

# EFFECT OF PROCESSING PARAMETERS AND ADDITIVES ON THE GRAPHITIZATION OF PHENOLIC RESINS

Ana P. Luz<sup>1</sup>, Carmen G. Renda<sup>1</sup>, Alessandra A. Lucas<sup>1</sup>, Christos G. Aneziris<sup>2</sup>, Victor C. Pandolfelli<sup>1</sup>

<sup>1</sup>Federal University of São Carlos (UFSCar), São Carlos, Brazil, <sup>2</sup>TU Bergakademie Freiberg, Freiberg, Germany.

## ABSTRACT

Most of the thermosetting resins are classified as non-graphitizing carbon sources. However, the chemical resistance and thermo-mechanical properties of refractories bonded with resole or novolak resins depend on the presence of crystalline carbon phases (preferentially with features close to graphite ones) in their compositions. Consequently, there is major interest in finding routes to induce the graphitization of such components at temperatures and conditions similar to the ones that refractories are submitted to in service. This work evaluates the role of processing parameters (mixing, curing and firing temperature) and additives (ferrocene and boric acid) on the graphitization process of two commercial resins (resole and novolak) and a synthesized one (modified-novolak). X-ray diffraction and Raman spectroscopy analyses were carried out to identify the microstructural evolution of the compositions. According to the results, carbon graphitization was already detected after firing the samples at 1000°C for 5h under reducing atmosphere. Ferrocene addition favored a more effective graphitization of the selected resins and H<sub>3</sub>BO<sub>3</sub> induced the rearrangement of the carbon derived from the commercial novolak product. The mixing and curing procedures used during the compositions' preparations proved to be very important steps as they affected in a greater extent the resulting graphitization degree of the fired samples.

## INTRODUCTION

A great effort has been made to find alternative routes to induce the rearrangement of the pyrolytic carbon (derived from thermosetting resins) and improve its features when submitted to temperatures similar to the ones reached by the refractories used in the steel-making processes [1,2]. Various techniques have been evaluated to activate the crystallization of non-graphitic carbon compounds and the incorporation of catalytic agents (such as organometallics, metal salts and oxides [2-4]) into the resin binder is a likely option to favor an effective graphitization of novolak and resole polymers.

Ferrocene [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] and boric acid (H<sub>3</sub>BO<sub>3</sub>) are some compounds that can be used for this purpose. The former can be decomposed during the resin pyrolysis (up to 900°C in an inert atmosphere), generating Fe and Fe<sub>3</sub>C nanoparticles, which will act as active sites for the rearrangement of the non-graphitic carbon. Based on previous work [4], adding 3 wt.% of ferrocene to a novolak resin resulted in graphitization level close to 33% after firing the mixture at 1000°C for 5h under reducing atmosphere. On the other hand, the processing of boron-containing phenol-formaldehyde resin (BPR) usually improve the ordering of the carbonized material due to the B incorporation into the backbone of the polymer, resulting in changes in the crystallite size and lower carbon interlayer spacing [5,6]. Another positive aspect is the higher B-O bond energy (561 kJ/mol) compared to the C-O one (384 kJ/mol), which explains the greater thermal stability (> char yield) of BPRs. This latter effect is associated with the antioxidant action of boron-based compounds, as they favor the formation of a non-permeable glass coating on the surface of the carbonaceous products upon their thermal degradation, preventing C interaction with oxygen [5-7].

Considering these aspects, this work addresses the evaluation of some processing parameters (mixing, curing and firing temperature) and different additives (ferrocene and boric acid) in the graphitization process of two commercial resins (resole and

novolak) and a synthesized one (modified-novolak) prepared by the authors.

## EXPERIMENTAL

The selected refractory binders comprised three different products: (i) a novolak (Nv), (ii) a resole (Rs) and (iii) a novel resin (Rc) synthesized via polymerization reaction using HCl as a catalyst compound. Table 1 shows additional information of the binders, the cross-linking agent and additives used in this study.

Table 1: Binders, cross-linking and graphitizing agents evaluated in this work.

	Raw materials	Supplier
Binders	Novolak resin (Prefere 88 5010R)	Dynea (Brazil)
	Resole resin (Prefere 88 5000R)	Dynea (Brazil)
	Synthesized resin (Rc)	-
Cross-linking agent	Hexamethylenetetramine (HMTA)	Dynea (Brazil)
Additives to induce carbon graphitization	Ferrocene (150 < d < 70 µm, 98% purity)	Aldrich (USA)
	Boric acid (d < 100 µm, 99.5% purity)	Labsynth (Brazil)

Rc synthesis was carried out by adding phenol (99% purity, Proquímios, Brazil) and formaldehyde (36-38 wt.% solution, Proquímios, Brazil) to a 250 mL beaker, keeping the phenol:formaldehyde ratio = 1:3. These reagents were mixed in a mechanical stirrer at room temperature and, after 30 minutes, hydrochloric acid solution 3.2M (Vetec, Brazil) was added to the reagents (equivalent to 2:3 vol of HCl:formaldehyde) to speed up the reaction rate. The obtained solution was continuously mixed for 150 minutes. After that, the mixture presented two distinct liquid phases: (i) a denser and colorless one found at the bottom of the beaker (pre-polymer = resin) and (ii) a whitish solution at the top (containing un-reacted reagents). The latter was withdrawn by using a pipette and the synthesized resin was collected for further tests [8].

Mixtures of 10 g of resin + additives (3 wt.% ferrocene or 10 wt.% H<sub>3</sub>BO<sub>3</sub>) were prepared according to the ML or MH procedures (Table 2) to ensure a suitable homogenization of the compositions. The choice of additive content was based on preliminary tests. The mixtures were placed in alumina crucibles (their top surface was covered with alumina lids) inside a sealed refractory box, and they were embedded in coke to provide a reducing atmosphere during the samples' pyrolysis. The curing step was carried out based on the CF and CS procedures (Table 2) to induce the release of a major amount of volatile compounds generated during the resin carbonization. The pyrolysis took place when the samples were submitted to temperatures in the 600-1000°C range, with a dwell time of 5 hours at the maximum evaluated temperature.

The prepared compositions obtained after the pyrolysis treatment were evaluated via XRD measurements (Siemens D5005 AXS equipment, using CuKα radiation [ $\lambda = 1.5418 \text{ \AA}$ ] and a nickel filter, using 40 mA, 40 mV and scanning step = 0.02°). The Peak Analyzer tool (OriginPro® 8.6 software) was used to simulate (based on mathematical functions) the regions of the XRD profiles related to graphitic or non-graphitic carbon, quantify their respective areas and then estimate the graphitization level of the compositions. A full description of this semi-quantitative method can be found in a previous publication by some of the authors [4]. In order to have a reference for the crystalline carbon source, flake graphite particles (Graflake® 9980, Nacional de Grafite, Brazil) were also analyzed.

Table 2 – Mixing and curing/firing procedures.

Mixing procedures	Description
ML (L = low energy)	Mixtures of resin + additives were prepared in a mechanical stirrer, using a mixing rotation speed of ~500 rpm for 20 min. After that the samples were placed in an ultrasonic bath for 10 min.
MH (H = high energy)	Mixtures of resin + additives were carried out in a high-energy mixer (StateMix VM-200 vortex mixer, Canada), using a mixing rotation speed of ~2000 rpm for 30 seconds.
Curing/Firing procedures*	Description
CF (F = fast)	This curing step of the compositions was carried out at 100°C for 4h, followed by a pre-pyrolysis treatment at 500°C for 1h and the pyrolysis itself took place when the samples were heated up to 1000°C for 5h (heating rate = 3°C/min).
CS (S = slow)	This slower curing procedure comprised various intermediate heating steps (80°C for 2h, 100°C for 30 min, 150°C for 30 min and 200°C for 1h), followed by a thermal treatment at 500°C for 1h and at 1000°C for 5h (heating rate = 3°C/min).

\*CF and CS treatments were performed in reducing atmosphere.

Raman spectroscopy measurements were carried out at room temperature using Labran HR equipment (Horiba Jobin Yuon). A He-Ne laser with a nominal wavelength of 632.8 nm was coupled to a microscope. The laser beam was reflected by a holographic beam splitter and was aimed at the ground ( $d < 325 \mu\text{m}$ ) and pyrolysed samples with a microscope objective (magnification of 10x and 50x). The backscattered Raman light was detected by a spectroscopic CCD and the integration time of 30s was chosen for each measurement to attain a spectra with good counting rates. The laser power of the incident beam was kept at 17  $\mu\text{W}$  to prevent irreversible thermal damage to the specimen surface.

## RESULTS AND DISCUSSION

### Phase evolution of the samples prepared according to ML procedure

Two curing procedures (CF = 100°C/4h + 500°C/1h or CS = 80°C/4h + 100°C/30min + 150°C/30min + 200°C/1h + 500°C/1h) were used before the thermal treatment of the compositions at 1000°C for 5h under reducing environment. Fig. 1 shows the XRD pattern of flake graphite (reference) and the plain resins (with and without HMTA addition to the novolak ones = Nv and Rc) after their fast (CF) curing. As the plain resins submitted to fast and slow curing resulted in similar XRD results, only the ones related to CF are shown here.

As received flake graphite (Graflake F9980) presented sharp and intense peaks located at the diffraction angles associated to the typical crystalline pattern of the graphitic structure (Fig. 1a). These features highlight the high crystallinity of this material. The pyrolysis of novolak (Nv = commercial product) and Rc = synthesized one, with and without 10 wt.% of HMTA and resole (Rs) resins resulted in a typical XRD pattern for non-graphitic carbon, showing broad humps located near the main diffraction lines of graphite (Fig. 1b). Only Rc+10%HMTA and Rs compositions subjected to fast curing (Fig. 1b) presented a defined peak around 26°, resulting in calculated graphitization levels (GL) of 15.2% and 12.7%, respectively. Furthermore, it is important to point out that: (i) the high hump observed at low angles ( $< 15^\circ$ ) is related to a feature of the used equipment to prevent the scattering of the X-ray signal at low angles, and (ii) the small peaks close to 31°, 35° and 48° are associated with the contamination of the prepared compositions with tungsten carbide, which is the lining material of the grinding equipment used to prepare the powders for the XRD measurements.

Resoles are commonly cured by acid and base compounds or thermal treatments<sup>[3,9]</sup>. While heating this sort of resin, molecular weight increase takes place firstly leading the mixture to a gel state. After that, with the solvent volatilization, a flexible phenolic intermediate material becomes rigid and crosslinked<sup>[9]</sup>. Nevertheless, the conditions under which these transformations may occur are not completely understood. Similar to the difficulties found for the resole cure, complete knowledge of the novolak curing mechanism via hexamethylenetetramine (HMTA)

addition has not been attained so far due to crosslinking and the complexibility of the product<sup>[3]</sup>. As reported in the literature<sup>[4, 9]</sup>, two main stages can be pointed out during the novolak curing reaction: (i) formation of initial intermediate compounds such as benzoxazines and benzyl amines, and (ii) decomposition, oxidation, and/or further reactions of these components generating methylene bridges between phenolic rings and other species (i.e. amines, amides/imides, imines, methyl phenol, etc.).

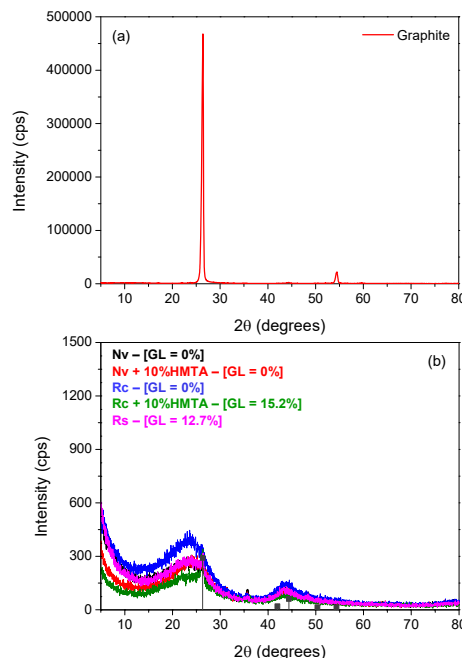


Fig. 1: XRD profiles of as received (a) flake graphite (Graflake F9980) and (b) ground samples of plain resins (Nv = novolak, Rc = synthesized material, Rs = resole) or resin + 10 wt% of HMTA after fast (CF) curing procedures and firing up to 1000°C for 5h under reducing atmosphere.

Based on the distinct crystallinity levels presented by the pyrolysed resins and the as received graphite (Fig. 1), it could be observed how difficult it is to induce the carbon graphitization of phenolic resins at intermediate temperatures, such as 1000°C.

Compositions comprising resin (Nv, Rc or Rs) + ferrocene (Fc, 3 wt%) or resin (Nv or Rc) + HMTA + ferrocene were prepared, cured using the fast (CF) or slow (CS) procedure and fired at 1000°C for 5h under a reducing atmosphere (heating rate = 3°C/min). XRD results of some these samples are shown in Fig. 2. Ferrocene may act as a catalytic agent<sup>[1-4]</sup>, favoring the evolution of the graphitic carbon peaks at ~26° and ~44.5° for both evaluated curing conditions. Nevertheless, using a slower heating procedure (CS, Fig. 2a) led to sharper and more intense peaks at ~26° for all compositions, indicating a better rearrangement of the graphitic carbon structure at an atomic level. Thus, higher GL were obtained for the samples subjected to various intermediate heating steps between 80°C and 500°C (see Table 2) which might have resulted in a suitable condition for the solvent volatilization and the interaction of the catalyst agent with the resin components, as well as the molecule rearrangement and crosslinking. Despite the lower intensity of the XRD peaks at 26° of the compositions containing Fc (Fig. 2a, when compared to flake graphite = Fig. 1a), the calculations of the graphitization level indicated that, in general, the resole (Rs) resin presented a greater tendency to generate graphitic carbon than the modified (Rc) and commercial novolaks (Nv).

Regarding the boric acid (Fig. 2b), many investigations have already highlighted the positive effect of incorporating boron into the phenolic resin structure during the polymer synthesis or curing processes<sup>[5-7]</sup>. However, despite the positive influence of boron on improving the thermal stability of resins<sup>[6,7]</sup>, there is

still a lack of studies focused on its ability to induce carbon graphitization at high temperatures and under reducing conditions. The most promising results were attained for the compositions of commercial novolak [without HMTA] or resole containing 10 wt.% of boric acid. A different trend was also detected in this case, as the highest GL levels (~56.9%) were obtained for the samples subjected to the CF procedure (Fig. 2b).

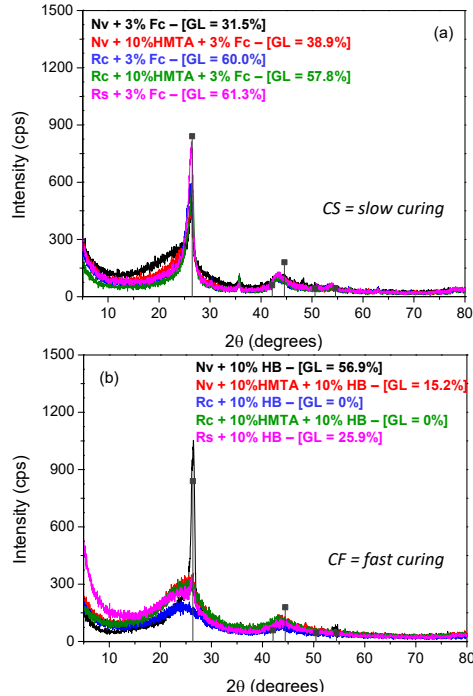


Fig. 2: XRD profiles of the ground samples of resins (Nv = novolak, Rc = synthesized material, Rs = resole) and resins + 10 wt.% HMTA + (a) 3 wt.% ferrocene (Fc) and (b) 10 wt.% boric acid (HB) after slow (CS) and fast (CF) curing procedure, respectively, and firing up to 1000°C for 5h under reducing atmosphere.

Table 3 presents additional information of the most promising compositions (higher GL levels) attained when using the low energy mixing procedure and firing the samples up to 1000°C/5h. According to these data, the use of ferrocene and the slow curing procedure was the more effective route for inducing the generation of graphitic carbon from the selected phenolic resins. The only exception was the Nv + 10% HB composition that led to better results when fast curing was carried out during the resin processing.

Table 3: The most promising compositions based on the low energy (ML) mixing procedure and the attained XRD results.

Compositions	Curing procedure	Graphitization level (%)	L <sub>c</sub> (nm)	d <sub>002</sub> (nm)
Nv + 10% HB	CF	56.9	10.37	0.3364
Nv + 10% HMTA + 3% Fc	CS	38.9	6.44	0.3409
Rc + 3 % Fc	CS	60.0	5.27	0.3417
Rc + 10% HMTA + 3% Fc	CS	57.8	12.27	0.3348
Rs + 3% Fc	CS	61.3	11.76	0.3380

CF = fast curing, CS = slow curing, L<sub>c</sub> = mean crystallite thickness, d<sub>002</sub> = interlayer spacing.

### Phase evolution of the samples based on MH procedure

Based on the previous data, the compositions which had a stronger trend to generate graphitic carbon were processed with the vortex mixer and submitted to the same curing and firing steps (CF or CS) used before. The samples presented a significant

temperature increase (~15°C) during the high energy mixing procedure, as well as a better homogenization of the resin + additives. However, this earlier heating of the resins might have sped up some reactions and transformations that were only expected to take place during the curing process. Rc + 3%Fc and Rc + 10%HMTA + 3%Fc compositions showed significant foaming due to the release of volatile compounds during fast curing (CF), which resulted in the opening of the alumina crucibles and their contamination with coke during the samples' pyrolysis. Consequently, these two specimens were not considered in further tests.

Table 4 presents the calculated parameters (graphitization level, L<sub>c</sub> and d<sub>002</sub>) of the prepared mixtures using the vortex mixer (MH), which samples were cured (CF or CS) and fired at 1000°C for 5h. Nv+10%HB and Rc + 3%Fc compositions, cured via the slowest heating method (CS), resulted in the highest GL values attained for this mixing condition. However, the MH mixing procedure negatively affected further resin graphitization as the observed peak at ~26° was less intense than the ones shown in Fig. 2.

Table 4: Results of the most promising compositions based on the high energy (MH) mixing procedure and the XRD measurements.

Compositions	Curing procedure	Graphitization level (%)	L <sub>c</sub> (nm)	d <sub>002</sub> (nm)
Nv + 10% HB	CF	23.4	9.87	0.3401
Nv + 10% HB	CS	38.9	11.68	0.3397
Nv + 10% HMTA + 3% Fc	CF	17.6	7.12	0.3428
Nv + 10% HMTA + 3% Fc	CS	19.4	5.90	0.3423
Rc + 3 % Fc	CS	44.7	6.12	0.3421
Rc + 10% HMTA + 3% Fc	CS	29.1	13.29	0.3409
Rs + 3% Fc	CF	17.9	14.56	0.3415
Rs + 3% Fc	CS	15.8	15.37	0.3423

CF = fast curing, CS = slow curing, L<sub>c</sub> = mean crystallite thickness, d<sub>002</sub> = interlayer spacing.

### Further graphitization when firing the samples at 1400°C

When submitting the samples previously fired at 1000°C for 5h to a second heating treatment up to 1400°C for another 5h under reducing atmosphere, an additional increase in the carbon graphitization was identified. The calculated graphitization level (GL) for the samples fired at 1000°C and 1400°C is presented in Table 5. All evaluated compositions showed an additional GL increase at 1400°C and, considering that these binders should be exposed to high working temperatures (1400-1700°C) when applied to MgO-C refractory products, it is expected that more graphitic carbon might still be formed in the resulting microstructure. Further tests with the incorporation of the analyzed resins + additives in MgO-C compositions should be carried out in order to investigate the effect of the resin graphitization in the overall performance of such refractories.

Table 5: Graphitization level increase of the most promising evaluated compositions after firing the materials at 1000°C and 1400°C for 5h under a reducing environment.

Compositions	Maximum firing temperature (°C)	Curing step	XRD results Graphitization level (%)
Nv + 10% HB-ML	1000°C	CF	56.9
Nv + 10% HB-ML	1400°C	CF	61.9
Rs + 3% Fc- ML	1000°C	CS	61.3
Rs + 3% Fc-ML	1400°C	CS	64.8
Rc + 3% Fc-ML	1000°C	CS	60.0
Rc + 3% Fc- ML	1400°C	CS	61.8
Rc + 10% HMTA + 3% Fc-ML	1000°C	CS	57.8
Rc + 10% HMTA + 3% Fc- ML	1400°C	CS	59.7

## XRD versus Raman technique

X-ray diffraction measurements are obtained from a volume of randomly particles (in the case of powdered samples), thus averaging any preferred orientation of the microcrystals, whereas the Raman microprobe signal results from a limited volume (a few micrometers wide and not much more than 100 nm deep) of a particle(s) surface(s). Hence, for the latter, orientation effects cannot be entirely eliminated even when a high number of signals from different particles are evaluated [10]. Despite the very different physical phenomena involved in these two methods, the structural data provided by them has traditionally been assumed as equivalent.

Regarding the Raman results, highly ordered graphite usually presents one band between 1100 and 1700  $\text{cm}^{-1}$  and shows second order features in the range of 2400 and 3300  $\text{cm}^{-1}$ . The G mode of graphite at about 1580  $\text{cm}^{-1}$  has  $E_{2g}$  symmetry and is related to the relative motion of  $\text{sp}^2$  bonded carbon atoms. In the case of disordered carbons, significant changes are observed in the attained spectra, as besides G band, the so-called D one ( $\sim 1350 \text{ cm}^{-1}$ ) is also detected (whose origin is attributed to double resonant Raman scattering) [10]. Nevertheless, the interpretation of Raman data is somehow ambiguous in the literature. Moreover, fluorescent background and band overlapping are always important issues (even though rarely mentioned), which adds further difficulties to detect D and G profiles [10].

The compositions reported in Tables 3 and 4 were also evaluated via the Raman technique. Based on peak fitting of the attained spectrum, the  $I_D/I_G$  and  $I_G/(I_D+I_G)$  indexes (considering the integrated area of the bands) were estimated for a direct comparison with the graphitization level (GL) values previously presented (Table 6). The  $I_D/I_G$  ratio is commonly considered as an indicative of the graphitization degree in the Raman spectrum of carbon materials, where the lower this parameter is, the more ordered the carbon structure will be. Consequently,  $I_G/(I_D+I_G)$  index provides a complementary data that can also be used to infer the equivalent graphite content of the samples.

Table 6: General comparison of the XRD and Raman results of the most promising compositions.

Compositions	Mixing procedure	Curing step	XRD results	Raman results	
			Graphitization level (%)	$I_D/I_G$	$I_G/(I_D+I_G)$
Plain Nv	-	CF	0	2.57	28.02
Nv + 10% HB	ML	CF	56.9	3.78	20.91
Nv + 10% HB	MH	CF	23.4	2.12	32.05
Plain Nv	-	CS	0	3.35	22.97
Nv + 3% Fc	ML	CS	31.5	2.75	26.68
Nv + 10% HMTA + 3% Fc	ML	CS	38.9	3.34	23.06
Nv + 10% HMTA + 3% Fc	MH	CS	19.4	2.82	26.15
Plain Rs	-	CF	12.7	3.90	20.42
Rs + 3% Fc	ML	CF	45.4	2.48	28.73
Rs + 3% Fc	MH	CF	17.9	2.91	27.32
Plain Rs	-	CS	0	2.22	31.01
Rs + 3% Fc	ML	CS	61.3	3.25	25.13
Rs + 3% Fc	MH	CS	15.8	2.98	26.84
Plain Rc	-	CS	0	2.49	28.67
Rc + 3% Fc	ML	CS	60.0	3.54	23.49
Rc + 3% Fc	MH	CS	44.7	3.46	22.44
Rc + 10% HMTA + 3% Fc	ML	CS	57.8	3.50	22.23
Rc + 10% HMTA + 3% Fc	MH	CS	29.1	4.08	19.67

Considering the issues mentioned above regarding the Raman technique in the analyses of carbon-based materials and the fact that it does not take into account the bulk order/disorder share on the calculations, some authors [10] stated that the use of XRD (instead of Raman) is highly advisable whenever possible, as the spectroscopy errors might be as high as  $\pm 100\%$  and they are likely to be underestimations rather than overestimations. In general, the calculated  $I_G/(I_D+I_G)$  values (Table 6) were lower

than the ones attained via XRD measurements. Nevertheless, one must keep in mind that the latter can be considered as a more accurate and reliable analysis of the pyrolyzed samples.

## CONCLUSIONS

The selected binders (resole, novolak or modified-novolak), as well as the processing procedures (mixing, curing and temperature used in the thermal treatments) and additives (ferrocene, boric acid and graphene) had a significant influence on the resulting amount of graphitic carbon derived from the pyrolysis of the resins. All resins presented the likelihood to generate, at some extent, graphitic carbon after thermal treatments at 1000°C and 1400°C under reducing atmosphere. However, an optimal condition was analyzed in order to minimize the non-graphitic carbon, as two parallel transformations might be developed during the samples' pyrolysis: graphitization and rearrangement of the non-graphitic carbon. According to the evaluated conditions, in general, the use of a low energy mixing procedure (ML) and a slower curing step (CS) resulted in a higher graphitization level ( $\sim 38\text{--}61\%$ ) for all analyzed compositions after firing at 1000°C/5h. The highest GL results attained for ferrocene containing compositions (after firing at 1000°C/5h) were: Rc + 10% HMTA + 3% Fc (57.8%), Rc + 3% Fc (60.0%) and Rs + 3% Fc (61.3%) for low energy mixing and slower curing procedures. Between the two used techniques (XRD and Raman spectroscopy), X-ray diffraction proved to be the most reliable and accurate one to evaluate the graphitization evolution of the fired samples, which is in agreement with various published papers presented in the literature.

## ACKNOWLEDGEMENTS

The authors are grateful to Magnesita Refratários, FIPAI and FIRE for supporting this work. The authors would also like to thank Prof. R. Bertholdo for his assistance with the Raman tests.

## REFERENCES

- [1] Bartha, P. Jansen, H., Daldrup, H.G. Carbonaceous refractory shaped body with improved oxidation behavior composition and method for producing the same, US6846766B1, 2005.
- [2] Jansen, H., Aneziris, C.G., Hampel, M., Li, Y.M. Microstructure and mechanical behaviour of magnesia-carbon bricks by catalytically activated resins, in: Proceedings UNITECR'07, Dresden, Germany, 2007; pp. 38–41.
- [3] Gardziella, A., Pilato, L., Knop, A., Phenolic resins: Chemistry, applications, standardization, safety and ecology, 2<sup>nd</sup> Ed., Springer, New York, USA, 2000.
- [4] Bitencourt, C.S., Luz, A.P., Pagliosa, C.S., Pandolfelli, V.C., Role of catalytic agents and processing parameters in the graphitization process of a carbon-based refractory binder, Ceram. Inter., 2015;41: 13320–13330.
- [5] Gao, J., Liu, Y., Yang, L., Thermal stability of boron-containing phenol formaldehyde resin, Polym. Degrad. Stab., 1999;63:19–22;
- [6] Bian, C., Wang, Y., Wang, S., Zhong, Y., Liu, Y., Jing, X., Influence of borate structure on the thermal stability of boron-containing phenolic resins: A DFT study, Polym. Degrad. Stab., 2015; 119:190–197.
- [7] Abdalla, M.O., Ludwick, A., Mitchell, T., Boron-modified phenolic resins for high performance applications, Polymer, 2003;44:7353–7359.
- [8] Renda, C.G. Study of a phenol/formaldehyde phenolic resin and its application as matrix for the preparation of polymeric nanocomposites containing carbon nanotubes, (Thesis) Federal University of Alfenas, Brazil, 2015; pp. 1–102 (in Portuguese).
- [9] Pilato, L., Phenolic resins: A century of progress, Springer, Heidelberg, Germany, 2010.
- [10] Cuesta, A., Dhamelincourt, P., Laureyns, J., Martínez-Alonso, A., Tascón, J.M.D., Comparative performance of X-ray diffraction and Raman microprobe techniques for the study of carbon materials, J. Mater. Chem. 1998;8:2875–2879.