



Role of catalytic agents and processing parameters in the graphitization process of a carbon-based refractory binder

C.S. Bitencourt^a, A.P. Luz^{a,*}, C. Pagliosa^b, V.C. Pandolfelli^b

^aFederal University of São Carlos, Materials Engineering Department, Rod. Washington Luiz, km 235, São Carlos 13565-905, SP, Brazil

^bMagnesita Refratários S.A., Research and Development Center Praça Louis Ensck, 240, Contagem 32210-900, MG, Brazil

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Abstract

The chemical resistance and thermo-mechanical properties of carbon-containing refractories are highly dependent on the presence of carbonaceous phases with structures similar to graphite ones. However, most of the thermosetting resins (used as binders) are classified as non-graphitizing carbon sources. Consequently, there is a high degree interest in finding alternative routes to induce an effective graphitization of such polymeric components at temperatures and conditions similar to the ones that refractories are submitted to in service. This research evaluates the effect of different catalytic agents (ferrocene, hematite and nano-Fe₂O₃ powder) and some processing parameters (i.e., temperature, dwell time, heating rate, amount of cross-linking additive) on the graphitization process of a novolak resin. X-ray diffraction, SEM/EDS and thermogravimetric analyses were carried out to identify the phase and microstructural evolution of the prepared compositions. According to the attained results, carbon graphitization was observed after firing the samples at 1000 °C and 1400 °C for 5 h under a reducing atmosphere. The addition of ferrocene (> 2 wt%) favored the generation of a higher amount of iron oxide particles in the microstructure at 1400 °C and led to a more effective graphitization, whereas the greater tendency for nano-Fe₂O₃ powder to agglomerate during the initial samples' mixing step inhibited carbon crystallization. Regarding the effect of the processing parameters, the use of a heating rate of 3 °C/min and dwell time of 5 h at the maximum temperature of 1400 °C, led to the generation of a maximum amount of graphitic carbon, 33.1%, in the composition with novolak resin +3 wt% ferrocene.

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1. Introduction

Carbon addition to refractory products results in specific and unique properties that allow these materials to reach the performance level (i.e., suitable thermal shock and corrosion resistances) required for the iron and steel-making industry. However, other benefits can be attained when carbon is incorporated to the compositions not only as particles, but also as a binder. Compared to the traditional binders (calcium aluminate cements, hydratable alumina, etc.), organic compounds do not affect the formulations' refractoriness and can be an additional carbon source [1–3]. Furthermore, as they do

not use water during their processing steps to develop green mechanical strength of the consolidated pieces, organic binders are also excellent options to be applied when combined with oxides susceptible to hydration reactions [such as magnesia (MgO) and doloma (CaO.MgO)].

The technology of carbon-bonded refractories has presented important advances in recent years. Among them, the following can be highlighted [4–9]: (i) the use of additives (catalytic agents) to induce carbon graphitization in thermosetting polymers, and (ii) the in situ generation of nano-structured phases due to their combination/reaction with antioxidant compounds. Increasing interest in investigating graphitizing agents is related to the fact that most of the thermosetting resins are classified as non-graphitizing carbon sources. In this case, it is accepted that the carbon derived from these

*Corresponding author. Tel.: +55 16 33518253; fax: +55 16 33615404.

E-mail address: anapaula.light@gmail.com (A.P. Luz).

compounds would not be spontaneously crystallized, even when the resin-containing composition is exposed to high temperatures. Consequently, some of the main refractory properties (i.e., chemical resistance and thermo-mechanical strength) might be negatively affected, as they depend on the presence of carbonaceous phases with features at least close to the graphite ones.

1.1. Catalytic graphitization

Various techniques have been evaluated to induce the crystallization of non-graphitic carbon compounds, based on the application of compressive forces, radiation, magnetic fields, and others [10–12]. However, catalytic graphitization is the most successful and viable method for use in the refractory area. This procedure consists of adding metallic elements or compounds (catalytic agents) to non-graphitic carbon sources and, after reaction at high temperatures, a rearrangement of the amorphous carbon structure should take place giving rise to graphite [5,6]. According to Oya et al. [13,14], this interaction of the graphitizing agent with carbon can take place based on two main mechanisms:

- *Generation-decomposition*: A carbide compound should be generated after the reactions involving the metallic particles and carbon. When exposed to high temperatures, this carbide will be further decomposed, giving rise to graphite and an original metallic compound that becomes available to carry on the reaction process;
- *Dissolution-precipitation*: The non-graphitic carbon is continuously dissolved into the metal structure, from which it is precipitated as graphite.

These investigations were carried out by Oya and colleagues between 1970 and 1990 [13–15]. Nevertheless, the catalytic graphitization method only presented significant and successful improvements in 2001, after the publication of a patent by Bartha, Jansen and Daldrup [4]. According to this document and Jansen's paper [5], the addition of many metallic compounds (ranging from 0.1 and 10 wt%, based on the total amount of the resin added) followed by thermal treatment of the resultant mixtures at temperatures lower than 1000 °C, which would result in high graphitization levels of the carbonaceous binder commonly used in refractory compositions.

Differences related to this technique [4–6] and the one presented by the Japanese researchers [13,15] are mainly associated with the selected catalysts, as the patent suggested the use of various compounds including: organometallics (i.e., metallocenes, benzoates, octoates and naphthenates), metal salt solubles in thermosetting resins, and metal oxides chemically precipitated or micronized [4]. All of them should be based on transition metals, such as copper, nickel, chrome, iron and cobalt. Furthermore, Bartha et al. [4] pointed out that in order to attain an effective graphitization, these additives must be available at the beginning of the resins' carbonization process (between 400 and 500 °C) as individualized molecules.

Aiming to obtain a suitable dispersion, the catalyst must be added directly to the compositions as micro or nano-powders, suspensions or even dissolved in a solvent.

Ferrocene [$\text{Fe}(\text{C}_5\text{H}_5)_2$, Fig. 1] is one of the organometallic compounds that can be used as a catalytic agent for carbon graphitization [4,16]. This additive is found as a solid orange powder, insoluble in water but soluble in certain organic liquids.

According to Stamatina et al [16], ferrocene can be decomposed during the resin pyrolysis (up to 900 °C in an inert atmosphere), leading to the generation of Fe and Fe_3C nanoparticles, which act as sites for the rearrangement of graphene sheets from the non-graphitic carbon. Hence, the graphitization would take place in a heterogeneous manner in the resulting microstructure. However, this graphitization route might not lead to relevant benefits to the macroscopic properties of carbon (such as thermal and electric conductivity), as the graphitic phase would be isolated in a non-graphitic carbon matrix [13–15,17]. Consequently, there are still some remaining questions to be addressed regarding the performance of ferrocene as a catalytic agent for the graphitization of thermosetting resins.

Another important aspect pointed out by Stamatina et al. [16] was related to the morphology of the graphitic carbon generated on the surface of the iron-based nanoparticles. These authors reported that nanoparticles or nanotubes of carbon with multiple walls were identified in samples containing novolak resin + ferrocene (with total iron amounts of 2.5 wt% and 5 wt%) after their pyrolysis at 900 °C. Besides that, the mechanism responsible for these transformations consisted of the diffusion and re-organization at an atomic level, resulting in graphene growth together with the crystalline planes of the Fe and Fe_3C particles [16]. Nevertheless, this latter work did not provide any information highlighting the actual content of these formed nano-graphite particles compared to the non-graphitic carbon matrix. Moreover, the samples' graphitization was only evaluated at temperatures lower than 900 °C [16]. Hence, further experiments are still required to analyze the carbon phase evolution at higher temperatures and under a reducing atmosphere (conditions that should be found during the processing and service of refractory products).

Based on these aspects, the aim of this work was to investigate the role of different catalytic agents (ferrocene, hematite and nano- Fe_2O_3 powder) and some processing parameters (i.e., temperature, dwell time, heating rate, amount of cross-linking additive) in the graphitization process of a novolak resin. Carbores® P (a coal-tar-based binder that should be naturally graphitized when subjected to high temperatures) and flake graphite were considered as

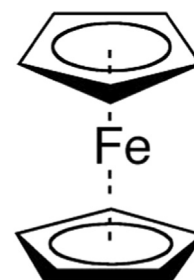


Fig. 1. Molecular structure of ferrocene [$\text{Fe}(\text{C}_5\text{H}_5)_2$].

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