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Physical, chemical and thermal characterization of alumina–magnesia–carbon refractories

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Abstract

Alumina–magnesia–carbon refractories (AMC) are of great technological interest for their use as linings for iron and steelmaking ladles. In this paper, the methodology implemented for the physical, chemical and thermal characterization of AMC refractories is presented along with the obtained results. These results are essential for the study of the chemical and mechanical behavior of these materials, which the present work frames. AMC bricks comprise different amounts of alumina, sintered or electrofused magnesia, graphite and antioxidant additives bonded together with a phenolic resin. The variety of components, be they oxidic, metallic or polymeric in nature, and the complexity of the final microstructure and texture make characterizing these refractories a difficult task. In the present work, several complementary techniques were used in combination: X-ray fluorescence, plasma emission spectroscopy, gravimetry, X-ray diffraction, differential thermal and thermogrametric analyses, reflection optical microscopy and scanning electron microscopy, density and porosity measurements, dilatometric analysis and permanent linear change measurements. The results of these different techniques were analyzed separately and together in order to obtain a detailed description of each refractory in relation to its physical and chemical characteristics and thermal evolution. In addition, the characterization was completed by evaluating the mechanical properties at room temperature, such as the mechanical strength and Young's modulus.

Keywords: B. Microstructure-final; C. Mechanical properties; D. Al_2O_3, MgO, carbon; E. Refractories

1. Introduction

Alumina–magnesia–carbon refractories (AMC) appeared in the 1980s as a solution to the drawbacks in performance shown by the linings of steelmaking ladles made of Al_2O_3–C bricks on one hand and MgO–C bricks on the other [1]. The excellent performance of AMC materials is due to the combination of high refractory oxides such as corundum (α-Al_2O_3) and periclase (MgO) with graphite (C). The oxidic components are highly resistant to mechanical loading, erosion and abrasion and moderately resistant to chemical attack by melts. The presence of graphite enhances refractory performance in several ways: (a) since it is not wetted by metals or slags, graphite prevents these liquids from penetrating through open pores, thus reducing chemical wear; (b) the low thermal expansion and high thermal conductivity of graphite increase the thermal shock resistance of the brick; and (c) graphite provides flexibility to the structure due to its ability to absorb thermal and/or mechanical stresses.

However, graphite oxidizes easily at high temperature, and this process could determine the behavior of these materials in service, particularly in the case of an open vessel such as a ladle. In order to increase their resistance to graphite oxidation, a controlled amount of antioxidants are added to these materials, the most common of which are metals and metallic alloys and, less frequently, carbides and borides. In service, these additives react with C and the gases inside the pores

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(O_2, CO and/or N_2) forming other compounds (carbides, oxides and nitrides); these reactions help prevent graphite loss by oxidation. The new compounds crystallize as plates or whiskers, which fill the pores and/or react with ceramic particles (alumina or magnesia) to form other solid phases. Both these processes also enhance the mechanical and chemical properties of the brick.

Besides the heterogeneous nature of their inorganic, organic and metallic components, AMC refractories comprise particles with a wide granulometric range, including coarse (1–6 mm), medium (1 mm–120 μm) and fine (< 120 μm) fractions. The oxidic components—alumina (tabular, electrofused and/or bauxite) and magnesia (sintered and/or electrofused) aggregates—are distributed in the medium and coarse fractions. The fine fraction, which is the matrix, is more heterogeneous and is formed by the same oxidic particles, graphite flakes (between 5 and 15 wt% [2]) and, in general, aluminum as an antioxidant (∼2–3 wt%). The total amount of MgO varies between 2 and 35 wt% [2,3]. The bonding between the inorganic particles is performed at room temperature using polymeric organic binders, usually phenolic resins (∼2–3.5 wt% [2]) such as novolaka or resol, which are cured in the range of 100–300 °C.

At high temperature, alumina, magnesia and the aluminum present in the fine fraction of AMC type refractories, react according to several mechanisms leading to the formation of spinel ($MgAl_2O_4$) *in situ* (due to these reactions, these refractories are referred to as 'alive' or 'mutant' materials). This spinelization is accompanied by volumetric expansion (∼8% when magnesia reacts with alumina) that counteracts the bricks' joint wear [1,3–7]. In addition, this expansion also induces microcracking due to differences between the thermal expansions of the reagents and the products, which could give rise to toughening mechanisms; however, these microcracks may also become points where chemically aggressive agents could enter into the brick. For these reasons, the reactions that cause spinel formation have to be controlled, which signifies that the MgO content has to be optimized.

The behavior of AMC refractories under mechanical, thermal and thermomechanical loadings and also their chemical behavior are directly related to the raw materials' composition, granulometry, purity and contents. All these factors determine the final microstructure and texture of the brick. The study of commercial refractories, which is quite uncommon due to the impossibility of controlling the chemical composition and/or the microstructure of the brick, does however have the advantage of avoiding the problems linked to reproducing the manufacturing process at a laboratory scale, which is not a trivial issue due to the low affinity between the main refractory components. Moreover, the results can be applied directly to the material's performance in the plant. However, the study of commercial bricks imposes the necessity of characterizing them in a comprehensive manner, particularly if the understanding of their behavior is to be based on relationships between their composition, microstructure and properties. By using several complementary analytical–chemical, mineralogical, microstructural, textural and thermal techniques, it is possible to obtain data that can be used to generate a detailed description of the material. For materials with such a high heterogeneity, *ad-hoc* methodologies are needed to obtain reliable information for certain aspects. For other aspects, however, no characterization technique has yet been developed.

Similar to other published papers dealing with the analytical characterization of MgO–C [8] and Al_2O_3–MgO–C [9] refractories, the aim of the this research is to establish a methodology for the comprehensive analysis of AMC-type commercial refractories while including other aspects besides their chemical and mineralogical composition, such as their microstructure, texture, thermal behavior and typical mechanical properties at room temperature. This methodology was applied to three commercial AMC refractories used to line the walls and bottoms of steelmaking ladles that come in contact with the melted metal. Analyzing these selected aspects required the use of several techniques, most of which are not standard for these types of materials. In addition, they were selected taking into account the experimental simplicity involved and the accuracy of the data obtained from them. The experimental data were then used in basic studies of the mechanical behavior and slag-corrosion resistance of these types of refractories, which will be the subject of future publications.

2. Experimental procedure

2.1. Materials

Three commercial Al_2O_3–MgO–C bricks used to line the walls and bottoms of ladles in a local steel shop were analyzed. They were made by the same manufacturer and labeled as AMC1, AMC2 and AMC3. According to the technical data sheets, these refractories were formulated with different proportions of alumina tabular aggregates and/or bauxite, sintered magnesia, graphite and an antioxidant and bonded with resin.

2.2. Methodology

The methodology established for characterizing the AMC commercial bricks includes those aspects considered as determining the performance of these materials in service, which is also related to their behavior under thermal and mechanical loads and/or chemically aggressive conditions. Several combined techniques were selected taking into account the experimental simplicity, the reliability of data as well as the heterogeneity of the studied materials. The aspects and the analytical techniques used to characterize them are listed below.

a) *Microstructure*: Reflected light optical microscopy and scanning electron microscopy coupled with X-ray energy dispersive spectroscopy (SEM/EDS) were used; the nature of raw materials used to prepare the bricks and their distribution in the granulometric fractions were among the aspects evaluated. The estimation of particle sizes larger