Effects of Metallic Additions on Fired Ceramic Materials

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This paper describes the effect of metal powder addition to a standard fired ceramic kiln-furniture product. Different amounts and combinations of aluminium and silicon are tested. Small additions have the metals completely oxidised forming secondary mullite or corundum. Higher amounts and suitable combinations lead to the formation of SiAlONs in the core. In any case physical properties could be kept or even improved, especially cold crushing strength, even if the firing temperature is reduced compared to standard.

1 Introduction

Metallic additions are definitely state-of-the-art in some fields of ceramic production. It is quite common to add powders of aluminium, magnesium or silicon to carbon containing refractories to reduce the burn-off loss of carbon at higher temperatures and at the presence of oxygen [1]. Aluminium powder is added to cement containing castables to facilitate the drying process [2]. In patents EP 0531378 B1 and WO 1991018846 A1 ceramic moulds are described which are made from fine-grained ceramic powders, where metals are added to create reaction bonding and to compensate the firing shrinkage of fine-grained systems. Here metal contents of more than 10 % are necessary. In patent DE 10134524 A1 metal additions are used as a foaming agent to create a directional porosity.

In literature [3] different procedures are described where powdery mixtures with metallic additions are fired under special gas atmospheres or ceramic shapes are infiltrated with metallic melts and consequently are fired under special gas atmospheres, mostly nitrogen.

In contrast the addition of metals to standard coarse-ceramic materials like refractories or kiln-furniture is neither common nor well-known. This paper describes the effect of metal additions to a standard coarse-ceramic formulation of a kiln-furniture product. The target was to see if it is possible to reduce the firing temperature while at least keeping physical properties and/or even improving them. The possible cost reduction for energy savings must be carefully calculated against increasing raw materials prices, because metal powders are expensive.

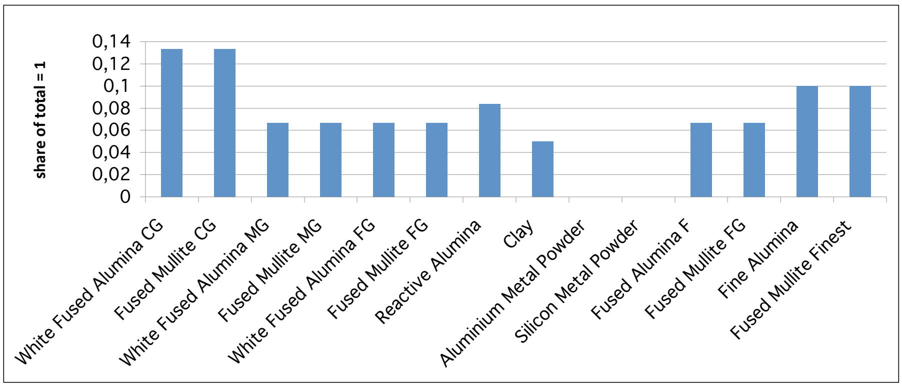

Fig. 1 Basic composition without metals

Tab. 1 Metal additions for different variations

Variation	0	1	2	3	4	5	6	7	8	9	10
Aluminium metal powder [%]	–	3,6	3,8	5,6	5,6	3,7	–	6,1	–	–	0,7
Silicon metal powder [%]	–	1,3	1,3	1,3	0,7	–	1,3	2,1	3,8	2,6	1,3
Fine alumina [%]	10	10	5	5	5	10	10	10	10	10	10

2 Experimental

The basis formulation (Var. 0) for the experiments was a standard ceramic mullite-corundum composition principally according to Fig. 1/Tab. 1. Aluminium and silicon were added as metal powders "on top" in different amounts and combinations, see Tab. 1. The components were mixed in a lab mixer and water was added until the right consistency for dry pressing was achieved. Samples were pressed as cylinders and bars (50 mm × 50 mm resp. 25 mm × 25 mm × 150 mm) so that testing of physical proper-

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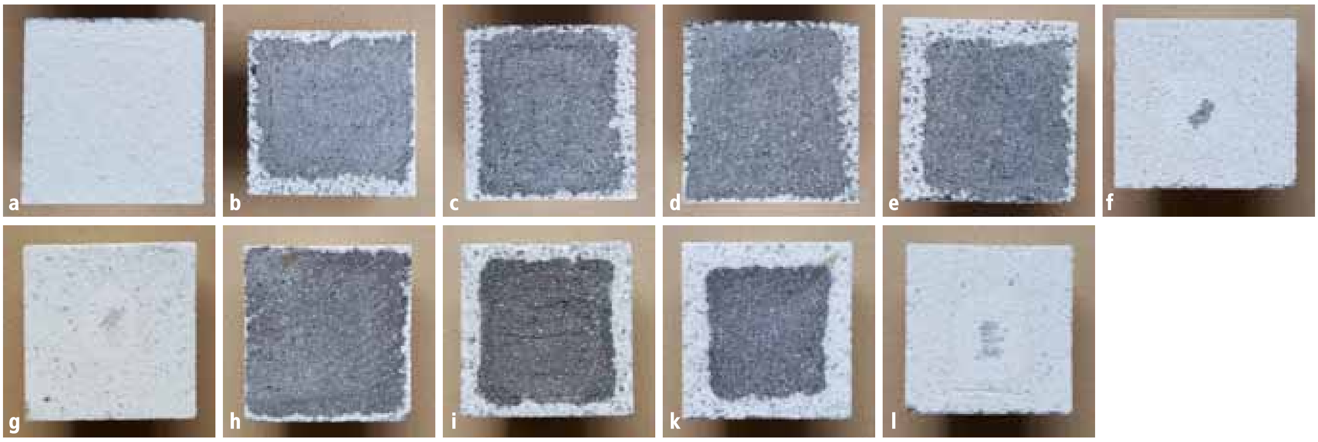

Fig. 2 a–l Cut sections of samples 0–10 fired at 1640 °C

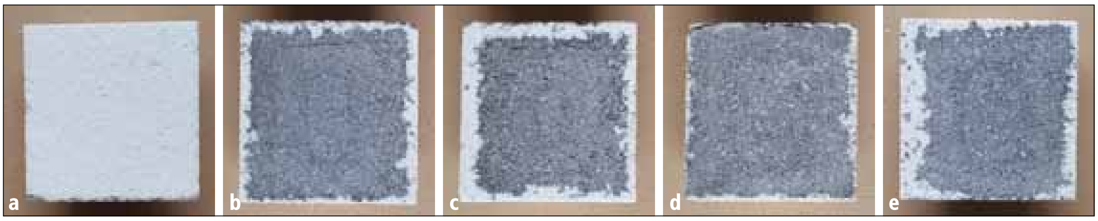

Fig. 3 a–e Cut sections of samples 0–4 fired at 1740 °C

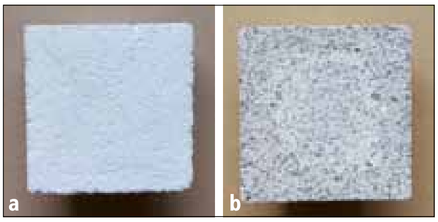

Fig. 4 a–b Cut sections of samples 0 and 1 fired at 1430 °C

ties according to the standard series DIN EN ISO 993 have been possible.

The first approach was to add a combination of aluminium and silicon in such a way that theoretically they form 10 % secondary mullite if fully oxidised and reacted (Var. 1 in Tab. 1). Var. 2 corresponds to Var. 1 with the exception that fine alumina is reduced adequate to the "on top"-addition of metals of Var. 1, to see if this is necessary and what the effect is.

The other variations are results of the first conclusions and considerations. Samples 0–4 were fired at the standard temperature 1740 °C and all at the reduced temperature of 1640 °C. Var. 0 and the startup Var. 1 was also fired at 1430 °C to see what the possible maximum measurement for cost and energy consumption reduction could be, see 4 a–b.

The variations in detail are (the contents of Var. 1 are here related as standard):

- Var. 3: aluminium increased, silicon standard, fine alumina reduced
- Var. 4: aluminium increased, silicon reduced, fine alumina reduced
- Var. 5: aluminium standard, no silicon, fine alumina standard
- Var. 6: no aluminium, silicon standard, fine alumina standard
- Var. 7: aluminium increased, silicon slightly increased, fine alumina standard
- Var. 8: no aluminium, silicon increased, fine alumina standard
- Var. 9: no aluminium, silicon slightly increased, fine alumina standard
- Var. 10: aluminium reduced, silicon standard, fine alumina standard.

One sample of each variation was cut after firing for visual observation. The rest was tested for physical properties:

Bulk density *BD*, water absorption *WA*, apparent porosity *AP*, cold crushing strength *CCS*, modulus of rupture *MoR* and modu-

Tab. 2 Phase contents of Var. 0–4

	Variation	**Var. 0**	**Var. 0**	**Var. 1**	**Var. 1**	**Var. 2**	**Var. 2**	**Var. 3**	**Var. 3**	**Var. 4**	**Var. 4**
Ausgangsstoffe/ source materials	**Temperature [°C]**	1640	1740	1640	1740	1640	1740	1640	1740	1640	1740
	Al [%]	0	0	3,6	3,6	3,8	3,8	5,6	5,6	5,6	5,6
	Si [%]	0	0	1,3	1,3	1,3	1,3	1,3	1,3	0,7	0,7
	"Fine alumina"	10	10	10	10	5	5	5	5	5	5
Ergebnisse/ results	**XRD/XRF**	mixed	mixed	core	core	core	core	mixed	mixed	mixed	mixed
	Si met	0,1	0,1	0,5	0,43	0,6	0,2	0,9	0,5	0,5	0,6
	Corundum	52	55	56	54	56	54	61	52	60	56
	Mullite	44	42	28	38	27	34	23	37	30	37
	SiAlON	0	0	15,4	6,9	16,5	11,6	14,9	10,1	9,8	6,4

lus of elasticity *E-M*. Variations 0 to 4 were also tested for quantitative X-ray diffraction. Var. 0, 1 and 6 were tested for creeping under load (Creep in Compression) *CiC* at about 1570 °C, abrasion resistance *AR* (both close to ASTM C 704 – 12 and DIN 52108 – 68 [Boehme]) and hot modulus of rupture *HMOR* at 1400 °C.

3 Results and discussion

The cut sections of the 1640 °C-fired series can be seen in photograph series Fig. 2 a–l and the series of 1740 °C in Fig. 3 a–e. It is obvious that all samples with a high metal content have a white seam and a dark core. X-ray diffraction shows that the dark core is caused by the formation of different SiAlONs and some residual silicon metal (Tab. 2). Var. 5 (no silicon) and Var. 6 (no aluminium, small amount of silicon) have (nearly) no black core at all. When aluminium is kept out and the silicon content is increased (Var. 8 and 9) the dark core reappears, the size being directly related to the silicon content. Also Var. 10 (reduced total metal contents) has nearly no black core.

The results of the physical properties are listed in Tab. 3 ff. It is not astonishing that the formation of SiAlONs results in higher strength than standard, but also the formation of secondary mullite (Var. 6) or secondary corundum (Var. 5) improves strength properties or keeps it on the standard level even when the firing temperature is lower. Without aluminium and within increasing silicon content (Var. 8 and 9) there is a further increase in strength. Presently we cannot say if this is only a SiAlON-effect or whether residual silicon plays a role.

Definitely metal addition has an upper and a lower limit for both content and relation to be effective. The drop of properties in Var. 7 and also Var. 3 and 4 against Var. 1 and 2 shows that the limit of total metal addition is surely below 10 %. The lower limit seems to be 1,3 % (only silicon, Var. 6). Presently we have no interpretation why Var. 6 with the small addition of silicon already has a positive effect, whereas Var. 10 with the same amount of silicon but a small aluminium addition has the worst values in our test series.

Tab. 3 a Physical properties of Var. 0 and Var. 1

Variation	Var. 0	Var. 0	Var. 1	Var. 1
Temperature [°C]	1640	1740	1640	1740
Al [%]			3,6	3,6
Si [%]			1,3	1,3
Fine alumina [%]	10	10	10	10
BD [g/cm^3]	2,87	2,88	2,85	2,84
WA [%]	6,1	6,0	6,4	6,5
AP [%]	17,5	17,1	18,3	18,3
E-M [GPa]	14,3	13,9	24,6	22,3
CCS [MPa]	103	109	167	147
MoR [MPa]	12,1	12,1	12,8	12,7
CiC Temperature max. [°C]	1564	1571	1571	1568
CiC 25 h [%]	1,12	0,49	0,15	0,37
Creep rate 5–25 h [%/h]	0,0285	0,0146	0,0045	0,0135

Tab. 3 b Physical Properties of Var. 5–10 fired 1640 °C

Variation	Var. 5	Var. 6	Var. 7	Var. 8	Var. 9	Var. 10
Temperature [°C]	1640	1640	1640	1640	1640	1640
Al [%]	3,7		6,1			0,7
Si [%]		1,3	2,1	3,8	2,6	1,3
Fine alumina	10	120	10	10	10	10
BD [g/cm^3]	2,80	2,84	2,78	2,80	2,82	2,77
WA [%]	7,0	5,7	7,5	5,6	5,6	6,6
oPO [%]	19,7	16,3	20,8	15,6	15,9	18,5
E-M [GPa]	20,9	24,6	22,0	24,5	32,4	12,6
CCS [MPa]	128	149	111	159	177	87
MOR [MPa]	14,0	13,5	12,1	17,0	14,7	12,8
CiC 25 h [%]		0,4316				
Creep rate 25–5 h [h/%]		0,012				

Tab. 3 c Physical properties of samples fired at 1430 °C

Variation	Var. 0	Var. 0	Var. 1	Var. 1
Temperature [°C]	1430	1430	1430	1430
Fired at	Lab El.	Plant Gas	Lab El.	Plant Gas
BD [g/cm^3]	2,82	2,81	2,85	2,86
WA [%]	7,0	6,8	6,1	5,9
oPO [%]	19,8	19,1	17,3	16,8
E-M [GPa]	6,5	7,8	19,9	22,1
CCS [MPa]	70	72	139	140
MoR [MPa]	12,0	12,0	12,4	12,5
CiC 25h [%]			0,9523	
Creep rate 25 h–5 h [h/%]			0,03326	

Remarkable is also the effect on hot properties. The creep rate of Var. 1 fired at 1640 °C and the total shrinkage is on the same level – slightly lower – than the standard fired at 1740 °C (Tab. 3 a).

The positive effect of metal addition can be extended to even lower temperatures. The standard composition fired at 1430 °C shows a dramatic loss in properties (Tab. 4), but Var. 1 has the same level as fired 1740 °C (Tab. 5). Considering all the results of the test series, it appears that a lower metal addition not only makes a lower firing

Tab. 4 Physical properties of Var. 0 fired at different temperatures

	Var. 0 (1740 °C)	Var. 0 (1640 °C)	Var. 0/13 (1430 °C)
BD [g/cm³]	2,88	2,87	2,81
WA [%]	6,0	6,1	6,8
AP [%]	17,1	17,5	19,1
E-M [GPa]	13,9	14,3	7,8
CCS [MPa]	109	103	72
MOR [MPa]	12,1	12,1	12

Tab. 5 Physical properties of Var. 1 fired at different temperatures

	Var. 1 (1740 °C)	Var. 1 (1640 °C)	Var. 1/ (11) (1430 °C)
BD [g/cm³]	2,84	2,85	2,86
WA [%]	6,5	6,4	5,9
AP [%]	18,3	18,3	16,8
E-M [GPa]	22,3	24,6	22,1
CCS [MPa]	147	167	140
MoR [MPa]	12,7	12,8	12,4
CiC 25 h [%]	0,37	0,15	0,43
Creep rate 5–25 h [h/%]	0,0135	0,0045	0,0120

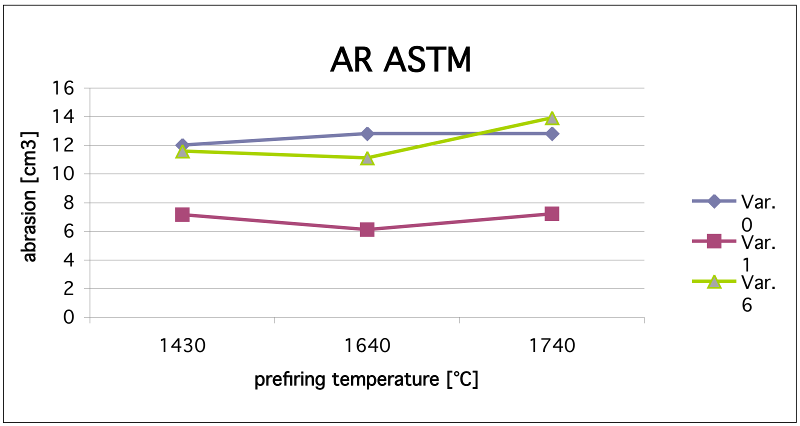

Fig. 5 Abrasion values for ASTM method

temperature possible, but necessary, probably because of decomposition of SiAlONs at higher temperatures.

The results of the abrasion resistance are similar with both methods (Figs. 5–6): The abrasion is only slightly dependent on the prefiring temperature with no visible tendency. There is a big tendency regarding composition: Again Var. 1 shows the lowest abrasion, especially fired at 1640 °C. The abrasion resistance of Var. 1 fired 1430 °C is even better than for Var. 0 fired at all temperatures. On average Var. 6 is on the same level as Var. 0. Prefired 1430 °C Var. 6 is slightly better than Var. 0 fired 1740 °C for ASTM method, slightly worse for Boehme.

Hot modulus of rupture measured at 1400 °C shows a more or less linear relationship to the prefiring temperature (Fig. 7). Only Var. 1 shows a little decrease from 1640 to 1740 °C, which supports the assumption that the prefiring temperature should be reduced. Var. 0 has the lowest values, Var. 6 is better through all temperatures and again Var. 1 has the highest strength.

4 Conclusion

Metal powder addition to fired ceramic materials improves their strength properties. The main impact is on cold crushing strength, smaller on bending strength, on creeping under load and temperature and on hot modulus of rupture. Hot and cold properties are even improved when the metal is completely oxidised (Var. 6).

The firing temperature compared to no addition can be reduced and it is recommended to do so. Properties can be adjusted to at

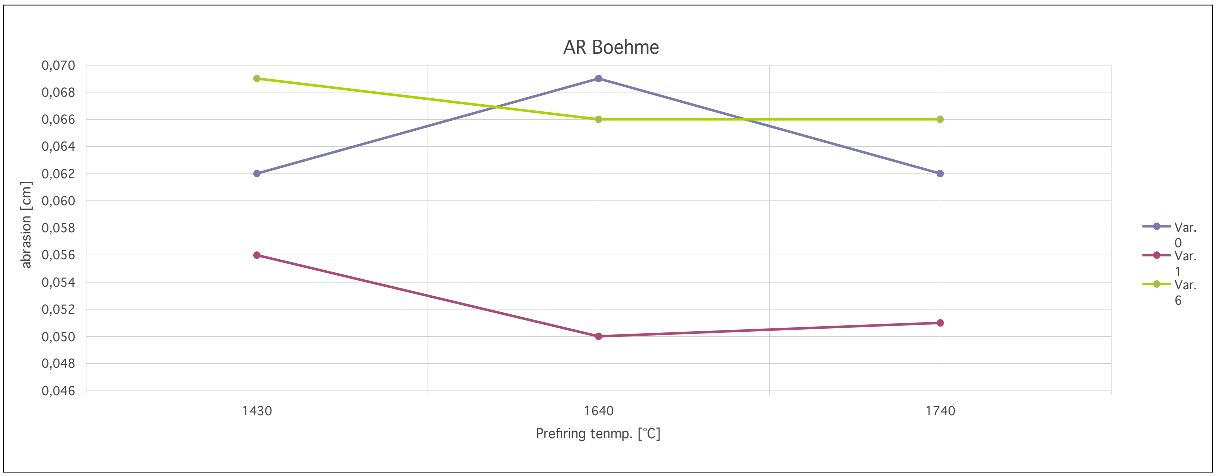

Fig. 6 Abrasion resistance according to DIN 52108 (Boehme)

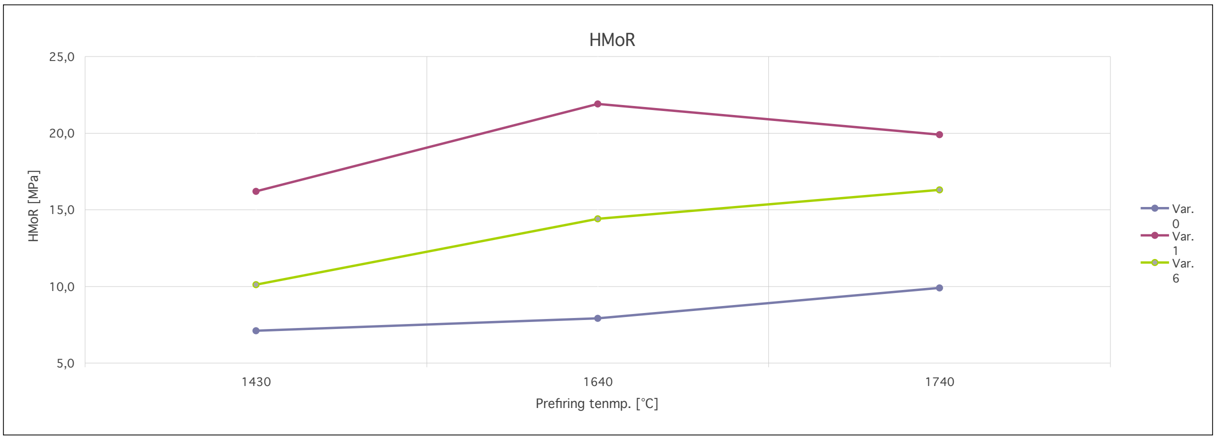

Fig. 7 Hot modulus of rupture at 1400 °C according to DIN EN 993-7

least the same level as the high fired standard.

Tab. 6 Physical properties of only silicon containing samples compared to Var. 0

	Var. 0 (1740 °C)	Var. 6 (1640 °C)	Var. 8 (1640 °C)	Var. 9 (1640 °C)
Silicon [%]		1,3	3,8	2,6
BD [g/cm³]	2,88	2,84	2,8	2,82
WA [%]	6,0	5,7	5,6	5,6
AP [%]	17,1	16,3	15,6	15,9
E-M [GPa]	13,9	24,6	24,5	32,4
CCS [MPa]	109	149	159	177
MOR [MPa]	12,1	13,5	17,0	14,7

Tab. 7 Creeping under load of Var. 0 and Var. 6

	Var. 0 (1740 °C)	Var. 0 (1640 °C)	Var. 6 (1640 °C)
CiC 25 h [%]	0,49	1,12	0,43
Creep rate 5–25 h [h/%]	0,0146	0,0285	0,0120

There is an upper and a lower limit for the metal content to have a positive effect. Final properties are dependent on amount and relation of the metals if more than one is added.

The mechanism for improving properties is the formation of secondary alumina in the case of Al addition, of secondary mullite in the case of Si, and of SiAlONs if both are added in a certain amount. Remaining metallic silicon can also have an influence. In cost/benefit-relation it makes more sense to add small amount of a single metal and to resign the formation of SiAlONs, but that depends on the application of the ceramics.

The presence of residual silicon and the absence of metallic aluminium indicate that aluminium – with the higher affinity to oxygen – traps most of the oxygen and most probably, like observed in the aluminium producing industry, a part of the oxygen of silicate phases. This assumption should be supported by some REM examination.

Our examinations open a wide field of more possible ceramic-metal combinations which could be reasonable. Not only silicon and aluminium – the most common ones – and their combinations are possible, but for example metallic magnesium (also in fired magnesia products), and they are some other metal powders available on the market that we currently do not think of.

This paper is a result of closing operations for a ceramic technician, therefore not all experiments and examinations that could be interesting could be made, but the playground is open.

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