

The Steel Industry in Germany – Trends in Clean Steel Technology and Refractory Engineering

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The permanent development of steel producing technology is a main driver for the development of new and improved refractories. The paper briefly discusses the trends in steel secondary metallurgy and how modern engineered refractories provide innovative solutions for challenging conditions in the steel making process. Examples are given how refractories contribute to steel quality and economical improvements in the process.

The steel industry is a key driver for new developments in the refractory industry due to the high market share of steel refractories in the range of 60 to 70 % and the harsh conditions for refractories in the steel making processes. A constant engineering of refractories is needed to cope with new and more demanding requirements in the steel making process. The first part of the paper briefly discusses trends in the steel making technology, and the second part describes examples how modern engineered refractories provide solutions for economical production of high quality steels.

Trends in secondary metallurgy

Trends in the steel making technology have been discussed in detail by Fahndrich et al. [1], and Bruckhausen and Fahndrich [2]. With regard to the focus of this paper, they can be briefly summarised as follows. There is continuous development of new steel grades with tailored properties for various, very different applications, and there are more than 2000 different steel grades on the market. These are high purity steel grades with tight specifications for undesired impurities and alloying elements. Fig. 1 shows the achievable content of im-

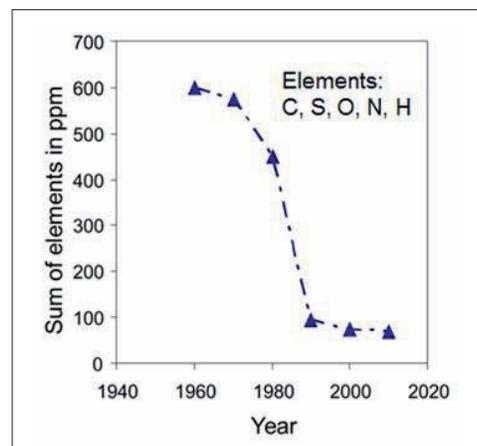


Fig. 1 Achievable contents after secondary metallurgical treatment between 1960 and 2010 [1]

purities in steel over the past 50 years, and Tab. 1 shows important alloying agents in steel production and possible minimum and maximum contents for different products. The improvement of steel is to a great extent achieved by treatment in the steel ladle. The strong impact of this so-called secondary metallurgical treatment in the steel ladle from 1980 onwards is obvious.

Tab. 1 Content of alloying agents due to treatment in secondary metallurgy [1]

Element	Min./Max. Content [%]	Relevant Secondary Metallurgical Aggregates
C	0,0010–2,50	VOD/VD, RH, RH-OB, stirring station
Si	0,01–3,70	RH, LTS
Mn	0,08–20,00	LF
Cr	0,03–25,00	VD, RH, LF
Mo	0,01–4,50	LF or primary steelmaking
Ni	0,03–80,00	LF or primary steelmaking
Cu	0,03–3,50	LF or primary steelmaking
N	0,0020–0,5000	VD, RH, LF, stirring station
Al	0,0020–5,50	VD, RH, stirring station
W	0,020–6,50	LF or primary steelmaking
Co	0,03–10,00	LF or primary steelmaking
V	0,01–1,50	VD, RH, LF, stirring station
Ti	0,01–1,50	VD, RH, stirring station
B, Se, Te, Ca, Pb, S	0,001–0,300	stirring station, LF

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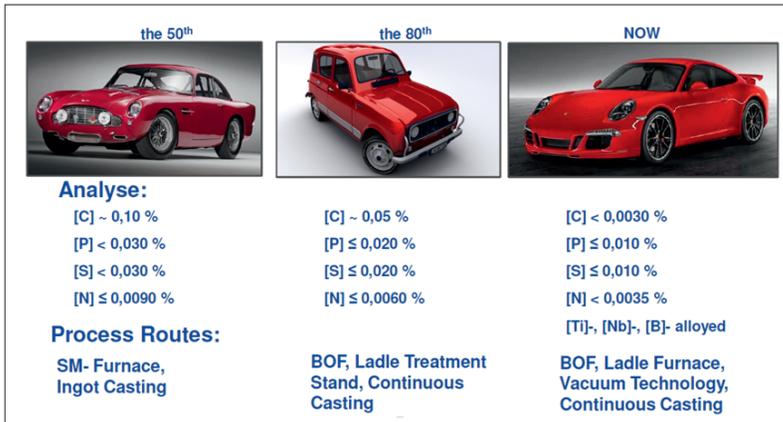


Fig. 2 Metallurgical challenges – example automobile industry [3]

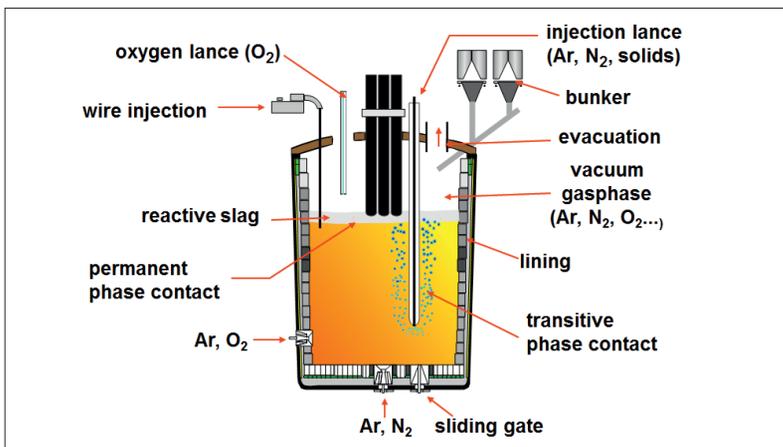


Fig. 3 The steel ladle as a “metallurgical reactor” [4]

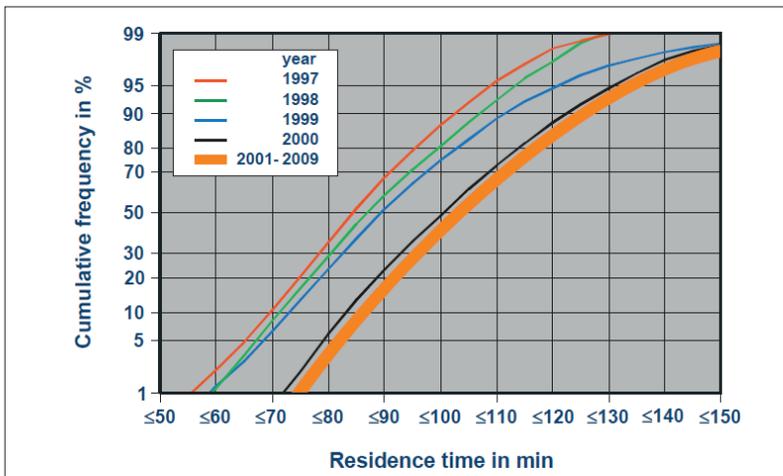


Fig. 4 Evolution of residence time of liquid steel in the ladle from tapping to start of casting [4]

Analyses of typical steel grades for automobiles in Fig. 2 demonstrate the increasing demand for low impurities and tight specification of steel.

An extended processing of liquid steel in secondary metallurgy requires continuous adjustment and improvement of the refrac-

tory linings and can be considered among the most important drivers for refractory innovations. Secondary metallurgy covers a broad range of processing such as de-oxidising, de-gassing, de-sulphurisation, de-carburisation to ultra-low carbon contents, alloying in tight specification ranges,

improvement of steel cleanliness by separation or modification of non-metallic inclusions, and last but not least homogenisation of composition and temperature. Lachmund [4] therefore refers to the steel ladle as a “metallurgical reactor” (Fig. 3).

The steel is constantly cooling down during the extended treatment times (Fig. 4) in the steel ladle. Therefore either higher tapping temperatures from BOF or EAF or re-heating of the steel in a ladle furnace or with thermochemical methods such as CAS-OB are required to compensate this temperature loss and ensure the right temperature for the casting of steel. The cost of temperature loss, specifically raising the temperature of steel by 1 K are between 3 and 5 [5] or even up to 10 [6] EUR per ton of steel according to different sources.

The high number of different steel grades (>2000) but also the different conditions in each steel plant, where none is exactly like another, require multiple and complex processing routes during secondary metallurgy in order to finally achieve the desired high quality steel product. Typical routes are shown in Fig. 5 considering primary melting, stirring, RH and VD/VOD degassing, ladle furnace and chemical heating installations. Careful and exact planning and performance of processing is needed for technically and economically successful steel production. Bruckhaus [2] therefore reported about “zero error strategies” with maximum productivity and flexibility as an important trend in modern steel making. Secondary metallurgy can only be performed with high performance refractory linings in the steel ladle. The following examples demonstrate how engineered refractories in steel ladle lining provide technical and economical solutions for challenging conditions in modern steel making. A special focus is given on high purity alumina refractories.

Developments in refractories engineering

Inert refractories for clean steel production

Refractories for steel ladle side walls must withstand slag attack by aggressive, metallurgical reactive slag e.g. calcium-aluminate slag with CaO/Al₂O₃ ratio around 1 for Al-killed steel (Fig. 6). In addition, the refractory lining must be thermodynamically stable in

contact with steel, e.g. excess dissolved aluminium in Al-killed steel, in order to avoid re-oxidation of the steel and problems with the steel cleanliness. This is normally not a problem with basic refractory linings such as doloma or magnesia-carbon bricks, the latter one being the standard material in the slag line of steel ladles.

Silica containing high alumina refractories such as andalusite or bauxite show high wear-rates with aggressive, low melting calcium aluminate slag. The SiO₂ in these refractories is thermodynamically not stable in contact with aluminium dissolved in the liquid steel and is reduced by the aluminium forming Al₂O₃, which degrades the steel cleanliness: $3\text{SiO}_2 + 4[\text{Al}] \rightarrow 2\text{Al}_2\text{O}_3 + 3[\text{Si}]$. Therefore high purity alumina-spinel refractories or magcarbon bricks have replaced andalusite and bauxite in ladle linings (Fig. 7).

Alumina-spinel refractories are successfully used in ladle side walls for both, Al- and Si-killed steel grades. They are applied either as castables or bricks. In steel ladle side walls, spinel forming castables provide advantages when compared with spinel containing castables due to slag resistance and thermoplastic behaviour at elevated temperature [8]. Bricks are either high-fired carbon free bricks or carbon bonded spinel forming AluMagCarbon (AMC) bricks.

Such fired spinel bricks must have a very low SiO₂ content in order to provide the desired performance. Franken et al. [9] reported that spinel bricks with 1 % SiO₂ achieved only 40 % of lifetime when compared to spinel bricks with 0,1 % SiO₂. Consequently, classical clay binder concepts for fired bricks must be modified e.g. by use of reactive alumina.

The performance of AMC bricks depends on the alumina aggregate used. Bauxite containing bricks represent the lowest quality. Such bricks cannot provide better performance necessary for more demanding and flexible processing of steel in the ladle. In the ladle bottom, high purity AMC bricks based on tabular alumina clearly outperform brown fused alumina bricks. Krausz et al. [10] reported about a 50 % lifetime reduction with brown fused alumina instead of tabular alumina in ladle bottom bricks.

The high purity tabular bricks provide higher creep and slag resistance and the most consistent rate of spinel formation during

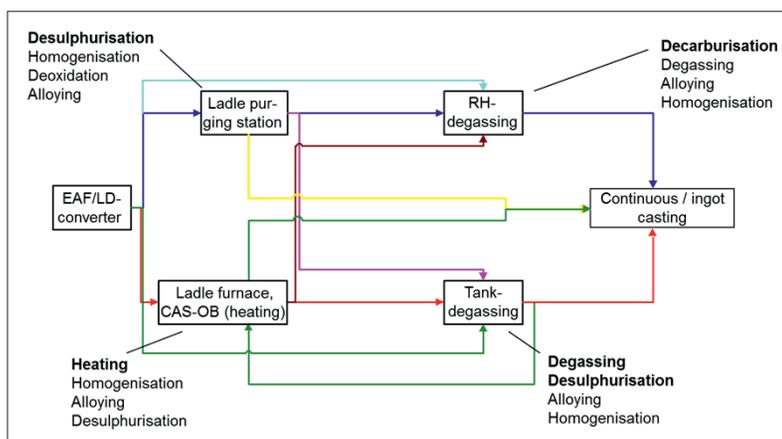


Fig. 5 Secondary metallurgy process routes – flexibility and diversity [1]

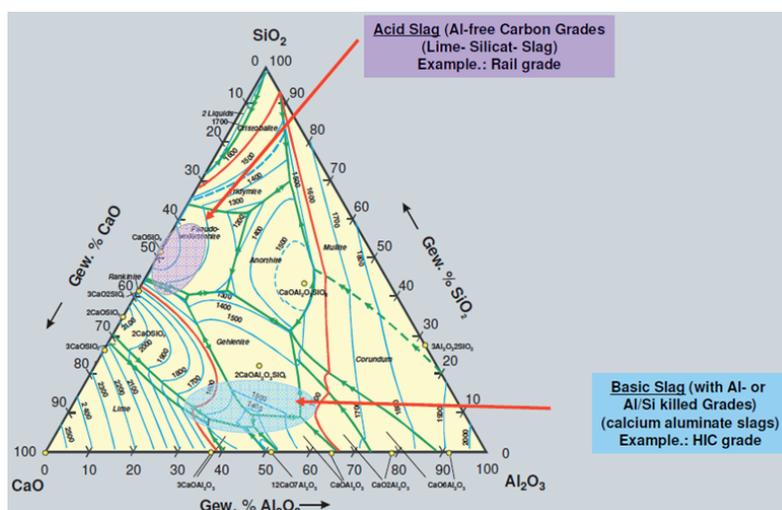


Fig. 6 Steel ladle slag compositions for metallurgically reactive top slags with low melting temperature and viscosity [3]

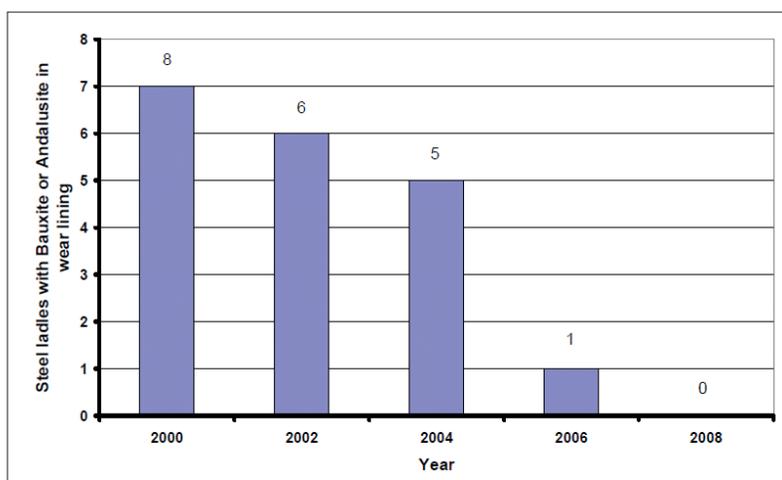


Fig. 7 Number of European steel works with bauxite or andalusite based wear linings in steel ladles, presented at international seminars on steel ladle lining in Europe 2000–2008 [7]

thermal cycling. Recent investigations with the new sintered alumina aggregate BSA 96 have shown a much more homogeneous

and earlier spinel formation in AMC bricks when compared to brown fused alumina [11].

Tab. 2 Typical data of ladle lining refractories

	MgO/C Bricks	AMC Bricks		AM	AM
		BFA	BSA 96	Fired Bricks	Castables
C [%]	10–15	6–8		–	–
Thermal Conductivity [W/m·K]	10	6,5	6,4	3,5	3,5
Bulk Density [g/cm ³]	2,9	3,25	3,08	3,0–3,2	2,9–3,0

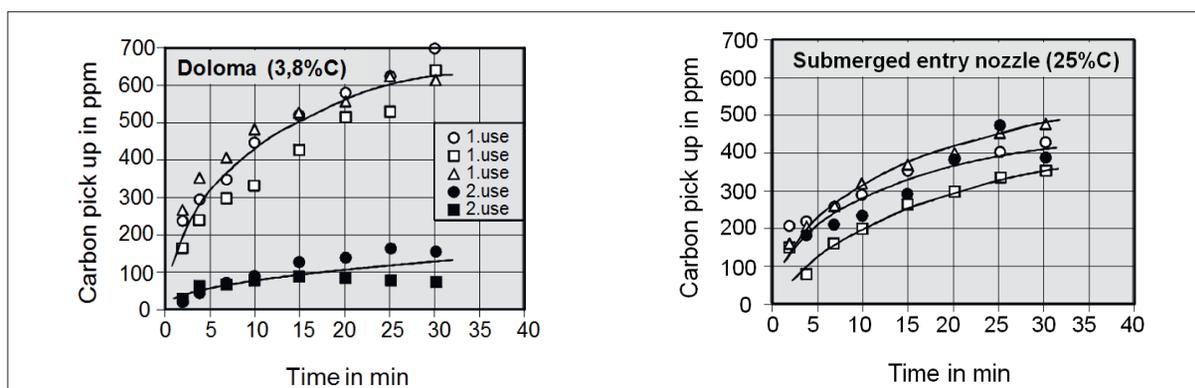


Fig. 8 Carbon pick up of steel from refractories in submersion laboratory testing: low vs. high carbon refractories [4]

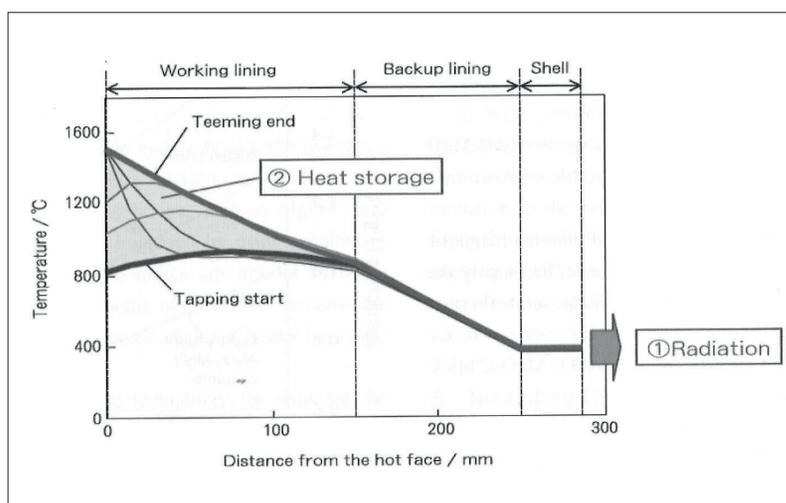


Fig. 9 Calculated temperature change in the refractory lining of a steel ladle during operation [12]

Ultra-low carbon steels, which are used e.g. for automotive steel sheets, are susceptible to carbon pick up from the refractory lining, if the refractories contain carbon and especially graphite. Such steel grades have specifications of max. 10–20 ppm carbon, so even few ppm carbon pick up are considered critical these days. Different to magnesia refractories, alumina refractories do not require carbon/graphite in their formulation for achieving the desired thermomechanical flexibility and thermal shock resistance. Even carbon bonded AluMagCarbon (AMC) bricks contain significantly less graphite when compared to magcarbon bricks (Tab. 2).

Lachmund [4] reports about clear differences in carbon pick up of steel from refractories when comparing just carbon bonded bricks with refractories containing a higher amount of graphite. With high amount of graphite in the refractory the carbon pick is high for the first and also the subsequent heats, whereas in the case of just a carbon bond, it is clearly lower for subsequent heats (Fig. 8).

Reduction of energy losses

During treatment and transport of steel in the ladle, it is cooling by typically around 1 K/min. Heat losses can be reduced by

covering the ladle, but this often cannot be applied in steelworks. The refractory lining is contributing to temperature losses in two ways. First, there is heat transport through the lining to the steel shell, which can be reduced e.g. by better insulation or lower thermal conductivity materials in the wear lining. This heat transfer achieves somewhat of a steady state situation once the lining is completely warmed up, typically after the first 3–4 heats.

Another heat loss comes from the thermal cycling of the ladle, where the hot face is cooling down during the empty phases from about 1550 °C to about 800 °C. It depends on the heat capacity and the thermal conductivity of the wear lining how much heat is lost during the empty period. This aspect has recently been discussed by Ogata et al. (Fig. 9).

Fig. 10 shows the temperature loss in a 180 t steel ladle with spinel forming castable in comparison to MgO/C bricks in the ladle side wall. Due to the higher thermal conductivity of MgO/C (Tab. 2) the temperature loss is 10–15 K higher in spite of an additional insulation layer in the permanent lining. Taking into account that 1 K temperature loss costs between 5–10 EUR per ton of steel, a 15 K higher temperature loss means cost of 0,75–1,5 EUR per ton of steel. In general, ladle refractory cost – without the sliding gate system – are in the range of 1,5–2 EUR per ton of steel.

So the cost of heat loss can be more than 50 % of the ladle refractory cost!

Alumina refractories with lower or no carbon content provide a clear advantage over basic refractories with higher carbon contents due to their lower thermal conductivity, and such aspects should be included in the economic evaluation of ladle lining concepts.

Wear resistant thin linings for increased ladle capacity

For a steel ladle with 200 t steel capacity, 2,5 t additional capacity can be gained by reducing the lining thickness by 10 mm. Except for input material cost, other processing cost remain the same so these additional tons can considerably improve the economic result of the steel works [14]. Consequently, the refractory lining thickness was reduced in many European steel works. Tab. 3 gives examples for extreme cases where high performance alumina-spinel materials enable wear lining thickness of only 110–140 mm for new installed linings and still achieving ladle campaigns of 114–140 heats on average.

Such capacity increases are possible until the maximum crane weight becomes the limiting factor. In such cases, a focus is also given on the weight of the refractory lining. Alumina refractories based on sintered aggregates typically have a lower bulk density than those with fused aggregates due to the inherent closed porosity in sintered aggregates. An example is given in Tab. 2 for AMC bricks with the new sintered aggregate BSA 96 vs. brown fused alumina [11].

Concept for advanced permanent linings

In order to increase the ladle capacity, the permanent lining thickness has also been reduced in many European steel ladles and special insulating layers have become a standard. Microporous boards have very low thermal conductivity of about 0,04 W/m·K but must be protected from over-heating because their temperature limit is only 900–1000 °C. The same applies for vermiculite based insulation boards (around 0,3 W/m·K). Therefore two brick layers are applied in front of the board: a dense material for safety purposes and an insulating brick for protecting the board (Fig. 11).

The disadvantage of such multilayer but thin permanent linings is the low mechan-

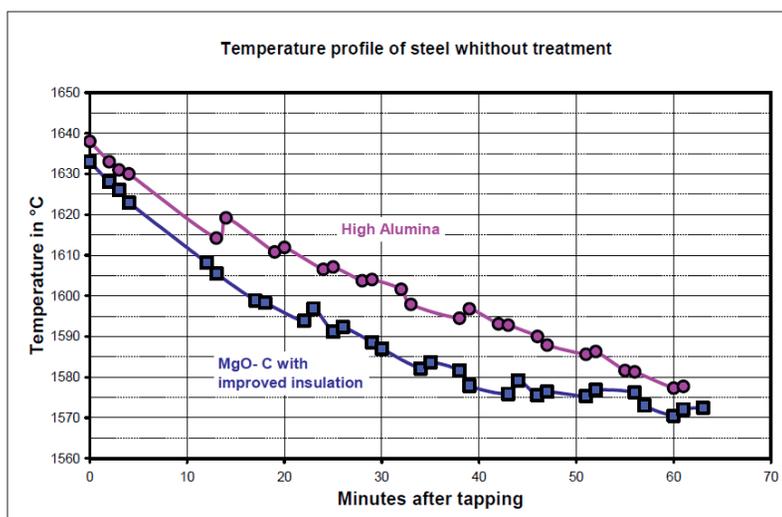


Fig. 10 Steel temperature development in a 180 t steel ladle with different lining concepts: alumina monolithic vs. MgO/C bricks [13]

Tab. 3 European examples for low lining thickness in steel ladles

	voestalpine Stahl GmbH Linz, Austria	TATA Steel IJmuiden, Netherlands
Ladle size [t]	180	332
Side wall wear lining	Alumina-spinel forming castable	Fired spinel bricks
Thickness [mm]	110–136	140
Ladle campaign [heats]	114	140

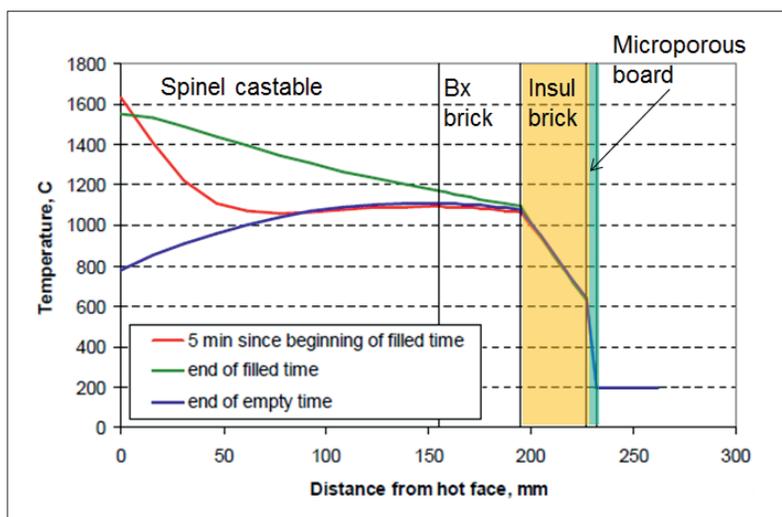


Fig. 11 Thermal modelling of steel ladle lining: spinel castable wear lining and permanent lining with dual brick layer and 5 mm microporous insulating board [15]

ical stability which requires frequent repairs and limits the campaign length of the lining. New calcium hexa-aluminate (CA₆) materials provide a combination of safety and reduced thermal conductivity for the permanent linings in steel ladles. Schnabel et al. [15] reported about the high slag resistance against calcium aluminate slag (Fig. 12) and the low thermal conductiv-

ity (Fig. 13) of dense CA₆ material bonite, which makes it an interesting solution for steel ladle safety lining.

A safety lining with low thermal conductivity based on bonite LD (low density) in front of the insulating layer can make an additional layer of insulating bricks obsolete (Fig. 14) and thus strengthen the whole mechanical stability of the permanent lining.

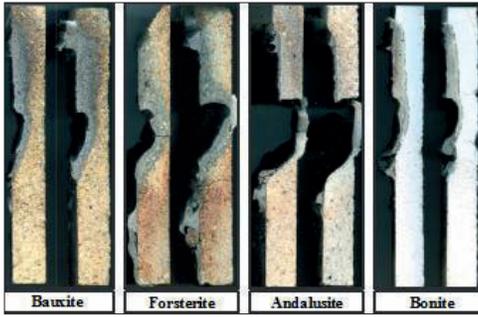


Fig. 12 Samples after slag test; CaO/Al₂O₃-ratio 1,08, (Induction furnace, 1600 °C/ 2 h; air) [15]

The newly developed bonite LD has a thermal conductivity in the range of chamotte bricks. Projects with bonite LD bricks [16] in steel ladle permanent linings are ongoing.

Functional refractories

Pre-cast shapes such as purging plugs and well blocks in the steel ladle bottom are an essential part of the ladle lining concept. The metallurgical treatment cannot be performed without stirring the steel in the ladle. Flow rates range from 100 NI/min up to 1500 NI/min per purging plug. Soft bubbling is applied for transferring oxide inclusions to the top slag and increasing the steel cleanliness. Stronger stirring is required for alloying and homogenisation, and especially for vacuum treatment in tank degassing.

The plugs can be exchangeable during hot cycling of the ladle but the well blocks can often be the bottleneck for achieving the desired campaign length of the whole ladle. Therefore highest quality tabular alumina-spinel materials have become the standard for this application. The water demand of the castables is reduced to 3–4 % by using reactive alumina and high performance additives such as dispersing aluminas ADS/W in the matrix fines. In order to achieve the required hot strength and erosion resistance, silica fume must not be used here as is discussed in detail by Schnabel et al. [8]. High purity spinel containing materials have hot modulus of rupture (HMoR) at 1500 °C of 30 MPa, refractoriness under load (RUL) T05 > 1700 °C, and creep rates at 1600 °C of 0,01–0,02 %/h, both at 0,2 MPa load. Purging plugs are exposed to severe thermal shock conditions as shown in Fig. 15. A thermocouple was placed in the purging plug as an indicator for the stirring performance

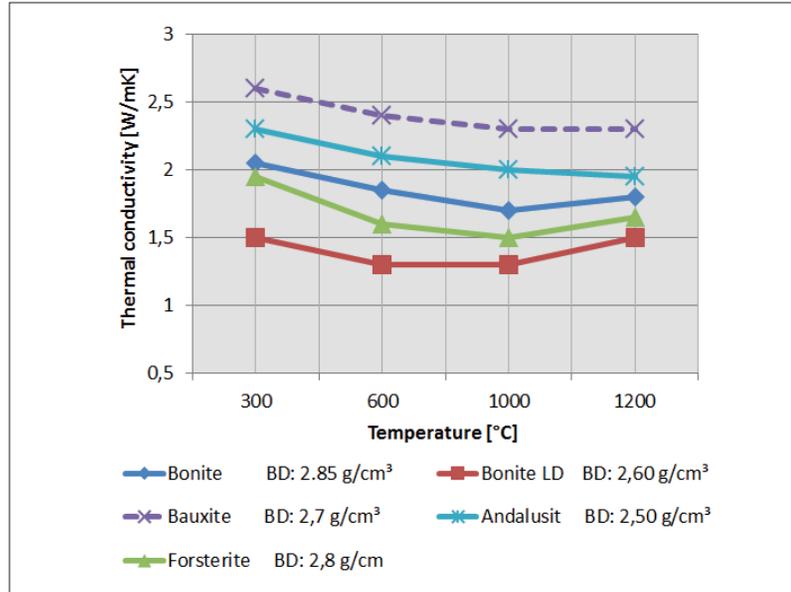


Fig. 13 Thermal conductivity of steel ladle permanent lining materials [15]

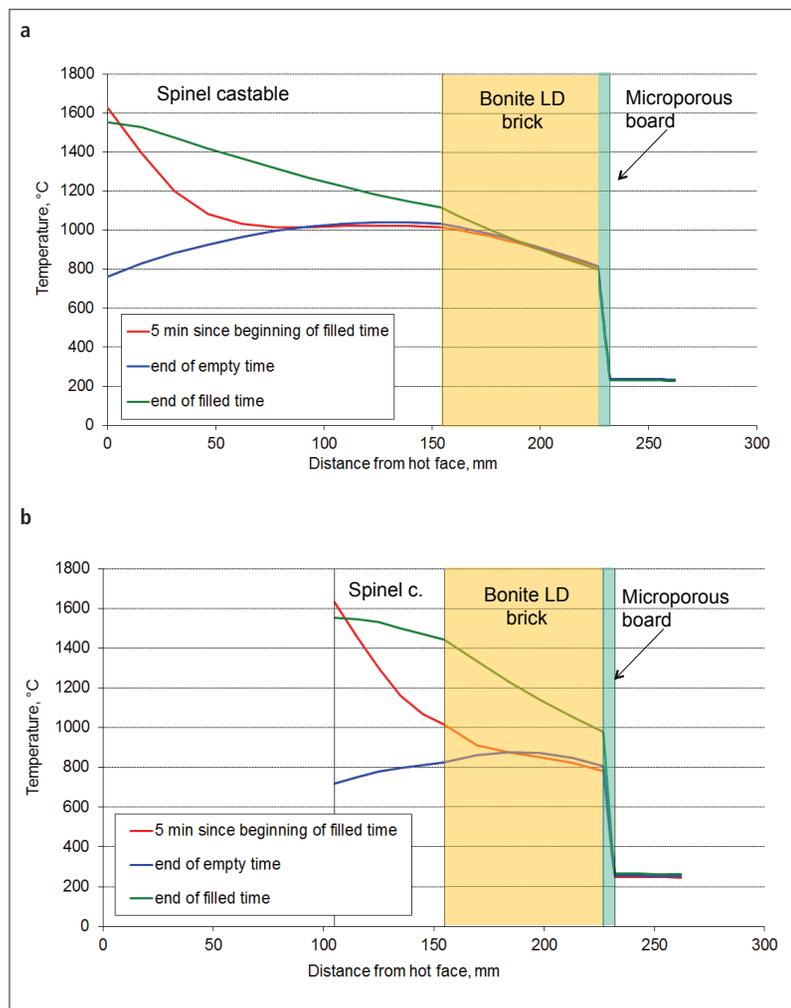


Fig. 14 a–b Thermal modelling of steel ladle lining: spinel castable wear lining and permanent lining with 72 mm bonite LD brick and 5 mm microporous insulating board [15]: new castable lining 155 mm (a), and worn 50 mm (b)

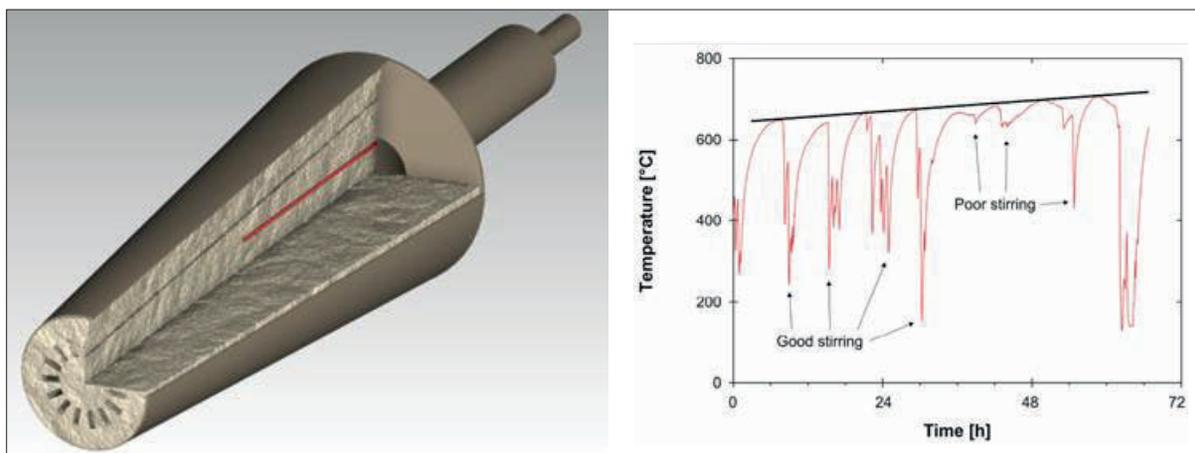


Fig. 15 Temperature changes in a steel ladle purging plug during ladle cycling and stirring [17]

[17]. When the purging plug is clogged and no stirring gas flows, the temperature remains high. When the plug is functioning, the cold argon stirring gas decreases the temperature quickly from about 700 °C to about 200 °C inside the plug. Temperature changes in this range are particularly critical because refractory material in general behaves more brittle at such lower temperatures when compared to temperatures beyond 1000 °C. Tabular alumina-spinel refractories provide the desired thermal shock resistance due to the blend of corundum and spinel with different thermal expansion, which reduces stresses in the material. In addition, the wetting angle of liquid steel on spinel-containing alumina refractories is increased beyond 90° so that an infiltration of the gas slits and clogging of the purging plug is hampered.

Conclusion

The examples of modern engineered refractories briefly discussed in this paper demonstrate the contribution of refractories to modern steel making, both technically and economically. When considering the economics of refractory solutions, it is important to also take refractory related operational costs into consideration, and not only focus on the directly spend refractory costs. Refractory related operational costs beyond purchase price and installation can be briefly summarised as follows: production losses due to unavailability of vessels (relining, lack of reliability, unexpected failure – or even worse, incidents), effect on steel quality, energy losses, yield losses, environmental, health and safety aspects, etc.

Experience shows that the refractory related operational costs have the same magnitude as the directly spent refractory cost, and a simple saving by purchasing cheaper, lower quality refractories is often a much more expensive solution when taking the refractory related operational costs into account. The flexibility required in modern steel making processes requires robust performance of refractories.

The examples given in this paper demonstrate what impact the ladle refractories can have on the economic results of the steel work and are supporting what Siebring [14] stated in the refractory seminar of the Steel Academy: "Refractory is a tool to produce steel."

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