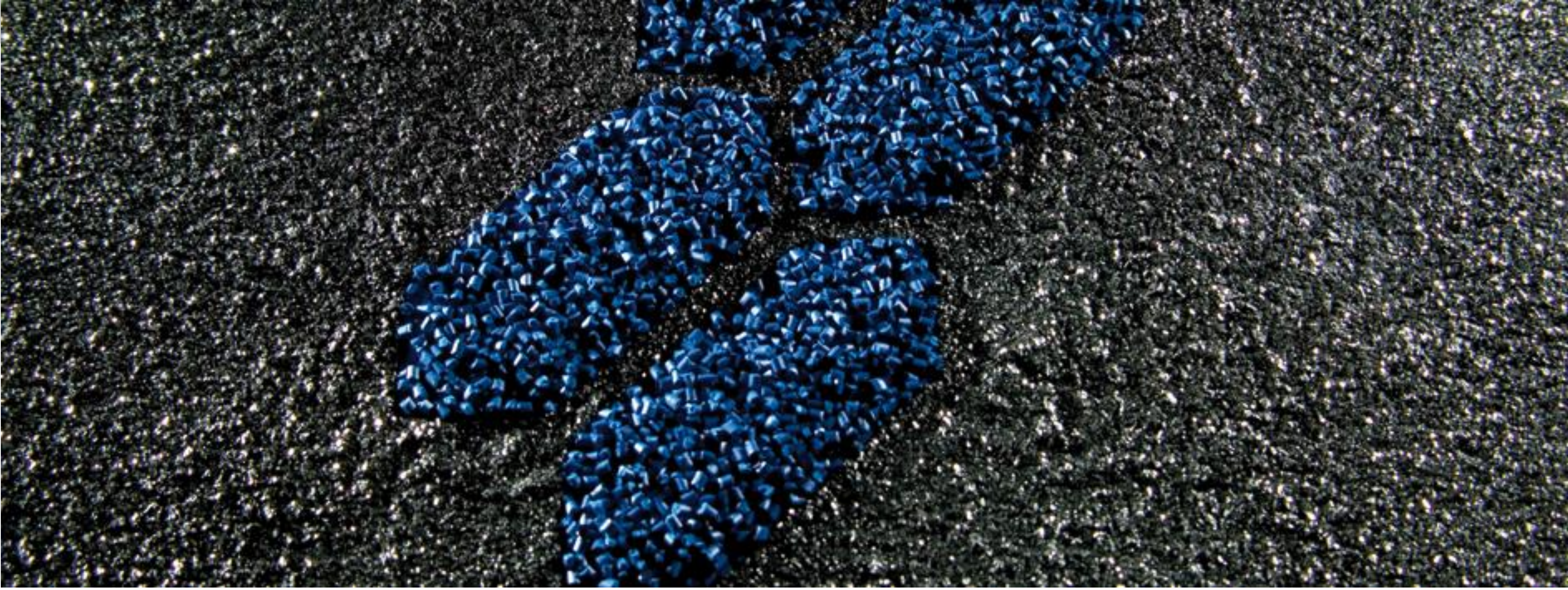

The Role of Graphite in Refractories such as $Al_2O_3/MgO/C$

Graphit Kropfmühl

AMG MINING

Overview

- **AMG Mining – Short introduction**
- **History of refractory production in Europe**
- **Crucibles**
- **Refractories**
  - High alumina refractories
  - Al_2O_3-MgO-C
  - MgO-C
- **Summery of the graphite role in refractories**



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AMG Mining - Company History


1870 Start of industrial Graphite mining in Kropfmühl
1877 Patent for a „Method to purify Graphite“
1916 Change into a public company
1916 First deliveries to the pencil industry
1980 Development of water based Graphite-Dispersions
1984 UF Graphite: Standard in PM Industry
1998 Acquisition of RW silicium GmbH
1999 Start of expandable Graphite production in Týn
1999 Introduction of SGB Graphite
2008 80% of GK shares were bought by AMG
2012 First increase to 93,59 %, then squeeze out
2012 Restart of mining in Kropfmühl

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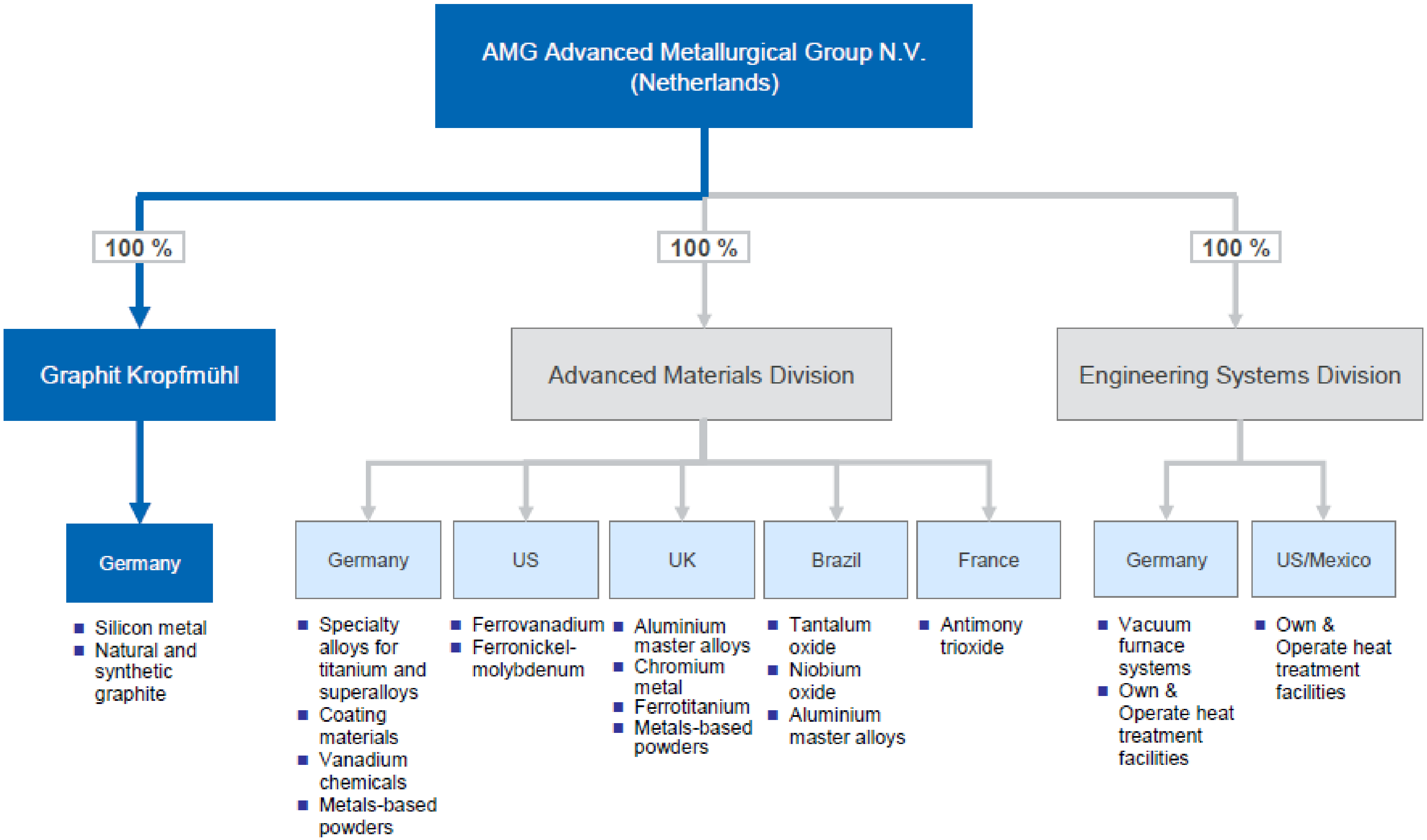
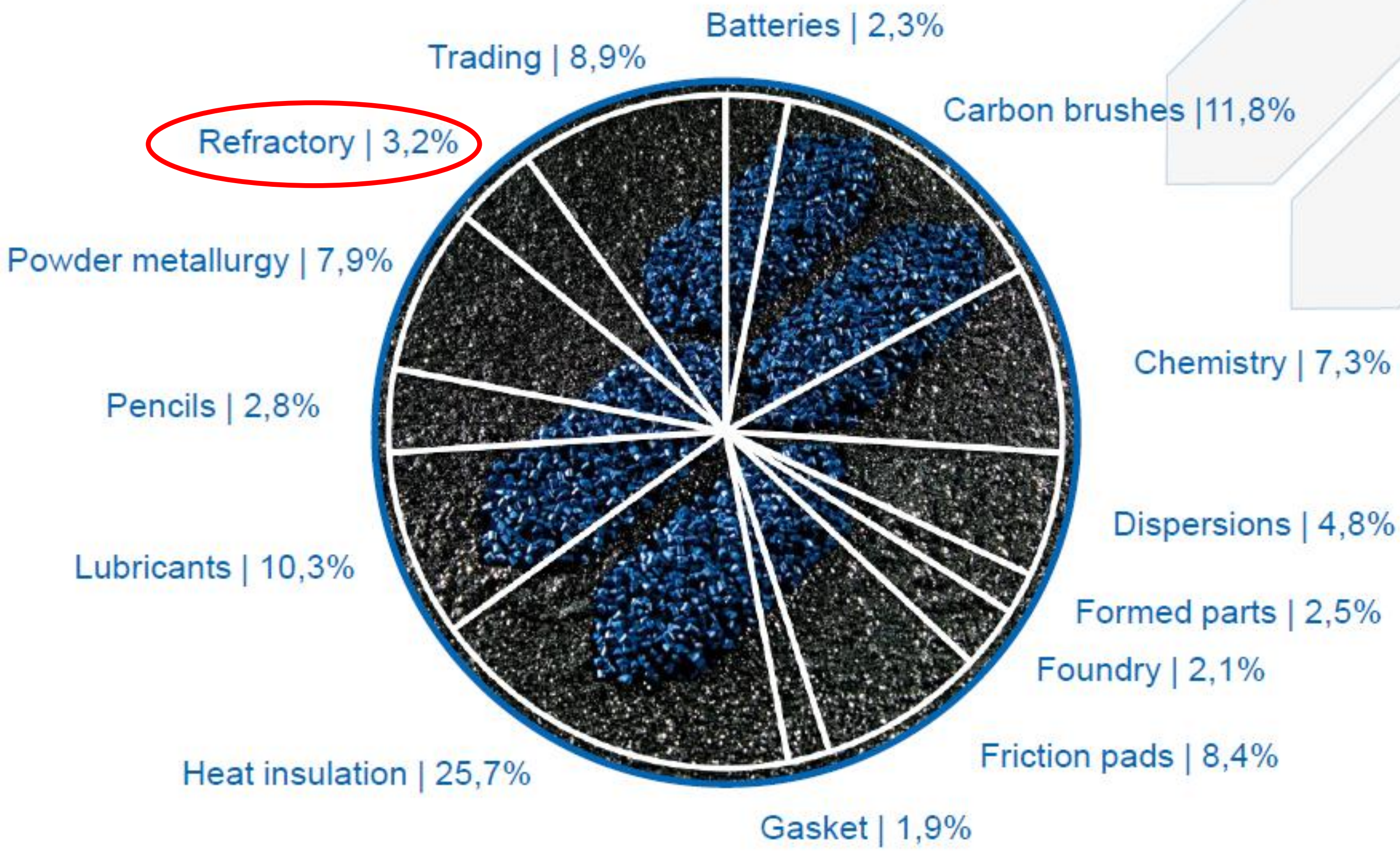
Worldwide companies AMG



Turnover AMG Mining 2012



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History – graphite in crucibles

- The melting of metals in crucibles has a long history, beginning in ancient Egypt and still continuing it`s traditions in today`s modern world. The first crucibles in the very advanced civilisation made in Egypt were based on silicates free of graphite.

- It is not clear when people first found out the advantages of mixing clay with graphite for crucibles. The German scientist Georgius Agricola was the first who made a report on the Passauer / Hafnerzeller crucibles for melting metals before the year 1556.

- The addition of graphite to pottery made it water proof even without glaze and better heat conductive. We can assume that the very first production of clay bounded graphite crucibles had taken place in the “Kropfmühl” area.

- In history, the celtics used graphite for production of ceramics already 2500 years ago.

Refractories

Market Size for Graphite in Refractories

- 2011: About 485,000 t graphite for 3.2 Mio t C-containing refractories
- 2 main groups at the center of attention:
- A) Crucibles:
  Main parts: Clay/tone, graphite
- B) Refractory stones (magnesite carbon stones)
  Main parts: Magnesite + coal materials

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Graphite containing crucibles

- Specs: Good thermal and el. conductivity
- Used in furnaces fired with fuel, electricity or induction, mostly for light non-ferrous metals
- Service temperature up to 1600 °C

- **Raw materials used in mixes for crucibles**:

Clay bonded	Carbon bonded
22-28% binder (refractory clays)	12-25% binder (refractory clays, pitch/phenolic resin)
6-10% Si	3-5% Si
15-25% SiC	38-45% SiC
40-50% Graphite	25-35% Graphite

- Isostatic pressing or screw-in (plastic) process
- Glaze formation during service protects graphite against oxidation

Refractories

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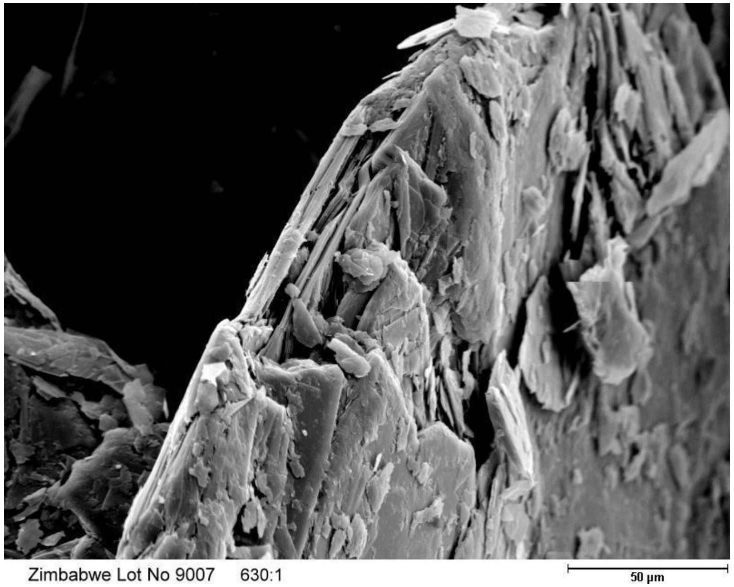
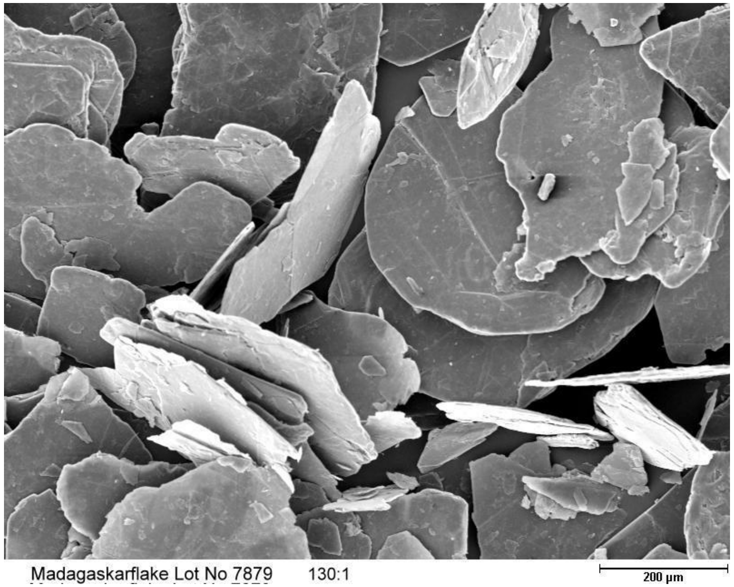
Graphite containing crucibles

- Specification for mostly used natural graphite:
- C= 85-94%, other important parameters: crystallite size, flake size and thickness , BET
  -> relative fraction of edge sites strongly influences oxidation
- Ash composition and melting point





- “thick” graphite flakes from Zimbabwe

“thin” flakes from Madagaskar

Graphit Kropfmühl

Al_2O_3-C (AC) high alumina refractories with ZrO_2

- Widely used as the lining materials in blast furnaces and electric furnaces

Important spec:

- Corrosion behavior in the melts of smelting reduction with the iron bath
- Thermal shock during filling and emptying

- Studied compositions:

Specimens	AC1	AC2	AC3	AZ1	AZ2	AZ3
Al_2O_3 (%)	76.75	74.60	72.45	71.58	68.35	66.02
SiO_2 (%)	11.20	10.40	10.12	10.17	9.50	8.14
C (%)	4.05	7.20	9.50	9.90	9.80	9.80
ZrO_2 (%)	0.12	0.51	1.50	3.00	6.00	9.00
CCS (MPa)	41.95	44.74	45.88	42.53	43.65	41.50
MOR (MPa)	15.45	16.68	17.81	15.36	14.45	15.66
Porosity (%)	5.38	4.52	4.03	4.18	4.92	5.14

Cold crushing strength
Modulus of rupture

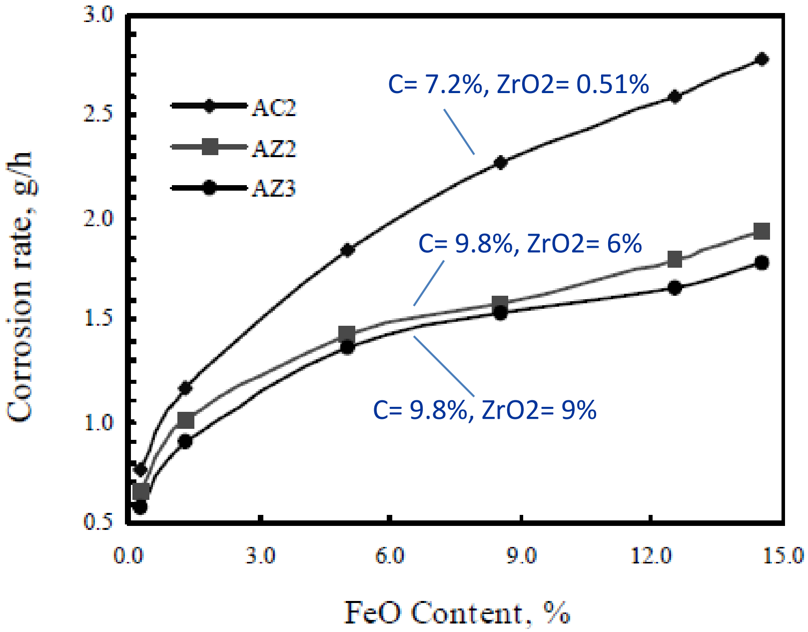
- LIU Qing-cai et al., Journal of Materials Science and Engineering 2(12) (2008) 49-53.

Graphit Kropfmühl

Al_2O_3-C (AC) high alumina refractories with ZrO_2

Testing

- Corrosion behaviors: rotary immersion and quasi-static immersion in electric resistance furnace
- Experimental temperatures were between 1400 °C and 1650 °C.
- The atmosphere above the molten bath was maintained at 30% CO, 60% N_2 and 10% CO_2 by volume.
- Slag composition: 10.0% FeO, 35.3% CaO, 33.2% SiO_2, 8.0% MgO, 11.0% Al_2O_3, 2.5% TiO_2. Iron bath formed by pig iron scrap, 4.16% C, 0.53% Si, 0.32% Mn, 0.10% P and 0.034% S.



-Dependence of the corrosion rate of refractories on the FeO content in melts , test temperature 1500 °C

- The refractories containing ZrO_2 exhibit a good anti-corrosion characteristic, especially in the melts of FeO concentration above 6%.

- Graphite carbon contained in the refractory is an active reducing agent of the iron oxides. The graphite of theAl_2O_3-C refractories was oxidized by the iron oxides of the melts. Pores and cracks are formed in the reaction zone.

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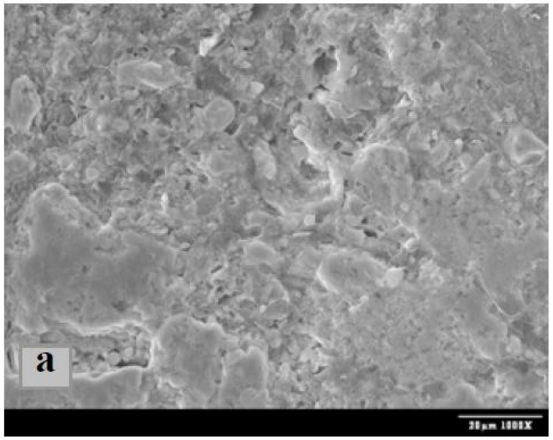
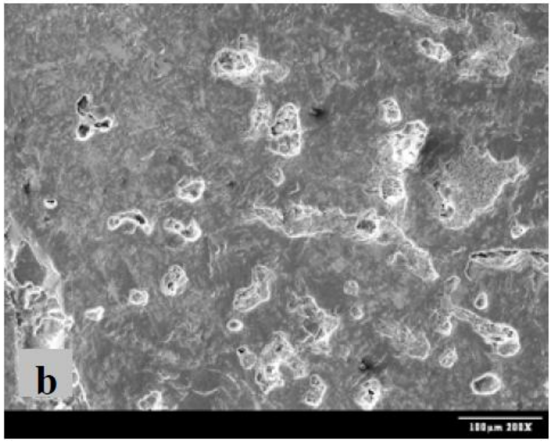
Al_2O_3-C (AC) high alumina refractories with ZrO_2

- SEM: AC2, immersed in slag and iron bath, test temperature 1773 K, rotary speed of refractory in melts 15 r/min.





Al_2O_3-C refractories are composed of corundum, mullite, Al_2O_3 and graphite.

EDS data: graphite carbon was oxidized over 90% and no graphite carbon was found in the interface between deteriorative layer of the refractory and slag film.

Corrosion mechanism of AC refractories in the smelting reduction melts with iron bath:

1. graphite oxidization
2. deteriorative layer formation.

The deteriorative layer of Al_2O_3-C refractory was corroded greatly by the smelting reduction melts.

Lot of new compounds formed by reaction with slag, such as $CaSiO_3$, TiO_2, $FeSiO_3$, Al_2SiO_5 and Fe_3C

Graphit Kropfmühl

Al_2O_3-MgO-C (AMC) refractories for steel ladle lining

Important spec:

- Residual expansion during the usage
- Temperatures from 1600 to 1750 °C, resistance against turbulence of steel bath during heating/purging
- Thermal shock during filling and emptying
- Corrosion contact with basic steel ladle slags

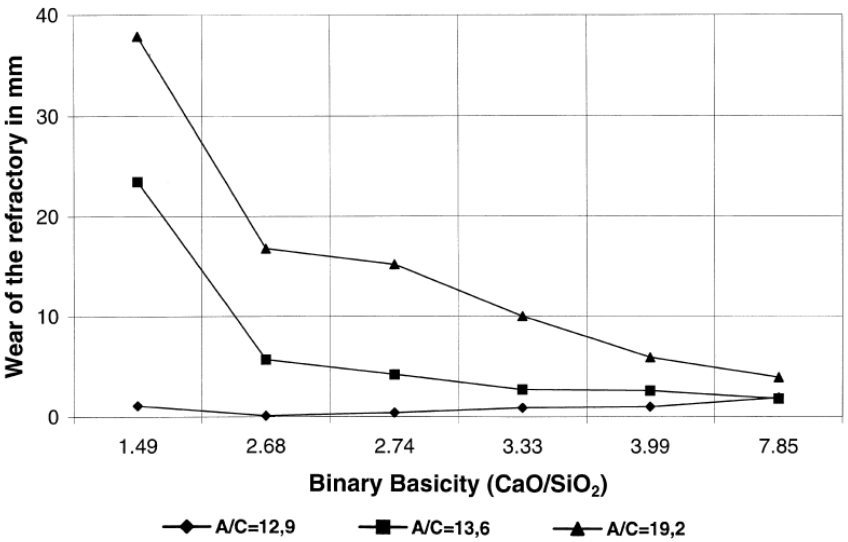
- AMC: Superior chemical and thermodynamic stability characteristics when compared to high alumina and doloma steel laddle refractories, but also excellent thermal and mechanical properties.
- Influence of alumina/carbon ratio and magnesia / silica contents on the refractories corrosion resistance.

- The carbon bond enables combinations of raw materials with varying expansion coefficient
- Usual compositions: 50-70% Al_2O_3 ,15-30% MgO, 2-15% C, 0.3-3% others (SiO_2, Fe_2O_3, TiO_2)

Graphit Kropfmühl

Al_2O_3-MgO-C (AMC) refractories for steel ladle lining

- Important spec: Residual expansion during the usage. responsible for the formation of a monolithic refractory lining resulting in a decreased steel penetration through the refractory joints.



- Wear results with rotary slag attack

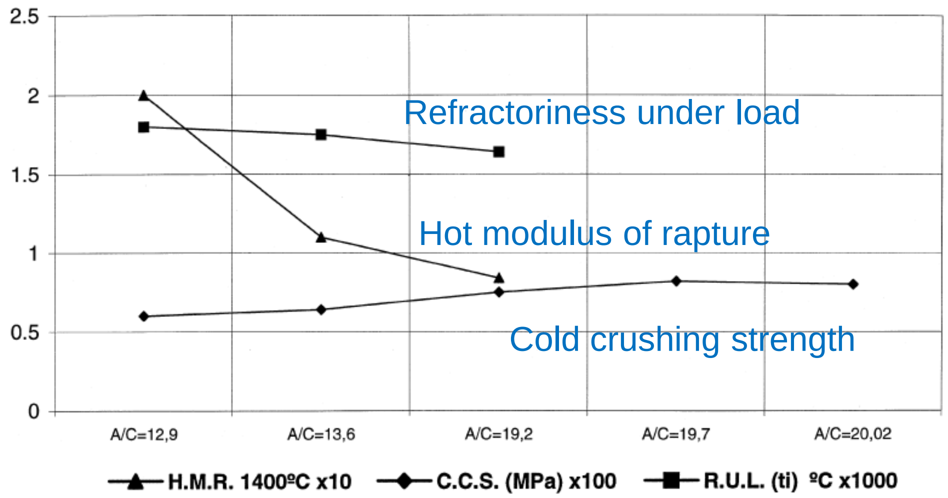
W. S. Resende et al., Journal of the European Ceramic Society 20 (2000) 1419-1427.

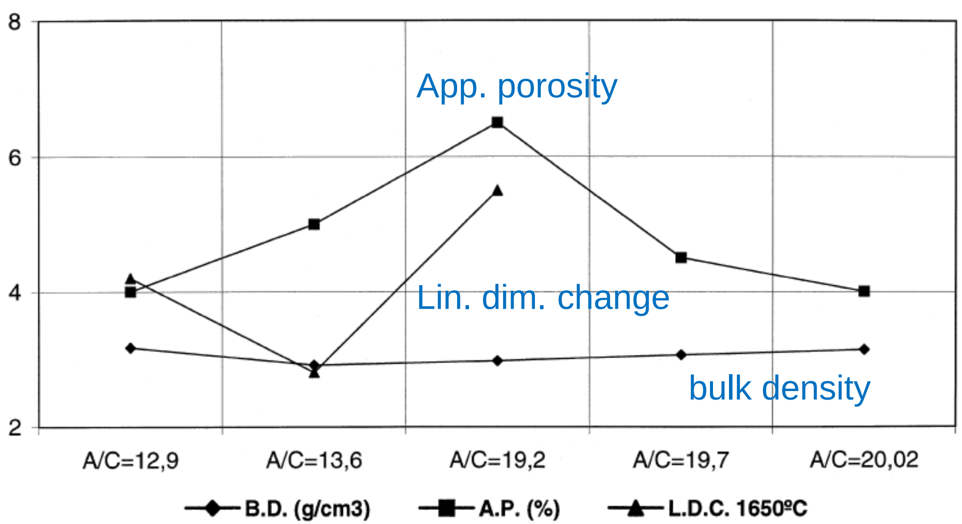
Al_2O_3/C (A/C) = 12.9

- Higher corrosion resistance for highest C content and smallest SiO2 content
- Present phases:
  - corundum Al_2O_3
  - mullite $3Al_2O_3 \cdot 2\ SiO_2$
  - periclase MgO
- Separate graphite phase with high refractoriness, λ, low thermal expansion, low wettability by slag
- High mullite conc. promotes Ca-aluminosilicat formation (eutectic at 1265 °C)
- Periclase consumes mullite and contributes corrosion resistance to high basicity slags

Graphit Kropfmühl

Al_2O_3-MgO-C (AMC) refractories for steel ladle lining





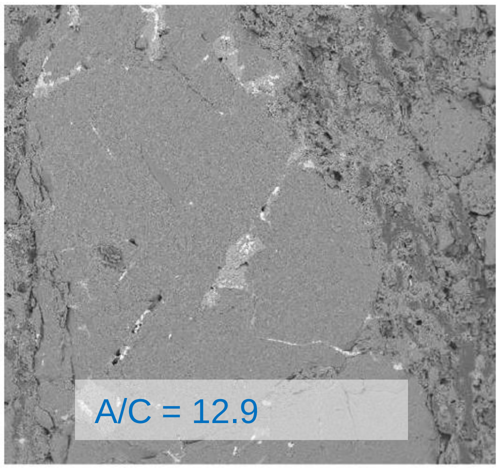
A/C = 12.9

- Better packing of microstructure, smaller pore size
- Higher conc. of graphite lead to best packing

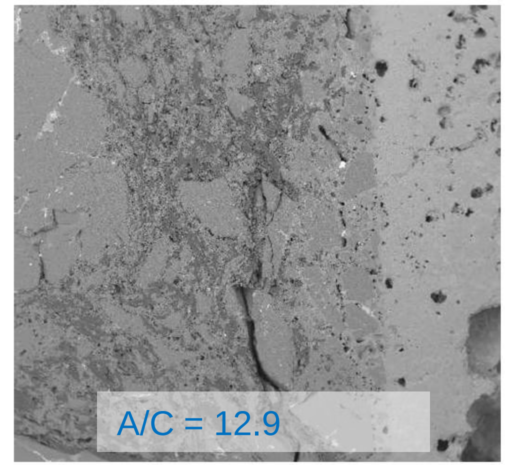
Refractories

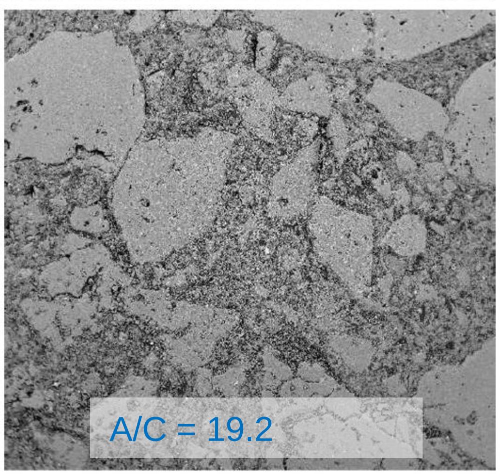
Graphit Kropfmühl

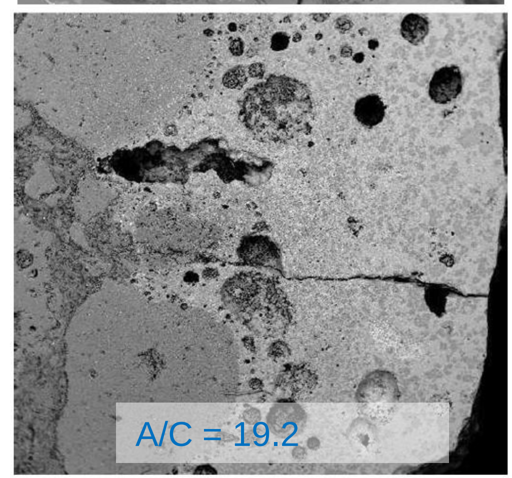
Al_2O_3-MgO-C (AMC) refractories for steel ladle lining



- Slag test at 2.74 bin. basicity
- 2h / 1750 °C







SEM before test (20x)

SEM after rotary slag test

Graphit Kropfmühl

MgO-C (MC) refractories for basic/electric arc furnaces

Important spec:

- Used in basic furnance, electric arc furnance, and steel ladles

Role of graphite

- Carbon specs: - macrocrystalline flakes with 90-96% C, -100 to +50 mesh, 3-25%
  - carbon black for optimal pore filling 1-2%)
  - pitch / phenolic resin for coaked binders (3%)

- Negative effects of oxidation of graphite: spalling and pore generation
  ->addition of antioxidants necessary

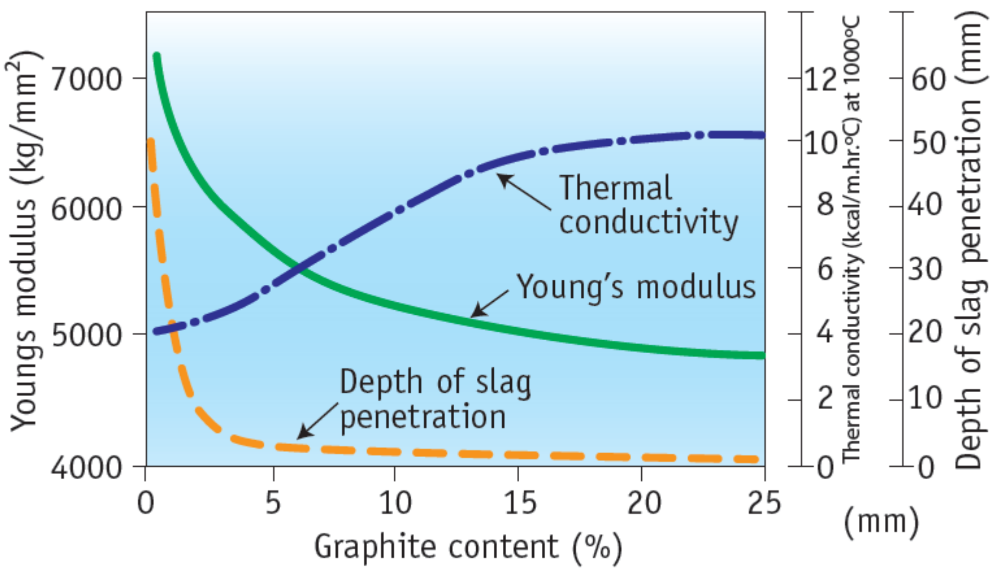
- Even better protection is possible by coating the antioxidant on top of the graphite particles

Graphit Kropfmühl

MgO-C (MC) refractories for basic/electric arc furnaces

Role of graphite

- Corrosion resistance by less wettability with a molten metal
- Excellent thermal shock resistance by low thermal expansion & high thermal conductivity
- Low elasticity, due to the presence of graphite
- Structure-flexible bond characteristic – C-bond usually forms in service
- Carbon changes the infiltration depth from cm to the mm range by:
  - Reduction of Fe_2O_3 in the infiltrating slag to Fe -< increase of the eutectic temp. from 1300 °C to >1600 °C
  - Non wetting behaviour between oxidic slag and brick carbon



T. Ayashi : Recent Trends in Japanese Refractory Technology, Transactions ISIJ, V21, 1981

R. Engel, The Refractories Engineer, (2013) 20-23

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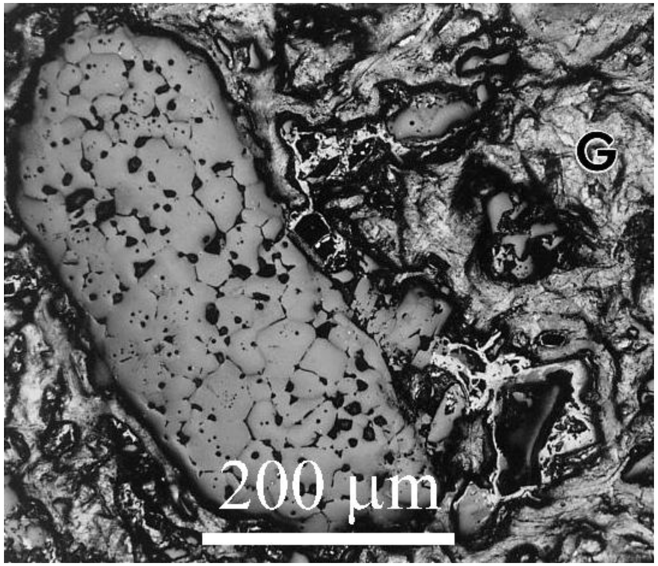
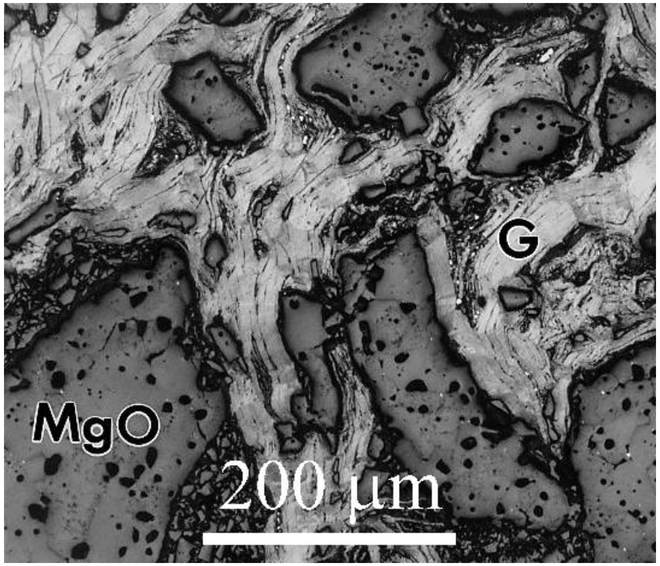
MgO-C (MC) refractories for basic/electric arc furnaces

SEM: Anisotropy of thermal conductivity by flake orientation





- Graphite flake alignment in MgO-C bricks, perpendicular (left) and parallel (right) to the bricks long dimension

W.E. Lee, http://core.materials.ac.uk

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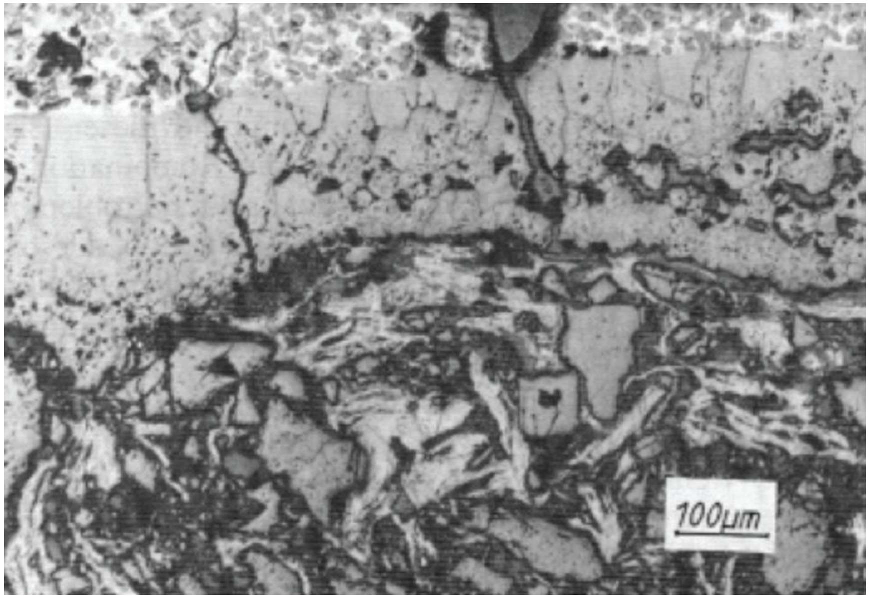
MgO-C (MC) refractories for basic/electric arc furnaces

SEM:



Hot face – slag

Dense zone

Unreacted brick

I. Strawbridge, D.G. Apostolopoulos: High Purity Magnesias and Graphites in Magnesia-Carbon Refractories, Stahl und Eisen, Special, 1994

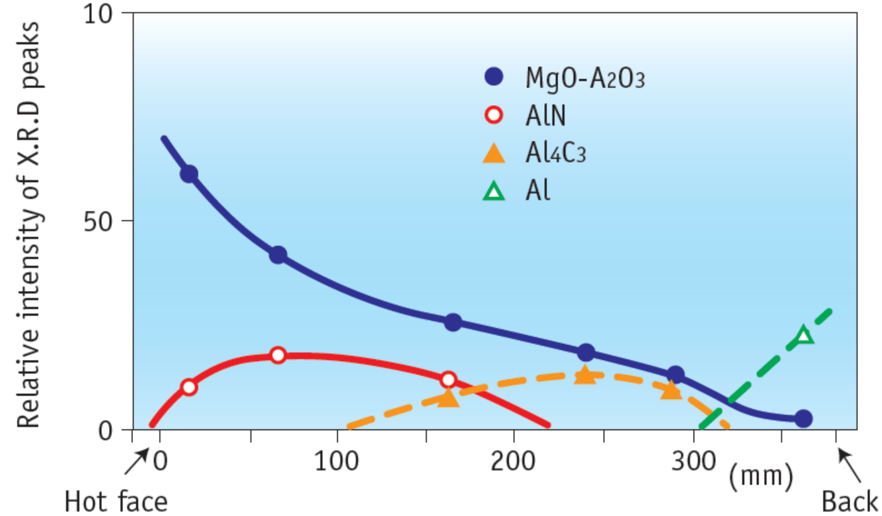
- Formation of a dense zone due to reduction of MgO with C at high T which vaporized the Mg and precipitated it in the dense zone.

MgO-C (MC) refractories for basic/electric arc furnaces

- Protection of the graphite in the dense zone: additions of metals like **Mg, Al, Si**

T

		$MgO + Al + C$	5. unreacted brick
	< 1380 K	$MgO + Mg + C$	4.
	> 1380 K	$MgO + Al_4C_3 + C$	
(N_2)		$MgO + AlN + C$	3.
(CO, N_2)	< 2080 K	$MgO + MgAl_2O_4 + C$	2.
	> 2080 K	$MgO + AlN + C$	
$(CO, CO_2, N2)$		$MgO + MgAl_2O_4$	1. hot face



T. Rymon-Lipinski: Reaktionen von Metallzusätzen in Magnesia-Kohlenstoffsteinen in einem Sauerstoffkonverter, Teil 1, p 1049 (47), Teil 2, p 1055 (53), Stahl u. Eisen, V. 108, # 22, 1988

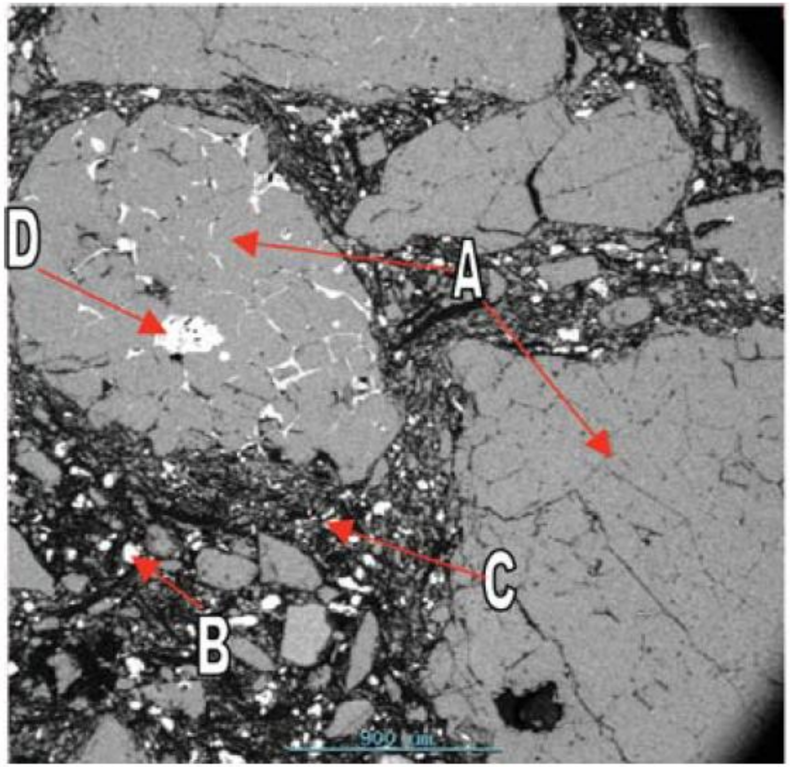
K. Ichikawa, et al., “Suppression Effects of Aluminum on Oxidation of MgO-C Bricks, Taikabutsu Overseas, V 15, #2, 1995

- Example of reactions inside different zones of the basic oxygen furnace with **Al** addition

Refractories

MgO-C (MC) refractories for basic/electric arc furnaces

- Protection of the graphite in the dense zone: additions of metals like **Mg, Al, Si**



YAMAGUCHI, A. Self-repairing function in the carbon-containing refractory, Int J Applied Ceramic Technology, vol. 4, no. 6, 2007, pp.490–495.

- Typical microstructure of a MgO-C brick which contains Al and Si as antioxidants.
- A=MgO; B=aluminium; C=silicon;D=merwinite ($Ca_3MgSi_2O_8$)

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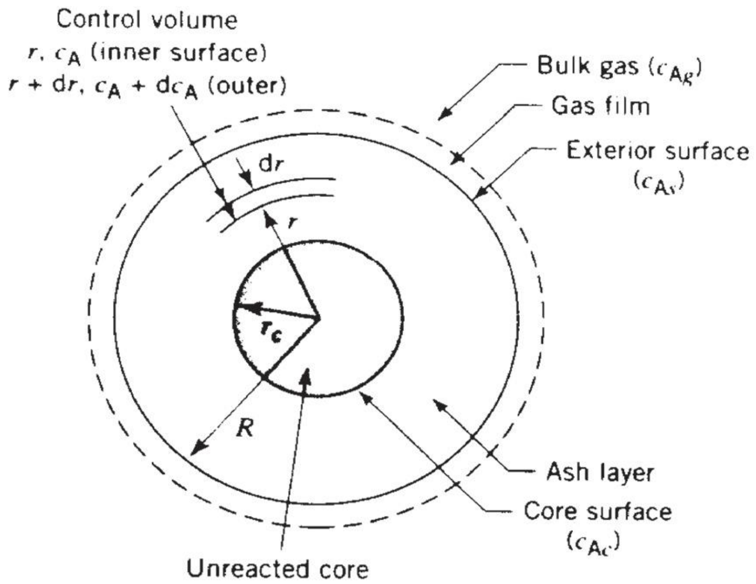
MgO-C (MC) refractories for basic/electric arc furnaces

- Further protection of the graphite particles by coating with **Al**



Z. Ali Nemati et al., Tehran International Conference on Refractories , 4-6 May 2004

Shrinking – Core Model (SCM)

- The shrinking core model for an isothermal spherical graphite particle (B) which reacts with gas (A)
- There is a sharp boundary (the reaction surface) between the no reacted core of the graphite and the porous outer shell (ash layer).
- The gas film reflected the resistance to mass transfer of gas (A) from the bulk gas to the exterior surface of the particle.
- As time passes, the reaction surface moves progressively toward the center of the particle.
- According to the SCM model, three processes involving mass transfer of gas in gas film, diffusion of gas in porous layer and reaction of gas with solid (B) at reaction surface, are rate controlling steps.

MgO-C (MC) refractories for basic/electric arc furnaces

- Further protection of the graphite particles by coating with **Al**

Shrinking – Core Model (SCM)

- 1. Oxidation increases exponentially with temperature because diffusion of oxygen and reaction of graphite with oxygen increase when temperature increases.
- 2. With increasing of the graphite content, the rate of weight loss increases due to the formation of a more porous oxidized layer, but the fractional weight loss decreases due to the increase of the initial carbon content. The weight loss increase is not, however, proportional to the enhancement of the graphite content. This may be attributed to the combined influences of the reaction front area change,CO/CO2 ratio change and inter diffusion coefficients variations.
- 3. Oxidation mechanism is pore diffusion, which means the diffusion of oxygen through decarburized layer is the process determining step.
- 4. With higher graphite content, the oxidation mechanism tends to slightly deviate from pure pore diffusion control. The gas volume variations due to the CO/CO2 ratio change may cause the slight shifting of the oxidation mechanism from pure pore diffusion to pore diffusion -external gas transfer mechanism.

MgO-C (MC) refractories for basic/electric arc furnaces

- Activation of graphite surface

Graphite particles

↓ Mixing with an acid solution

↓ Sonicating for 3h at RT & stirring for 24h at RT

↓ Filtering

↓ Washing with distilled water

↓ Drying at 80 ℃ for 48 h

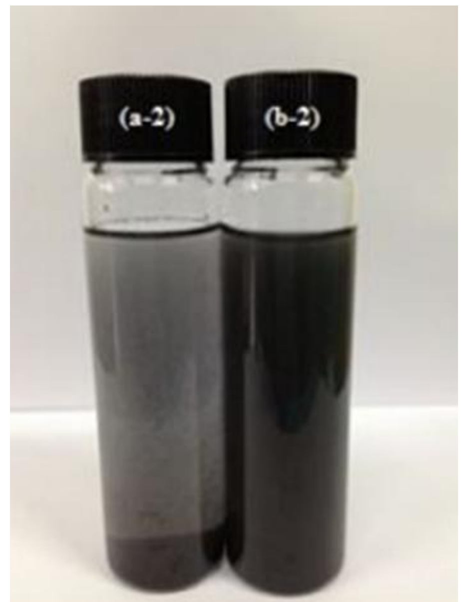
Surface modified graphite

↓ Mixing with Al precursor in an aqueous solution

↓ Drying at 80 ℃ for 1h

↓ Heat treatment at 300 ℃ for 1h

Al-coated graphite



Increased sedimentation stability of surface treated graphite in water after 3d

Geun-Ho Cho et al., “Improvement of Oxidation Resistance in Graphite for MgO-C Refractory”, 9th International Conference on Fracture & Strength of Solids, June 9-13, 2013, Jeju, Korea

Graphit Kropfmühl

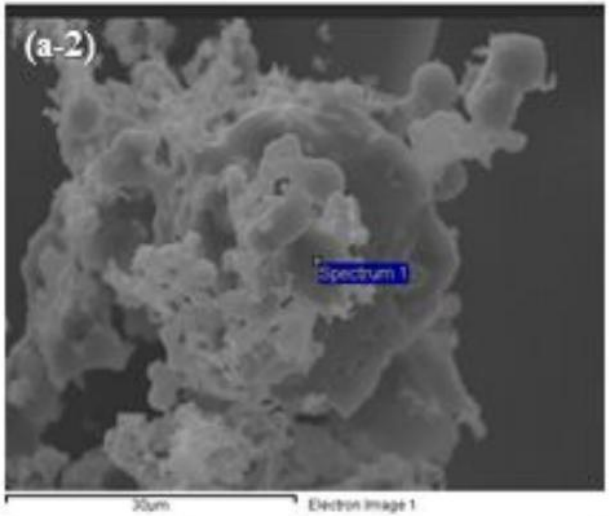
MgO-C (MC) refractories for basic/electric arc furnaces

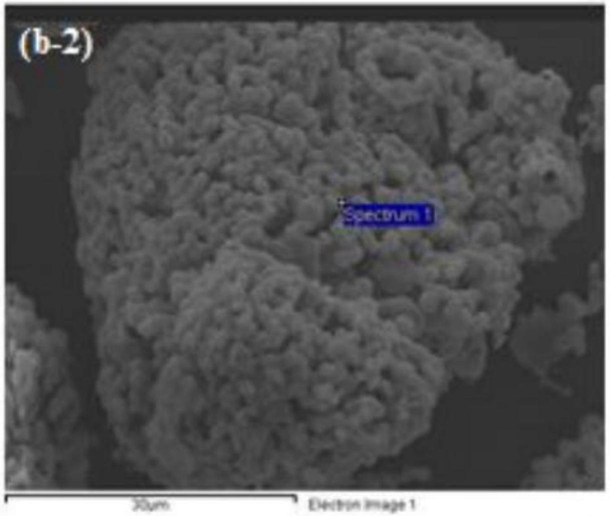
- Combustion tests at 500 – 1200 C for 1h

Element	Weight%	Atomic%
C K	10.73	16.03
O K	55.56	62.33
Na K	3.49	2.73
Mg K	0.74	0.55
Al K	6.21	4.13
Si K	20.19	12.90
Fe K	3.08	1.35
Totals	100	

Element	Weight%	Atomic%
C K	49.66	59.70
O K	36.36	32.82
Al K	13.98	7.48
Totals	100	

SEM morphologies and results of EDS analysis for modified graphite particles without and with coating by Al precursor:
(a) without coating layer and
(b) with coating layer.





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MgO-C (MC) refractories for basic/electric arc furnaces

- Combustion tests at 500 – 1200 °C for 1h

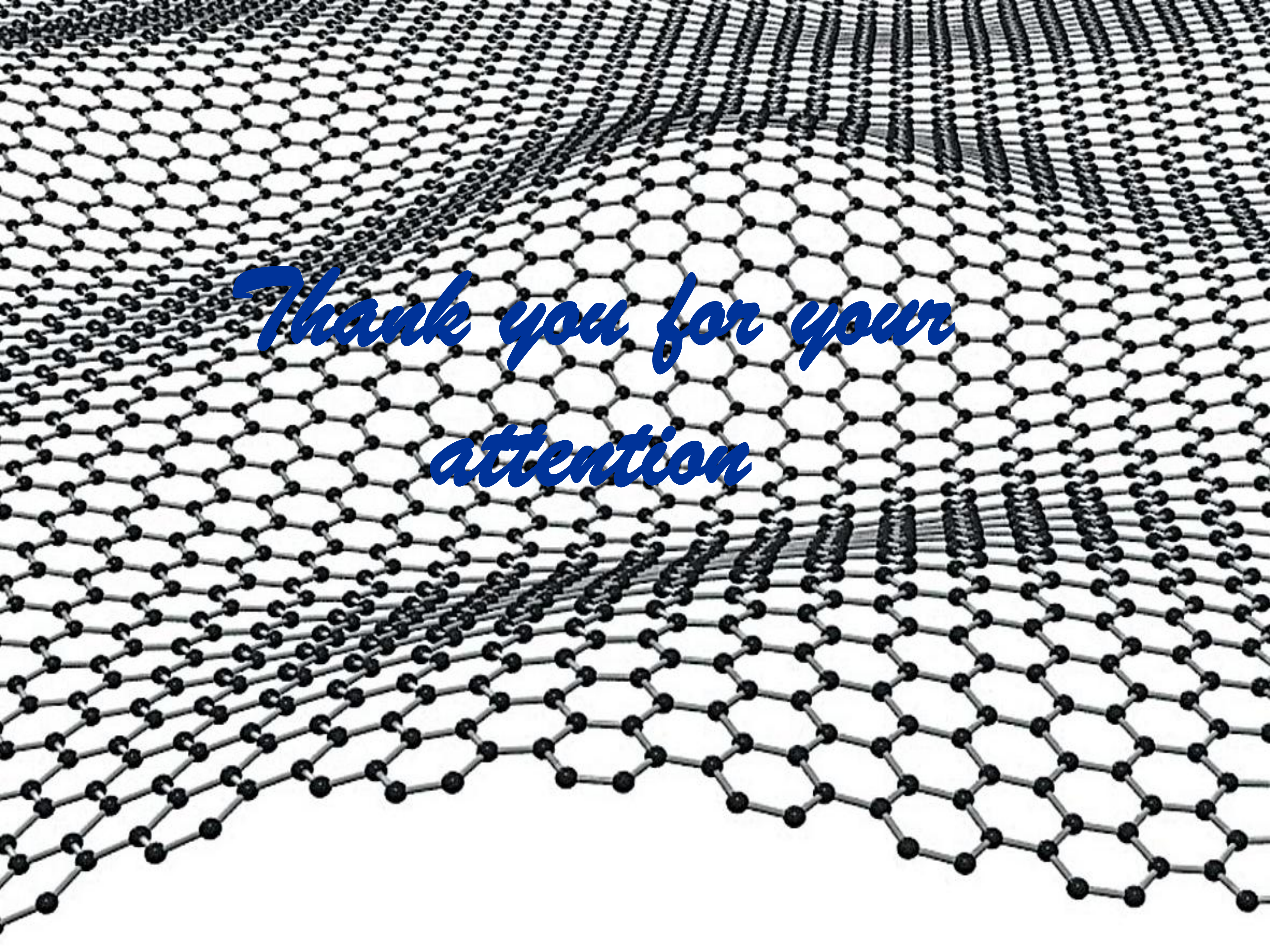
- Graphite without coating layer starts oxidizing at 700 °C and is fully reacted at 900 °C
- With coating: Oxidation starts at 900 °C and is fully oxidized at 1200 °C

- Further development of antioxidants: Binding resins that contain antioxidants attached to its polymeric chain in the form of complexation cations.

- TANAKA, P. and BALDO, J.B. A new friendly resin with coupled antioxidants protectors for carbon containing refractories. UNITECR 2007,Dresden, Germany, pp. 30–33.

Summary – Role of graphite

- **Refractory Specification**
  - oxidation resistance
    - graphite characteristics
      - particle size distribution
      - graphite impurities
      - crystallinity
        - macrocrystalline flakes
        - microcrystalline powder
    - presence of antioxidants
      - by mixing into the formulation
      - by coating onto the graphite
  - thermal shock resistance
    - anisotrpy of graphite flake
    - thermal conductivity
  - wear resistance
    - infiltration depth of slag
      - optimal pore filling by fine graphite or CB
      - nonwetting of graphite by oxidic infiltrate
    - structural strength
      - bonding strength inside the C lattice
      - adhesion of C (coke) lattice to the base material
      - formation of favorable strong phases by reaction of the antioxidant at higher T
    - reduction of slag components with a low mp
      - FeOx + C
  - mechanical strength
    - aspect ratio of graphite flake
    - orientation



Thank you for your attention