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Preliminary investigations of the production of MgAlON bonded refractories

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Abstract

The aim of the work was to find an appropriate composition for the formation of MgAlON bonding phase for Al_2O_3 and MgO based refractories. The first step was the preparation of pure MgAlON. AlN and Al_2O_3 were used as starting powders and either MgO or $MgAl_2O_4$ was added as a source of magnesium. The results verified the possibility to produce MgAlON under the prevailing conditions. Afterwards, MgAlON bonded alumina and magnesia refractories were investigated. The obtained results confirmed the possibility of the production of MgAlON bonded alumina refractories. However, in the case of magnesia-based samples MgAlON was not formed and instead stoichiometric spinel, AlN and alumina rich spinel were detected in the bonding phase. Additionally, the joining between the MgO grains and the matrix was poor with wide gaps on the interface.

Keywords: Sintering; Refractories; MgO; Al_2O_3; MgAlON

1. Introduction

Oxide/non-oxide composite refractories become more and more interesting because of the high requirements on refractory materials, e.g. for the production of high quality steel. A very interesting material is AlON, a solid solution of Al_2O_3 and AlN, because of its high corrosion resistance, low thermal coefficient of expansion and its high thermal conductivity.[1] However, the disadvantage of this phase is its small stability region.[2] AlON is only stable under a certain oxygen and nitrogen partial pressures, at temperatures higher then $1640 \pm 10\,^{\circ}C$. For the stabilization MgO can be added and a solid solution, spinel-type phase is formed, called MgAlON. MgAlON is characterized by interesting properties too, like a high compressive strength, high flexural strength and especially a high resistance to slag and metal attack and by a low thermal coefficient of expansion ($5.3 \times 10^{-6}\,K^{-1}$–$7.4 \times 10^{-6}\,K^{-1}$).[3–5] MgAlON can be produced in several ways, by solid state reaction,[6,7] by nitridation reaction sintering[8,9] and by carbothermal reaction and nitridation.[10,11] MgAlON can be used as a bonding phase for refractory materials. Especially the in situ formed MgAlON prepared by solid reaction of AlN, Al_2O_3 and MgO or by nitridation reaction sintering of Al, Al_2O_3 and $MgAl_2O_4$ are suitable for this purpose. Yang et al.[5] and Wang et al.[12] reported about MgAlON bonded composite refractories, using spinel and magnesia as the main components. However, the achieved results of these materials were not satisfying, especially if MgO was used, because of their low density and strength and high porosity. In this work MgAlON bonded refractories were prepared and investigated with a focus on proceeding reactions and the resultant phase composition. The processing parameters of MgAlON bonded alumina and magnesia refractories, like sintering temperature and atmosphere were also investigated.

2. Experimental

The first step was the verification that MgAlON could be produced under the prevailing conditions. For the production of MgAlON AlN and Al_2O_3 were used as starting powders and either MgO or $MgAl_2O_4$ was added as a source of magnesium. The powder characteristics are shown in Table 1 and the investigated compositions are listed in Table 2.

The MgO–Mg_3N_2–AlN–Al_2O_3 phase diagram of Sun et al.,[13] including the exact positions of the selected compositions M1–M4, is shown in Fig. 1.

The raw materials were mixed in isopropanol with an attritor to achieve a good homogeneity. The mixtures were dried in a rotary evaporator for 1 h and afterwards for 12 h in a

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Table 1
Characterization of the raw materials.

Raw materials for the bonding phase	d_{50} [μm]	Purity [%]	Specific surface area [m^2/g]
Al_2O_3 (Martoxid MR70, Albemarle Corp.)	0.5–0.8	≥99.8	6–10
AlN (grade C, H.C. Starck)	1.8		4.5
MgO (GR for analysis, Merck)	2	≥97	
$MgAl_2O_4$ (S30CR, Baikowski)	0.2	≥99	30
Coarse Al_2O_3 (tabular alumina)	300–1000	99.5	
Coarse MgO (sintered magnesia)	300–1000	98.5	

Table 2
Molar composition of investigated mixtures.

Sample	AlN [mol%]	Al_2O_3 [mol%]	$MgAl_2O_4$ [mol%]	MgO [mol%]
M1a	17.9	32.1	50.0	
M1b	11.9	54.8		33.3
M2	35.0	41.0	24.0	
M3	38.5	38.5	23.0	
M4	42.0	35.5	22.5	

vacuum drying chamber. Cylindrical samples were prepared with a diameter of 12 mm and a height of 6 mm with a uniaxial pressure of 100 MPa. Afterwards, the samples were isostatically pressed with a pressure of 250 MPa to obtain homogeneous compaction. The samples were sintered in a graphite resistance furnace for 5 h at two different temperatures, 1550 °C and 1650 °C. Slight overpressure of nitrogen (0.15 MPa) was used during sintering to avoid the loss of nitrogen from the samples. Two test series were investigated for each composition. The first test series were embedded in a powder bed consisting of BN, MgO and Al_2O_3 in the ratio of 90:5:5% by weight. The other test series were sintered without any powder bed.

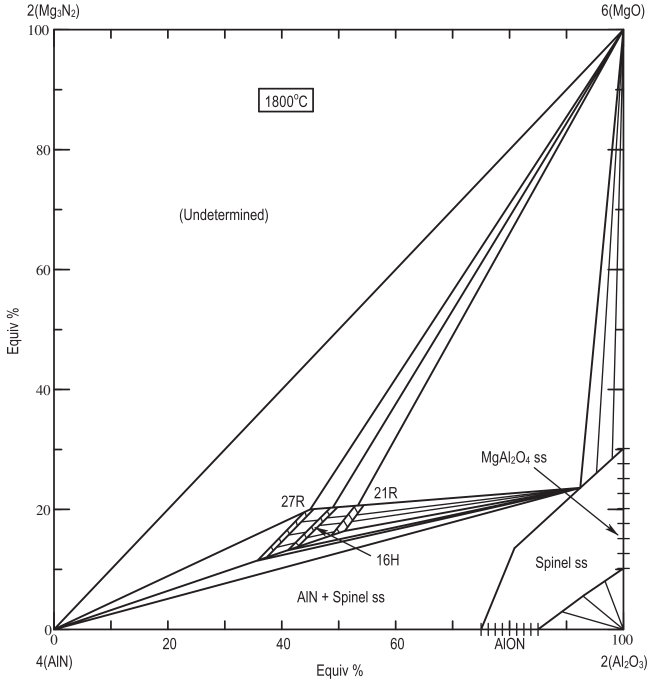

Fig. 1. MgO–Mg_3N_2–AlN–Al_2O_3 phase diagram[13] showing the investigated compositions: +, M1; ▼, M2; ●, M3; ▲, M4.

The next step was the preparation of MgAlON bonded alumina ceramics. Composition M2 was selected for the in situ formed MgAlON bonding phase. The fine fraction was premixed and dried before adding the coarse alumina grains with a grain size of 0.3–1 mm (Table 1). The whole batch, containing 20 wt% of alumina, was mixed for three hours on a roller homogenizer. Then samples were prepared and sintered in an analogous manner as pure MgAlON samples. The maximum sintering temperature was 1650 °C, based on the preliminary test. The influence of the powder bed was also investigated for these samples.

Similar processing was used also for the preparation of MgAlON bonded magnesia samples. 20 wt% of MgO with a grain size up to 1 mm (see Table 1) was added to the pure MgAlON matrix composition. For these samples four matrix compositions were used, meaning all mixtures except composition M1b, because of its high porosity. Due to the difficulties of the production, the maximum temperature was increased to 1800 °C while the dwell time remained 5 h at this high temperature.

After preparation, the samples were investigated in detail. The weight and size of the samples were measured before and after sintering to quantify the shrinkage or volume expansion. The densities were determined by the Archimedes principle in mercury. The structure of the samples was clarified with a reflected light microscope (Olympus GmbH) and the phase composition was analysed by X-ray diffraction with a Siemens D5000 diffractometer. Further microstructural details were obtained by investigation with a scanning electron microscope (Carl Zeiss GmbH) including energy dispersive X-ray spectroscopy for the elemental analysis.

3. Results and discussion

The investigation of the pure matrix compositions confirmed the formation of MgAlON for all samples. However, several differences could be observed. Composition M1 contained the lowest nitrogen content with an average value lower than 1 mol%. Furthermore, the raw materials had a big influence on the structure of the newly formed MgAlON. If MgO was used as magnesium source, the structure was very porous and volume expansion occurred due to the in situ formation of spinel

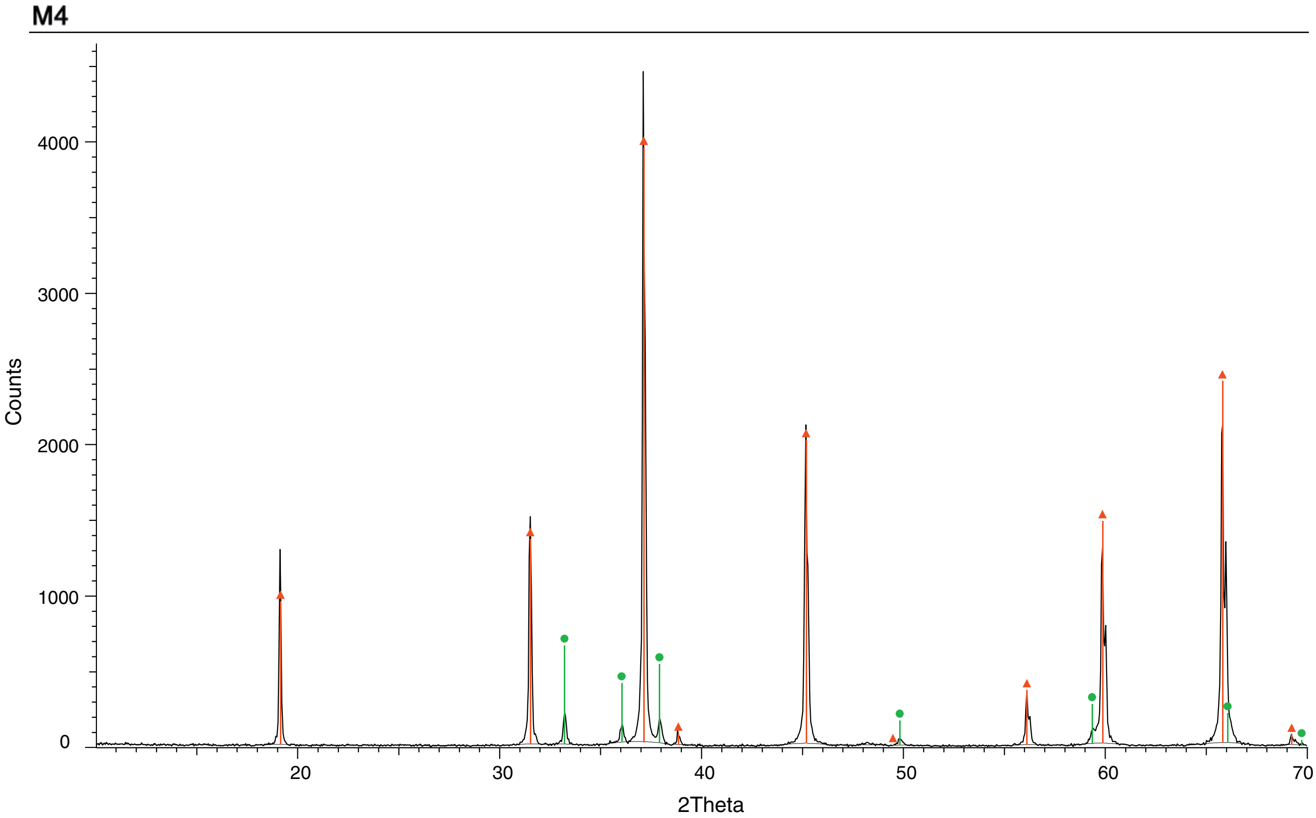

Fig. 2. XRD analysis of the sample M4 confirming AlN as secondary phase. ●, AlN; ▲, MgAlON.

leading to a low density of approximately 2.1 g cm^{-3}. The addition of $MgAl_2O_4$ led to a slight shrinkage during firing and a denser structure could be proved with a density of 3.3 g cm^{-3}. The phase composition of both samples was similar. The samples M2, M3 and M4 showed similar structure and the densities were between 3.4 and 3.7 g cm^{-3}. The mass and also some nitrogen loss might be attributed to the formation of volatile Mg_3N_2. The results are summarised in Table 3.

MgAlON with a higher nitrogen content (~5 mol%) could be produced from compositions M2, M3 and M4. MgAlON was the main phase beside AlN as a secondary phase. According to the phase diagram (see Fig. 1), AlN was expected for composition M4. However, it could be detected also in the other samples M2 and M3, but in a different quantity. Sample M4 contained the highest amount of AlN (see Figs. 2 and 3), while its content was lowest for composition M2.

Table 3
Changes of weight and dimensions and measured density of the samples M1–M4. The density was measured by the Archimedes principle.

	Weight change [%]	$\Delta d/d_0$ [%]		Density [g cm^{-3}]
M1a	−1.69	−17.41	Shrinkage	3.32
M1b	1.33	2.83	Expansion	2.14
M2	−2.06	−13.03	Shrinkage	3.44
M3	−2.18	−14.15	Shrinkage	3.71
M4	−1.46	−13.87	Shrinkage	3.53

The used temperature had a big influence on the MgAlON formation. The higher temperature of 1650 °C led to MgAlON with a lower content of secondary phase, therefore, this temperature was applied for all further experiments. The omission of the powder bed had only a low influence on the nitrogen content of the MgAlON phase. The structure and the phase composition of the two test series, i.e. with and without powder bed, were similar. The composition of MgAlON is presented in Table 4.

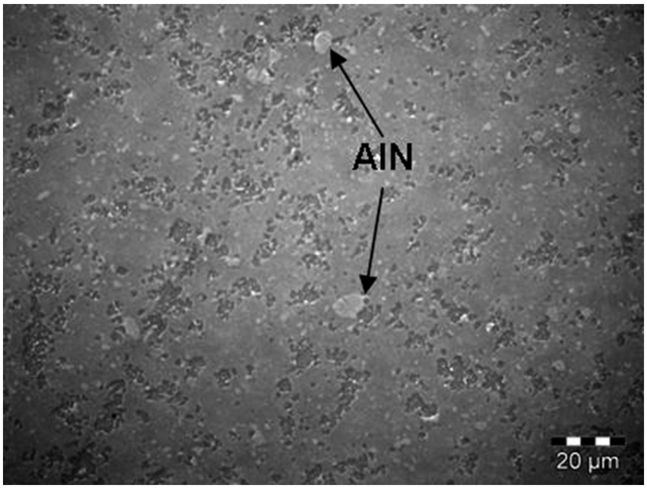

Fig. 3. Composition M4 consisting of MgAlON and AlN (light phase). The phases were determined by XRD and EDX.

Table 4
Composition of MgAlON of the samples M2, with and without powder bed, M3 and M4. The elemental analysis was measured by EDX.

Sample	Powder bed	N [mol%]	O [mol%]	Mg [mol%]	Al [mol%]
M2	90/5/5	5.1	53.5	5.2	36.2
M2	Without	4.9	53.1	5.3	36.7
M3	90/5/5	5.3	53.0	5.2	36.5
M4	90/5/5	5.6	53.6	5.3	35.5

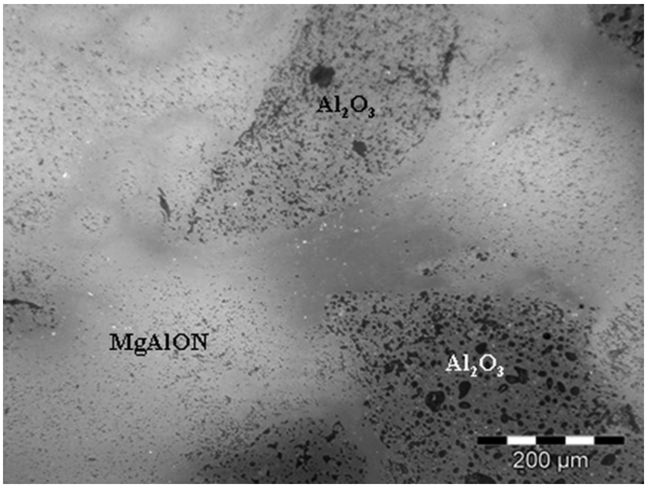

Fig. 4. Microstructure of an MgAlON bonded alumina refractory. A good bonding between the Al_2O_3 grains and the MgAlON bonding phase was achieved.

Composition M2 was selected for the production of MgAlON bonded alumina refractories. A good bonding between alumina grains and the MgAlON matrix phase was obtained (Figs. 4 and 5). The bonding phase consisted of MgAlON as main phase and small amounts of AlN and Al_2O_3-rich spinel, in the transition zone of grains and matrix (Fig. 6). A linear shrinkage of approximately 10% occurred during firing and the density of the samples was very high, 3.42 g cm^{-3}.

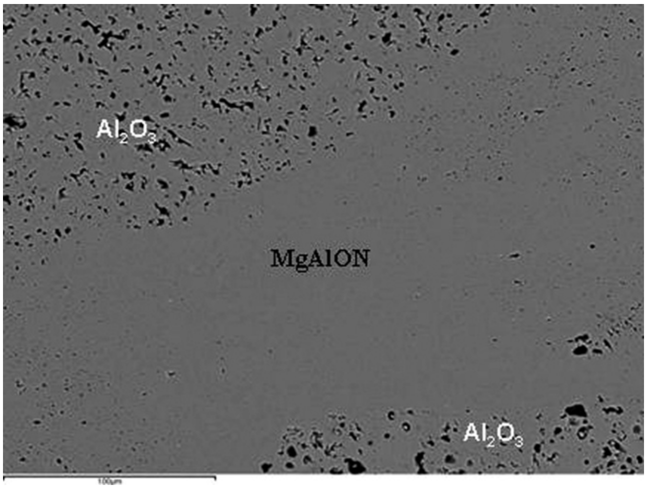

Fig. 5. SEM picture of MgAlON bonded alumina refractory. The investigation with SEM confirmed the good bonding between Al_2O_3 grains and the bonding phase. A smooth transition without gaps was formed.

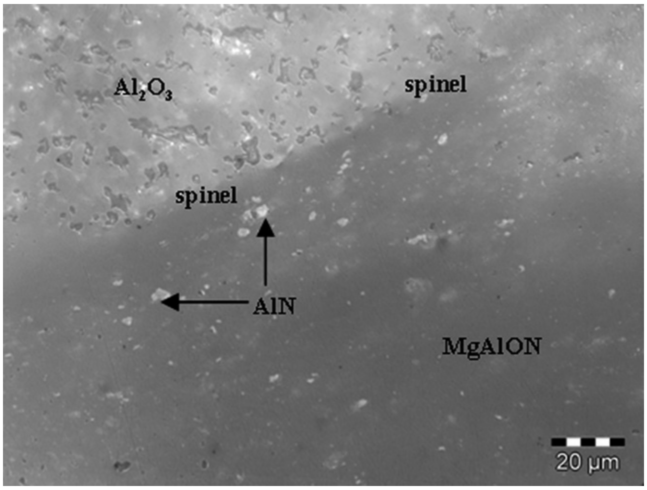

Fig. 6. Microstructure of MgAlON bonded alumina consisting of MgAlON, spinel and small amounts of AlN (white phase). Spinel without nitrogen was formed in the transition zone. The phases were determined by XRD and EDX.

Due to the good results for Al_2O_3–MgAlON composites, MgAlON bonded magnesia samples were prepared under the same conditions. The best results were expected for M1 composition as a bonding phase for magnesia ceramics, considering the phase diagram presented in Fig. 1. A bonding phase consisting of MgAlON phases with different amounts of nitrogen, or a bonding phase containing MgAlON and spinel was assumed. The prepared samples were sintered at 1650 °C for 5 h. However, instead of MgAlON, the bonding phase consisted of pure alumina rich spinel with small amounts of locally occurring AlN. Nitrogen was not detected in the spinel phase by EDX analysis. From this it follows, that AlN was not dissolved in the spinel phase.

Additionally, the properties of the samples were unsatisfying because the bonding between magnesia grains and matrix phase was very poor with wide gaps on the interfaces. Partially, even break-outs of magnesia grains occurred (see Fig. 7). The main reason for this might be the difference in the coefficient of thermal expansion of magnesia and spinel. While magnesia has a coefficient of thermal expansion of $13.63 \times 10^{-6}\,°C^{-1}$ for 25–1000 °C,[13] the coefficient of stoichiometric spinel is

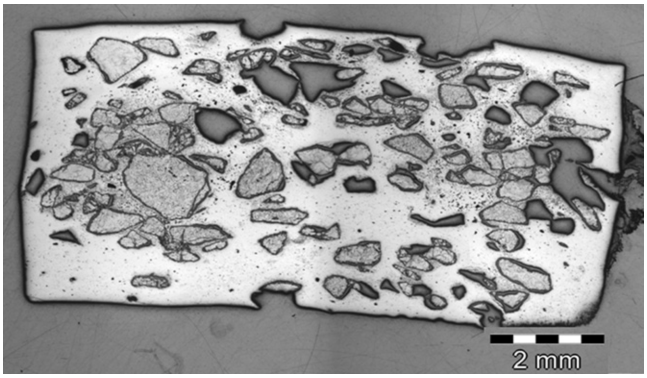

Fig. 7. Poor bonding between magnesia grains and matrix phase.

Table 5
Composition of the phases occurring in the MgO samples.

Phases	N [mol%]	O [mol%]	Mg [mol%]	Al [mol%]
MgO		51.6	48.4	
Stoichiometric spinel		59.6	13.3	27.1
Alumina rich spinel		57.2	8.8	34.0
AlN	49.5	2.5		47.9

$8.41 \times 10^{-6}\,°C^{-1}$ for 25–1000 °C.[13] During cooling the bonding between these phases was not strong enough to resist the occurring stresses.

Due to the undesired results, the matrix composition was changed and the mixtures M2, M3 and M4 were applied. It was expected that the higher amount of nitrogen in these composition support the MgAlON formation. However, the results were still not satisfying. Again the bonding between MgO and the matrix was poor with break-outs at the surface of the samples. Additionally, a partial decomposition of the magnesia grains could be observed because of a reaction between MgO and the matrix phase. This led to the formation of a rim of stoichiometric spinel around magnesia grains. With greater distance alumina rich spinel and a high amount of undissolved AlN could be found. Again, AlN was not dissolved in the spinel phase. The composition of the phases determined by EDX analysis is shown in Table 5.

The phase distributions are presented in Figs. 8 and 9. MgAlON was not formed in the bonding phase of magnesia refractories. Even at the high temperature of 1800 °C, AlN and spinel were still present.

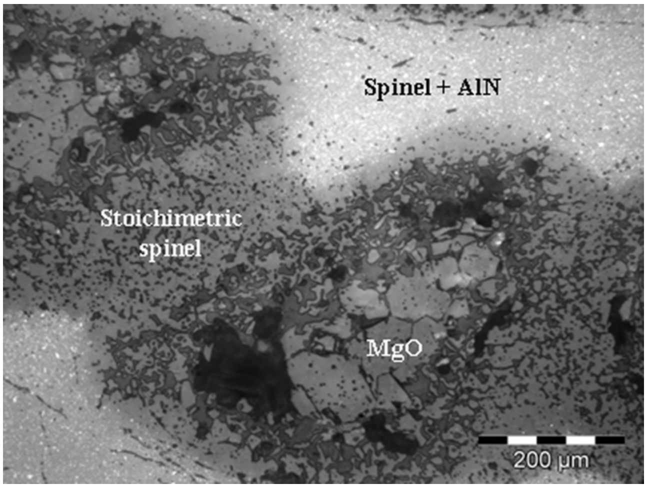

Fig. 8. Microstructure of magnesia refractories. Stoichiometric spinel was formed around the magnesia grains. The bonding phase consisted of alumina rich spinel and AlN.

Granon et al.[6] and Bandyopadhyay et al.[7] described that the final reaction of the MgAlON formation is the slow incorporation of AlN into the spinel phase. No MgO is present in this advanced state. In our case, however there was still MgO left in the form of magnesia grains which can react with the spinel phase. According to the kinetic of the reaction alumina rich

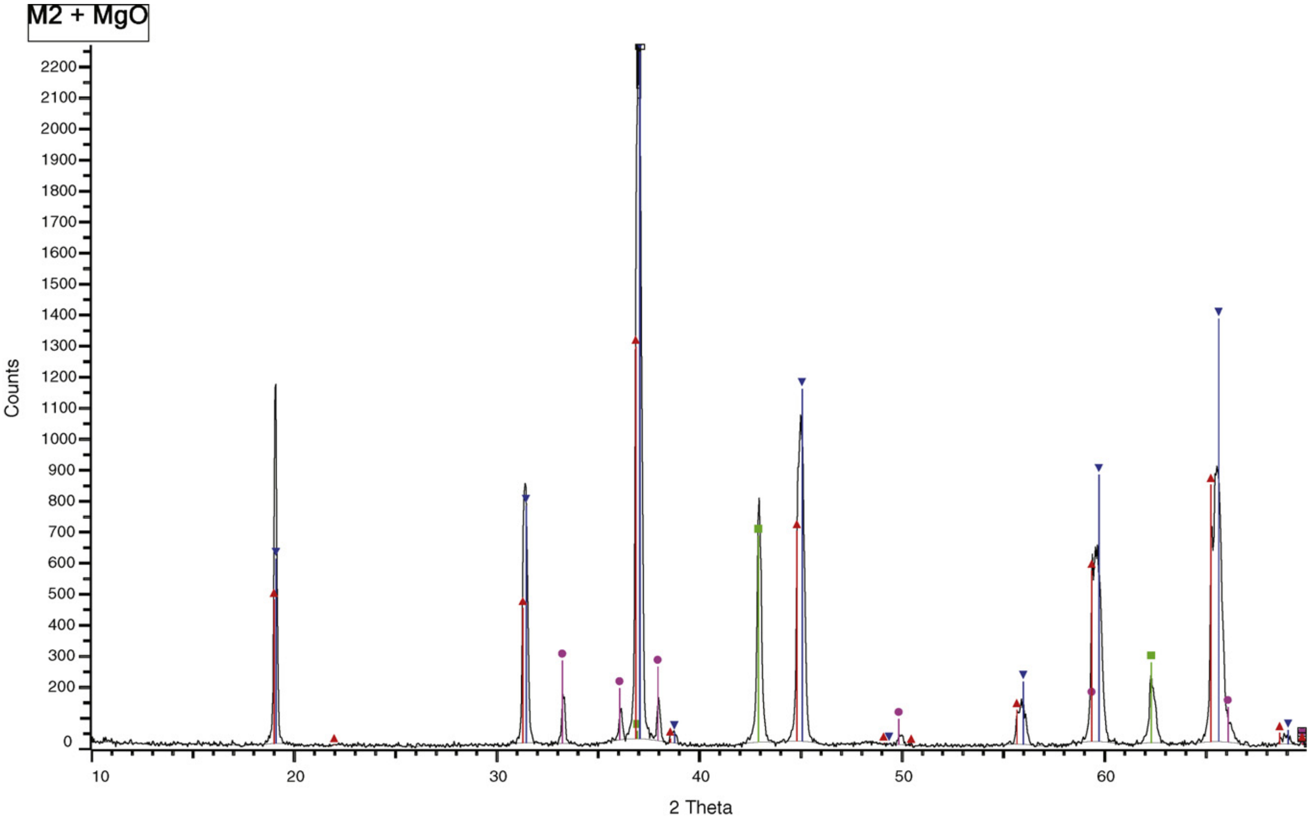

Fig. 9. XRD analysis of MgO samples. The bonding phase consisted of stoichiometric spinel, spinel and AlN. ■, MgO; ▲, stoichiometric spinel; ▼, alumina rich spinel; ●, AlN.

spinel, which was found in the bonding phase besides AlN, will first react with magnesia to form $MgAl_2O_4$ before incorporating AlN. These proposed reactions require further investigations.

4. Conclusion

The production of pure MgAlON in a graphite resistance furnace at a temperature of 1650 °C in nitrogen atmosphere was carried out. MgAlON was detected in all investigated samples, but differences occurred concerning the structure and the amount of secondary phases. If MgO was used as raw materials a volume expansion occurred due to the in situ formation of spinel. This should be avoided and therefore $MgAl_2O_4$ was added as magnesium source for MgAlON bonded refractories.

The production of MgAlON bonded alumina refractories was successful. The MgAlON bonding phase contained only a very small amount of AlN as secondary phase. It is expected that an increase of dwell time may help to produce a pure MgAlON phase.

The production of MgAlON bonded magnesia samples, however, was not possible. Stoichiometric spinel, alumina rich spinel and AlN were formed instead of MgAlON. Even at 1800 °C the AlN was not dissolved into spinel. One explanation might be that the equilibrium of the system was not yet reached and more time or a higher temperature would be necessary for the dissolution of AlN. A higher amount of fine magnesia might enable the formation of MgAlON bonded magnesia refractories. However, further investigations are necessary to fully clarify the possible reaction mechanisms.

Acknowledgements

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