MICROSTRUCTURE EVOLUTION DURING FIRING AND RESULTING MECHANICAL PROPERTIES OF STEEL FLOW CONTROL REFRACTORIES CONTAINING VARIOUS ADDITIVES

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ABSTRACT

Alumina-carbon refractories are widely used in the continuous casting of steel, e.g. for ladle shrouds, monobloc stoppers and submerged entry nozzles. They are responsible for the steel flow control and its protection against oxidation. To improve their own oxidation resistance, several additives such as carbides, metals or low melting point compounds are added as antioxidants. In this study, the influence of those additives on the thermomechanical properties of carbon-bonded refractories was studied.

Model materials having simplified composition compared to the real industrial ones were investigated so as to facilitate comprehension of mechanisms responsible for the modification of mechanical properties. Behavior of both cured (before pyrolysis) and fired (after pyrolysis) materials was studied.

The evolution of Young's modulus during firing was followed thanks to an ultrasonic pulse echography device. Damage occurrence within the material was investigated by the acoustic emission technique. X-ray diffraction measurements with Rietveld refinement enabled identification and quantification of phases after firing. Stress-strain curves were obtained by tensile testing at room temperature.

Obtained results showed that the carbonaceous binder undergoes transformation into pyrolytic carbon and that micro-cracks in material's matrix are created during firing. What is more, boron carbide transforms partially into boron oxide and carbon which does not have important influence on the mechanical properties. The metallic additive reacts with surrounding carbon to form carbides which rigidify the refractory. One of the low melting point compounds forms a liquid phase at high temperature which causes micro-cracks healing, thereby leading to a stiffening of the material. The second one undergoes irreversible softening and only slightly modifies the mechanical properties.

This study proved that even a small quantity of certain additives might modify the mechanical behavior of a refractory and thus have an influence on its reliability and performance.

Keywords: alumina, carbon, antioxidants, mechanical properties

INTRODUCTION

Refractory products such as ladle shrouds, monobloc stoppers and submerged nozzles find their application in the continuous casting of steel (Fig. 1). They are principally made of alumina-carbon composites which possess suitable thermomechanical and thermochemical properties such as high thermal conductivity, low coefficient of thermal expansion, low value of E-modulus, resistance to molten metals and slags as well as high thermal shock resistance.

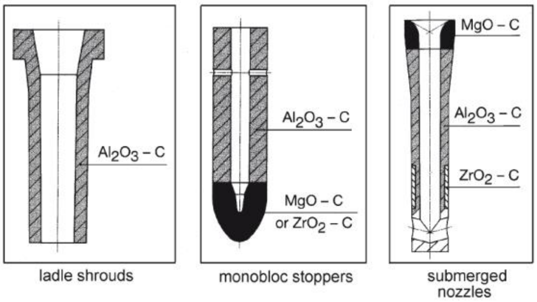

Fig. 1: Steel flow control refractories [1].

Complex compositions of those refractories have been developed through trial and error approach in order to cope with changing requirements from steel plants. It has led to numerous formulations containing many different constituents and additives. Their complexity made the comprehension of relations between microstructure and resulting thermo-mechanical properties quite difficult, thus hindering an effective progress in refractories science. It is then necessary to investigate model materials (having simplified composition) so as to improve the knowledge about basic mechanisms governing the properties of steel flow control refractories.

A few recent works [2-4] treated the influence of different volumetric aggregates/matrix ratios on various properties such as pore size distribution, coefficient of thermal expansion, mechanical strength and evolution of E-modulus with temperature. However, those materials did not contain any additives which in reality are present in all carbon-bonded refractories. That is why the main goal of this work was to investigate the influence of antioxidants on the properties of steel flow control refractories. The particular emphasis was put on their mechanical behavior.

STUDIED MATERIALS

Model materials having simplified composition compared to the real industrial ones were investigated in order to facilitate the comprehension of interactions between different constituents. Material R was treated as a reference since it did not contain any antioxidants (Tab. 1). Each of the materials labelled with letters A, B, C and D contained an antioxidant such as boron carbide, aluminium-silicon alloy, borax and a glass frit respectively.

Tab. 1: Composition of investigated materials in wt%.

Material	R	A	B	C	D
Alumina	84.5	84.5	84.5	84.5	84.5
Graphite	6.5	6.5	6.5	6.5	6.5
Carbonaceous binder	9	9	9	9	9
B_4C	-	2.5	-	-	-
Al-Si	-	-	2.5	-	-
Borax	-	-	-	2.5	-
Glass frit	-	-	-	-	2.5

Materials for this study, the so-called test tubes, were produced in accordance to a standard industrial procedure (Fig. 2).

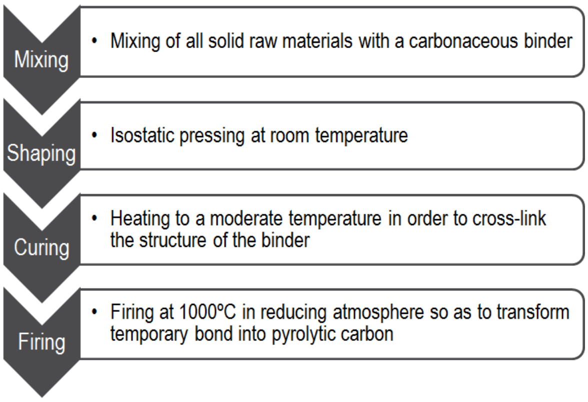

Fig. 2: Manufacturing process of studied materials.

EXPERIMENTAL PROCEDURE

All samples for this study were cut from test tubes. Both cured (before pyrolysis) and fired (after pyrolysis) materials were investigated.

Bulk density and open porosity were determined with the use of Archimedes' method. Analysis of microstructure was done thanks to SEM observations. XRD analysis with Rietveld refinement enabled identification and quantification of phases present in studied materials. Evolution of Young's modulus with temperature was followed thanks to an ultrasonic pulse echography device. Damage occurrence within the material was recorded by the acoustic emission technique. Tests at high temperature were carried out in argon atmosphere in order to avoid carbon oxidation. Mechanical properties were studied by tensile testing at room temperature. Incremental loading/unloading cycles were applied so as to highlight the particular behavior of these heterogeneous coarse grained materials.

BASIC CHARACTERIZATION

The microstructure of the cured reference material is presented in Fig. 3. All constituents shown in Table 1 are clearly seen. The material is principally made of two different fractions of alumina aggregates as well as graphite flakes. Its matrix is composed of fine alumina particles and a carbonaceous binder which provides cohesion to the refractory.

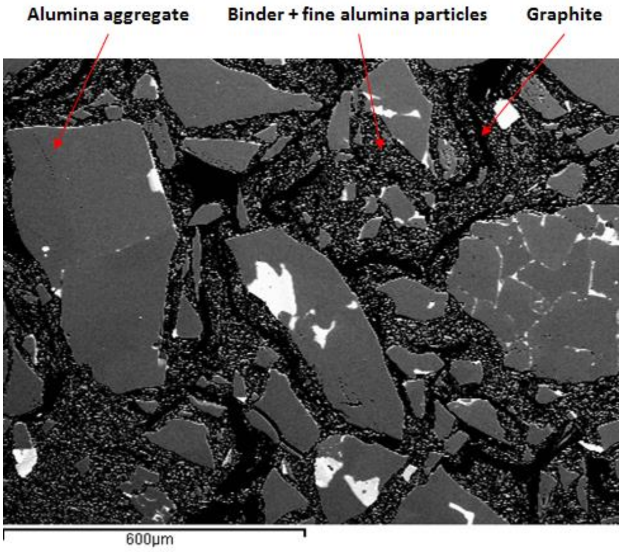

Fig. 3: Microstructure of the reference material before firing.

A significant difference between the cured and fired materials is seen in their bulk density and open porosity (Tab. 2). It was then interesting to study the evolution of cured materials during firing.

Tab. 2: Bulk density and open porosity of the reference material.

Material	Bulk density [g/cm^3]	Open porosity [%]
R - cured	3.07 ± 0.01	3.2 ± 0.2
R - fired	2.94 ± 0.01	16.3 ± 0.1

EVOLUTION DURING FIRING

Reference material

The evolution of Young's modulus and acoustic activity of the reference material during firing are presented in Figure 4. Its dilatation curve as well as variation of the coefficient of thermal expansion (CTE, during heating) are shown in Figure 5.

It is clearly seen that the behavior during firing process may be divided into four stages:

1. In the beginning, the refractory material simply expands up to the curing temperature. When this temperature is reached, the CTE decreases due to further cross-linking reactions and some evolution of their by-products. The resin pyrolysis starts at around 300°C which leads to an abrupt decrease in CTE. During this stage, the value of Young's modulus drops from 53 to 25 GPa. Various gases are emitted from the resin which generate porosity.
2. In the temperature range from 450 to 750°C, the temporary bond transforms into pyrolytic carbon, becomes stiffer, which leads to an increase in elastic modulus. During this stage, the resin shrinks while alumina particles expand. Nevertheless, the carbonaceous binder still shows some plasticity and is able to accommodate increasing expansion of alumina which leads to an almost constant value of CTE.
3. Above 750°C, the resin pyrolysis is almost completed. The carbon bond now is too rigid to accommodate further expansion of alumina, which induces compressive radial and tensile circumferential stresses in the matrix. It leads to the formation of micro-cracks around alumina grains (Fig. 6). This micro-cracking is responsible for the slight decrease in Young's modulus and is detected by the acoustic emission technique. Since there are many contacts between alumina particles and the pyrolytic carbon, the coefficient of thermal expansion of the refractory has a similar value to that of alumina.
4. During cooling stage, alumina grains shrink more than the pyrolytic carbon which induces tensile radial and compressive circumferential stresses in the matrix. It results in the formation of decohesions (Fig. 6) whose appearance is also detected by the acoustic emission technique.

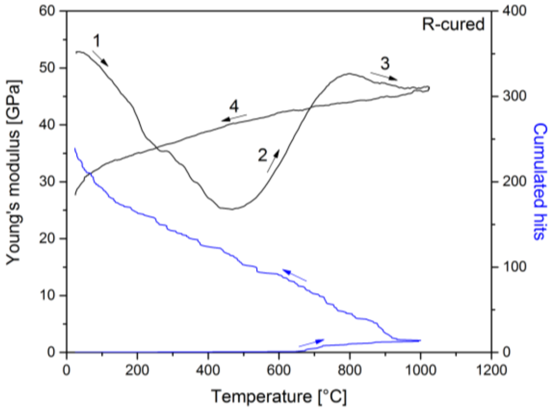

Fig. 4: Evolution of Young's modulus and acoustic activity of the reference material during firing.

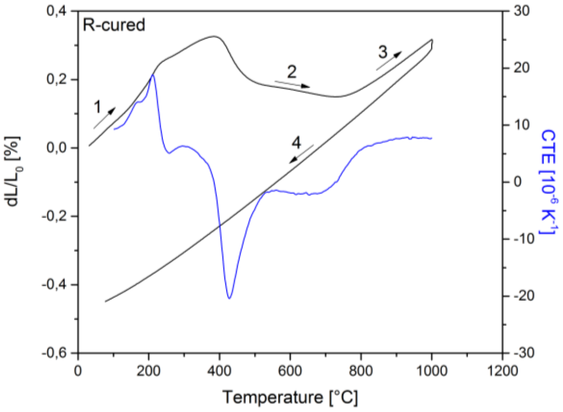

Fig. 5: Dilatation of the reference material during firing.

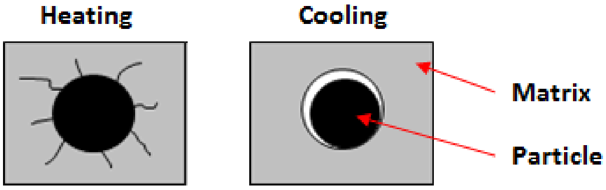

Fig. 6: Scheme of the damage formation within the material.

Influence of boron carbide

The refractory A containing boron carbide as additive exhibits similar behavior to the reference one up to 650°C (Fig. 7). At this temperature boron carbide reacts with carbon monoxide released during resin decomposition to form boron oxide and carbon [5]:

$$B_4C\ (s) + 6CO\ (g) \rightarrow 2B_2O_3\ (l, g) + 7C \qquad (1)$$

The appearance of a liquid phase within the material is responsible for the abrupt drop in E-modulus. During further heating, the elastic modulus increases due to a growing number of contacts between alumina particles and the carbonaceous binder. The behavior during cooling stage is very similar to the reference material.

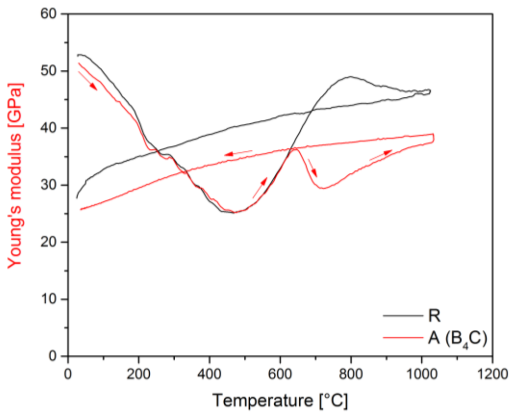

Fig. 7: Evolution of Young's modulus of the material A containing boron carbide as antioxidant.

Influence of Al-Si alloy

Aluminium-silicon alloy was added to the material B as antioxidant. Its behavior during firing resembles that of the reference below 600°C (Fig. 8). Around this temperature, the alloy melts and starts to react with surrounding carbon to from carbides and oxycarbides, which are responsible for the significant increase in E-modulus at high temperature [6]:

$$4Al\ (l) + 3C\ (s) \rightarrow Al_4C_3\ (s) \qquad (2)$$

$$Al_4C_3\ (s) + 2CO\ (g) \rightarrow 2Al_2OC\ (s) + 3C\ (s) \qquad (3)$$

Behavior during cooling stage is similar to the reference material, which indicates that decohesions between alumina particles and the pyrolytic carbon are created.

Rietveld refinement enabled quantification of phases after firing. It was found out that the alloy transformation into new ceramic phases (Al_4C_3 1.8wt% and Al_2OC 1.3wt%) was incomplete since 0.5wt% of Al-Si was still present in the material.

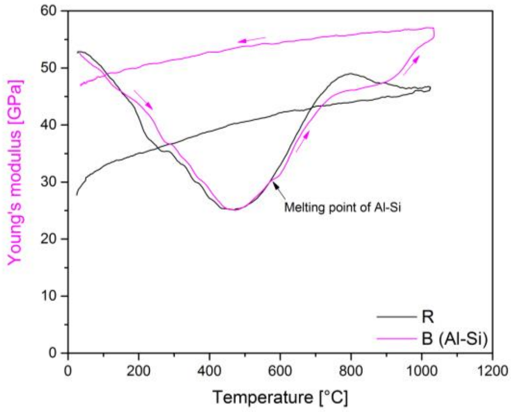

Fig. 8: Evolution of Young's modulus of the material B containing aluminium-silicon alloy as antioxidant.

Influence of borax

As presented in Figure 9, the material C containing borax as antioxidant exhibits significantly different behavior than the reference. Similar decrease in elastic modulus is registered below 500°C due to resin decomposition. However, at higher temperatures borax melts and the superposition of two effects, rearrangement of the temporary bond into pyrolytic carbon and the presence of a liquid phase [7], provides almost a constant value of E-modulus until the maximum firing temperature. During cooling stage, down to 700°C, the Young's modulus increases due to a progressive solidification of the viscous phase. Below this temperature, a slight decrease in E-modulus is detected which indicates formation of decohesions between alumina particles and the pyrolytic carbon.

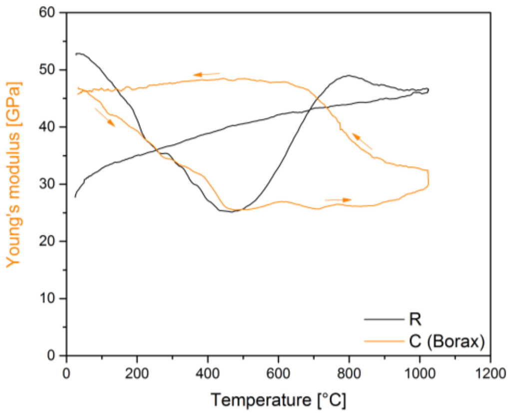

Fig. 9: Evolution of Young's modulus of the material C containing borax as antioxidant.

Influence of a glass frit

The refractory D containing a glass frit as antioxidant exhibits quite similar behavior to the reference material. The only difference can be seen around 800°C. At this temperature, the glass frit undergoes an irreversible transformation, which results in a progressive drop in Young's modulus. During cooling stage, decohesions are created in the material's matrix which are responsible for the further decrease in elastic modulus.

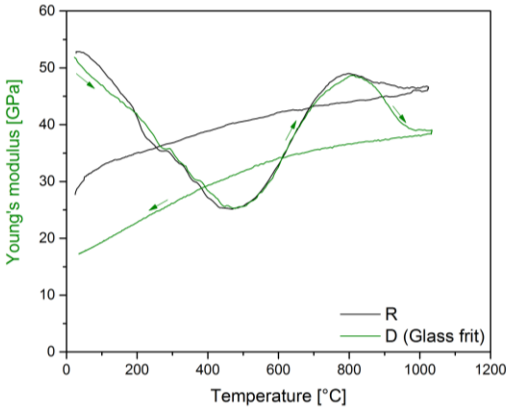

Fig. 10: Evolution of Young's modulus of the material D containing a glass frit as antioxidant.

MECHANICAL PROPERTIES AFTER FIRING

Corrosion resistance along with thermal shock resistance are key features of steel flow control refractories. According to different approaches [8-10], a refractory material may exhibit a good thermal shock resistance if it has a low value of CTE, high thermal conductivity, low E-modulus as well as large strain to rupture and an important rupture energy. In order to evaluate the three latter parameters, tensile tests with incremental loading/unloading cycles were carried out at room temperature.

Reference material

A stress-strain curve of the reference material is presented in Figure 11. Its behavior does not resemble that of traditional ceramic materials. Alumina-carbon refractories exhibit a strong nonlinearity. It is a result of the presence of micro-cracks and decohesions in the matrix, and also probably due to some microplasticity of the carbonaceous binder. Low value of Young's modulus (E_0 is measured at the beginning of loading during first cycle), large strain to rupture and a sufficient strength indicate that this material should exhibit a good thermal shock resistance.

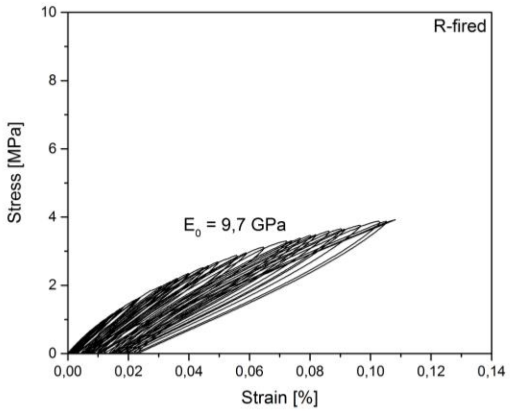

Fig. 11: Stress-strain curve of the reference material.

Influence of additives (antioxidants)

Stress-strain curves of all studied material are presented in Figure 12. It is clearly seen that the studied additives may have an important influence on the mechanical behavior.

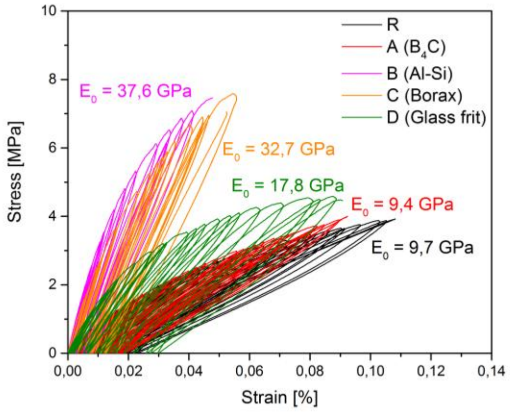

Fig. 12: Stress-strain curves of all investigated materials.

Boron carbide has only little influence since the quantity of a liquid phase (B_2O_3) created during firing was too small to cause micro-cracks healing.

Aluminium-silicon alloy significantly rigidifies the refractory through formation of new ceramic bonds (Al_4C_3 and Al_2OC).

Material C containing borax as additive exhibits similar behavior to that with Al-Si alloy, however, in this case the mechanism of stiffening is completely different. Namely, the liquid phase which was formed at high temperature solidified in micro-cracks during cooling, which led to their healing.

The glass frit slightly rigidified the material because the amorphous phase was able to penetrate into some defects at high temperature and provide more contacts between the matrix and alumina particles.

Comments

In terms of thermal shock resistance, the material A should exhibit the same behavior as the reference once. Al-Si alloy (B) and borax (C) significantly rigidify the refractory and reduce its strain to rupture by 50% which should have a negative effect on the thermal shock resistance. The glass frit seems to increase the rupture energy of the refractory D which should have a positive impact on its thermal shock resistance.

CONCLUSIONS

Alumina-carbon refractories are advanced heterogeneous composites. During firing, the carbonaceous binder undergoes transformation into pyrolytic carbon. At this stage, various gases are emitted from the resin which generate open porosity. What is more, due to the difference in CTE between alumina and carbon, micro-cracks and decohesions are created in the material's matrix. It results in a nonlinear stress-strain behavior. The material exhibits large strain to rupture, low value of Young's modulus and a sufficient strength which should result in a good thermal shock resistance. Nevertheless, this study showed that even a small quantity of certain additives might significantly modify their mechanical properties through different mechanisms such as micro-cracks healing or in situ formation of new ceramic bonds. It may have an influence on refractories' reliability and performance. Since the metallic additive has the most significant influence of the mechanical behavior, further studies will treat that type of additives in more detail.

REFERENCES

[1] Routschka G, Wuthnow H. Handbook of Refractory Materials. 4th ed. Germany; 2012

[2] Werner J, Aneziris CG, Dudczig S. Young's modulus of Elasticity of Carbon-Bonded Alumina Materials up to 1450°C. J. Am. Ceram. Soc. 2013; 1-8.

[3] Dupuy D, Huger M, Chotard T, DeBastiani D, Guillo P, Dumazeau C et al. Basic Understanding of Physical Properties of Carbon Bonded Refractory Composites. Proceedings of the UNITECR 2013 Conference; 2013 Sep 10-13; Victoria, British Colombia, Canada.

[4] Dupuy D, Huger M, Martelli S, Guillo P, Mazerat S, DeBastiani D et al. Carbon Bonded Refractory Composites. Proceedings of the UNITECR 2015 Conference; 2015 Sep 15-18; Vienna, Austria.

[5] Yamaguchi A. Self-Repairing Function in the Carbon-Containing Refractory. Int. J. Appl. Ceram. Technol. 2008; 4(6): 490-495.

[6] Yamaguchi A. Fundamentals of Refractory Technology. Chapter 8: Application of Thermochemistry to Refractories. The American Ceramic Society; 2001.

[7] Wacławska I. Thermal Decomposition of Borax. Journal of Thermal Analysis 1995; Vol. 43: 261-269.

[8] Kingery WD. Factors Affecting Thermal Stress Resistance of Ceramic Materials. The American Ceramic Society; 1955, Bd. 38, Nr. 1, S. 3-15.

[9] Hasselman DPH. Elastic Energy at Fracture and Surface Energy as Design Criteria for Thermal Shock. J. Am. Ceram. Soc. 1963.

[10] Gogotsi GA, Groushevsky YL, Strellov KK. The Significance of Non-elastic Deformation in the Fracture of Heterogeneous Ceramic Materials. Ceramurgia International; 1978, Bd. 4, Nr. 3, S. 113-118.