEM of the unpolished microstructure of AR 78

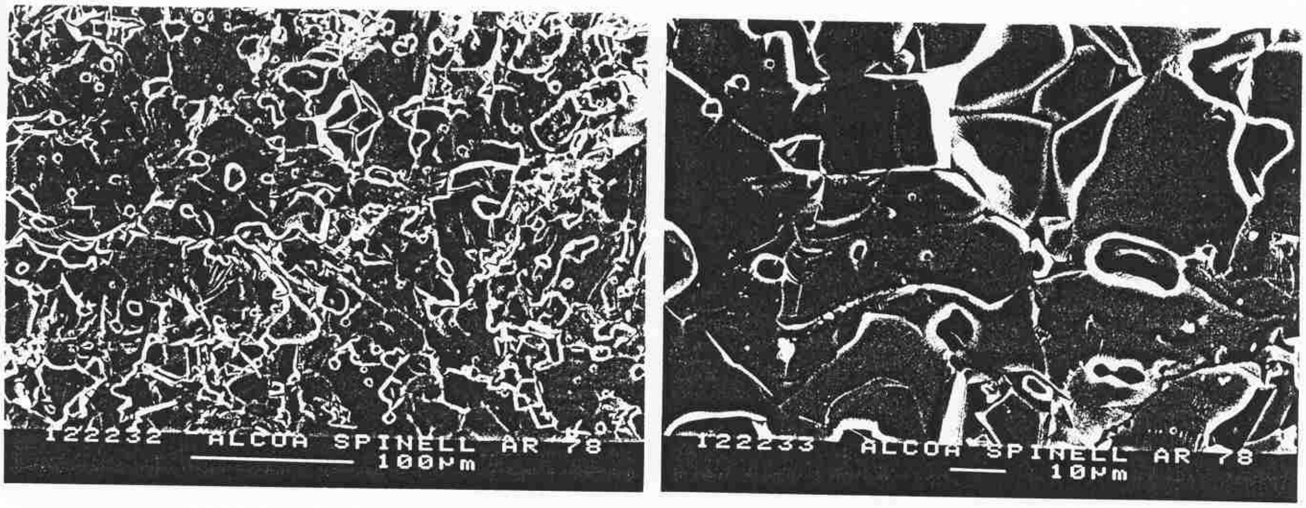


Fig. 7: SEM of the unpolished microstructure of AR 90

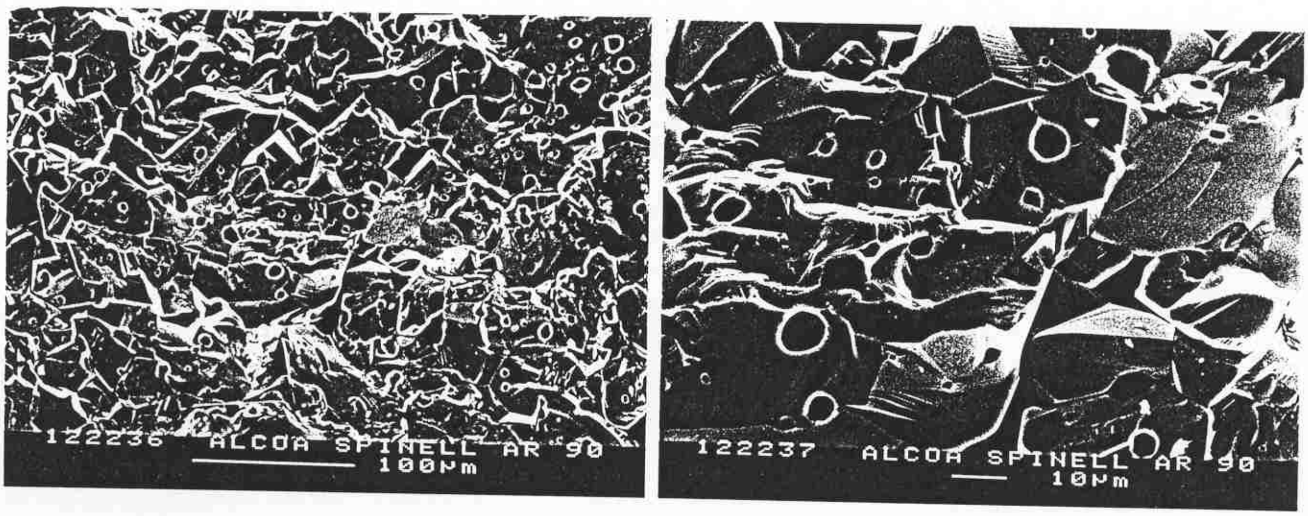
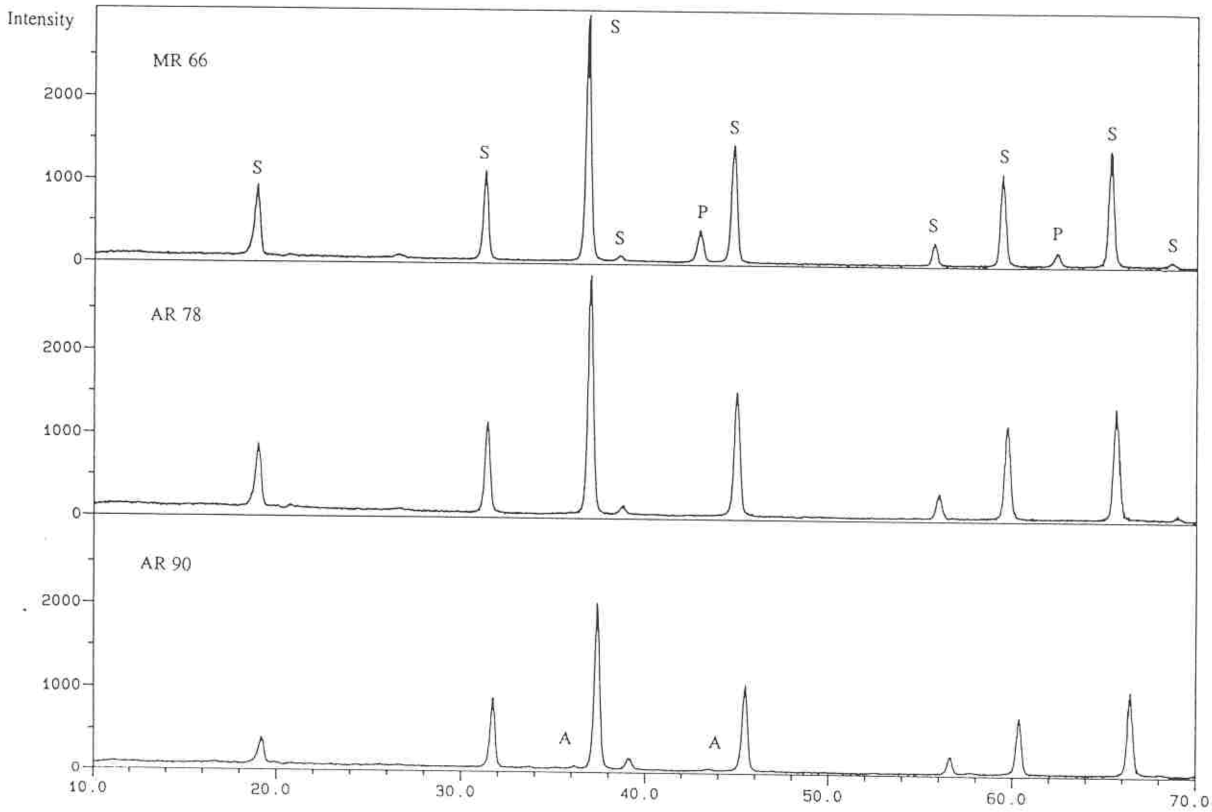


Fig. 8: SEM of the polished microstructure of AR78

3.4 Phase analysis

Fig. 9 Powderdiffraction of MR 66, AR 78 and AR 90



In figure 9, the x-ray diffraction patterns of the different Spinels are shown. MR 66 contains as expected from the chemical composition and from the results of the microprobe analysis besides Spinel also Periclase. AR 78 only has Spinel and AR 90 has besides spinel a minor concentration of corundum.

Looking to the phase diagram (fig. 10) the almost pure Spinel composition of AR 90 is understandable because the production temperature is at a level where pure Spinel phase exists even at 90 % Al2O3. Rapid cooling conserves that composition at room temperature.

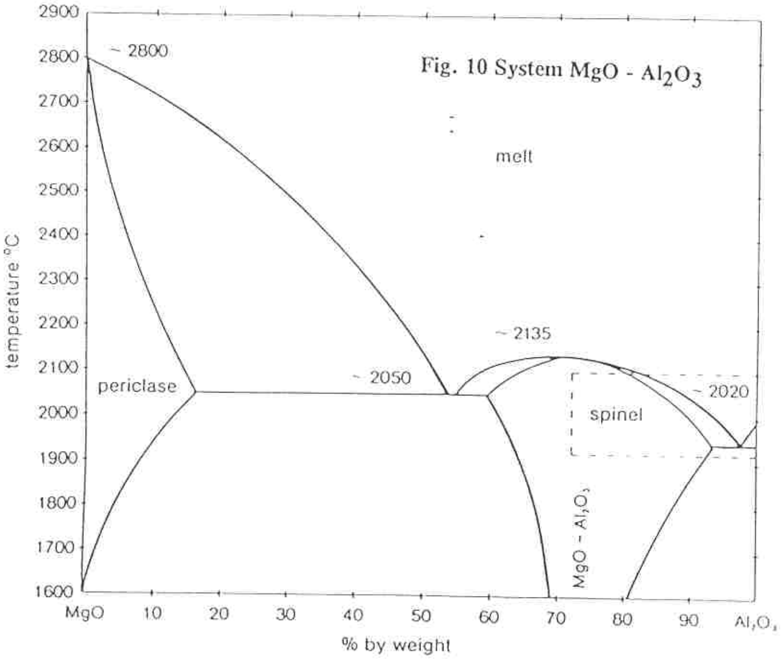


Fig. 10 System MgO - Al_2O_3

4. CORROSION TESTING

4.1 Castable design

	8 / 4	4	16	10	1
Tabular Al2O3					
G¹)	X		X	X	X
M	X		X	X	X
F	X		X	X	X
Spinel					
AR 90 G					
M				X	X
F				X	
AR 78 G					
M			X		
F			X		X
MR 66 G		X			
M		X			
F		X			
Content of Spinel	0	85	25	23	28
CA-Cement [%]					
70% Al2O3	10	5	7	7	7
Reactive Alumina [%]	0	10	10	10	10
H2O [%]	4.7	6.5	5	4.5	4.5

¹) G = 3 - 11 mm M = 0.09 - 3 mm F = 0 - 0.09 mm

Tab. 3: Castable Compositions

All three Spinels have been tested in low cement castables (tab. 3). Spinel has been used in the size range 0 - 3 mm with the exception of mixture 4, where Spinel grain up to 6 mm is present. Tabular Al2O3 up to 11 mm is used as aggregate beside Spinel. To improve green and hot strength, 10 % of a newly developed reactive Al2O3 with very low water demand has been applied. Besides strength improvement the presence of a reactive Alumina supports the slag resistance by the potential of forming CA 6 phase with the CaO of the slag [4]. Some physical properties of this Al2O3 are given in tab. 5. Cement amounts between 5-7 % have been used. No microsilica was added because of its known negative effect on corrosion resistance [2].

The physical properties of the castables are given in tab. 4. Material 10 based on AR 90 shows with 3.05 g/cm3 the highest density. The MR 66 based castable 4 had the highest water demand and consequently with 2.7 g/cm3 the lowest density. This goes along with the results of the strength test. The material 10 had the highest MOR with 36 N/mm2 compared to 21 N/mm2 of material 4. The linear shrinkage of material 4 was almost zero after 12h at 1650°C. An additional test at 1650°C/5h showed a linear expansion of 0.3 %. This is caused by the reaction of free Magnesia with Alumina, forming Spinel. After the completion of this reaction the castable starts to sinter.

CHEMICAL ANALYSIS	CL 370 C
Al2O3 [%]	99.8
Na2O [%]	0.08
Fe2O3 [%]	0.03
SiO2 [%]	0.02
CaO [%]	0.02
TiO2 [%]	0.004
PHYS. CHARACTERISTICS	
BET surface area [m2/g]	3
d1oo [μm]	12
fired density (1600°C/2h) [g/cm3]	3.5

Tab. 5: Chemical and physical properties of CL 370 C

Tab. 4: Physical properties of castables

CASTABLE	DENSITY [g/cm3] 110°C	DENSITY [g/cm3] (1650°C/12h)	lin. Shrinkage [%] (1650°C/12h)	MOR [N/mm2] 110°C	MOR [N/mm2] 1650°C/12h	CCS [N/mm2] 110°C	CCS [N/mm2] 1650°C/12h
8/4	2.88 ¹)	2.81 ²)	-0.13	-	28	-	68.3
4	2.7	2.6	+0.01 ³)	4.7	21	25	60
16	3.02	3.01	-0.25	5.9	23	37	129
10	3.05	3.02	-0.43	6.9	36	61	164
1	2.99	2.99	-0.55	4.9	34	35	79

¹) 300°C ²) 1600/3h ³) +0.3%, 1650°C/5h

4.2 slag testing

COMPONENTS	SLAG I	SLAG II
SiO2 [%]	3.6	37
Al2O3 [%]	13	9.9
CaO [%]	56	42
Fe2O3 [%]	1.4	0.3
TiO2 [%]	0.2	0.6
MgO [%]	25.5	8.8
K2O [%]	0.1	0.6
Mn3O4 [%]	0.1	0.3

Tab. 6: Slag compositions

A static slag test was performed at 1650°C for 5 h. The prefired (1100°C) test bodies were filled with 60 g of slag (composition see tab 6). Tab. 7 gives a summary of the obtained corrosion results. The pure Al2O3 castable 8/4 was fully penetrated by the slag and extensive cracks have been formed in the castable. A similar situation was found in the MR 66 based material 4. Almost the full amount of slag has penetrated into the refractory and has formed a penetration zone > 10 mm. The material in this zone shows high porosity and very low strength. A very different corrosion behavior was detected in samples 16,10 and 1. All these castables contain the Aluminarich Spinels in an amount of 23 to 28%. No penetration zone is detectable in this samples. Obviously a different corrosion mechanism takes place. The castable is dissolved in the slag. The highest loss of material can be seen in the sample 16, containing AR 78. Corrosion was slightly less in castable 10 based on AR 90. The best performance has been seen in sample 1. This castable was composed out of AR 90 in the medium size range up to 3 mm and AR 78 was present as fine powder. The Spinels were used in equal quantities.
The slag test with the acidic slag II (tab. 6) was performed on castable 4 and 1. The MR 66 based sample was detoriated similar to the basic slag test. Castable 1 shows almost no loss due to corrosion but showed about 5 mm of penetration.

castable	Spinel type	corrosion loss 1650/5h slag I	slag II
8/4	No Spinel	full slag penetration	n. d.
4	MR 66	strong slag penetration, pen. zone = 10 - 12 mm	
16	AR 78	4 mm	n.d.
10	AR 90	3 - 4 mm	n. d.
1	AR 90/AR 78	2.5 - 3 mm	<2 mm (4 - 5 mm pen.)

Tab. 7: Results of the static corrosion tests

5. CONCLUSIONS

A process for the production of sintered Spinels in a wide compositon range has been developed. Using this sintered Spinels Alumina-Spinel-castables can be made which have compared to pure Alumina castable improved corrosion resistance agains steel slags. The corrosion results indicate that Aluminarich Spinel is superior in that application compared to Magnesiarich Spinel. The castable which showed the best performance was a combination of a 76 % Al_2O_3 Spinel in the fine size and 90 % Al_2O_3 Spinel in the medium size. Further application testing in steel ladles will be necessary to have more detailed information on the performance of the different Al_2O_3-rich Spinels.

6. REFERENCES:

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