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Dynamics of Defects and Surface Structure Formation in Reticulated Vitreous Carbon

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Morphological and microstructure properties of reticulated vitreous carbon (RVC) were analyzed by scanning electron microscopy (SEM), micro-Raman spectroscopy and x-ray diffraction (XRD) techniques as a function of heat treatment temperature (HTT). Samples produced in the HTT range of 1000 to 2400 K have demonstrated a strong dependence of HTT in their structural order mainly attributed to the presence of hydrogen and oxygen (heteroatoms), originated from precursor. In this range, the material is changed from pyropolymer to carbon. The polyfurfuryl alcohol precursor has furanic groups and its cure originates methylenical bonds and sulphur atoms. At HTT higher than 1300 K, these atoms are gradually liberated from the material generating a discrete structure ordering.

Keywords: Defects; Surface Structure; Vitreous carbon

I. INTRODUCTION

Reticulated vitreous carbon (RVC) is an important material known by its high mechanical resistance, porosity, biocompatibility and relatively high electric conductivity. The morphological and structural properties of such singular material have been extensively explored in the last decades, mainly due to their wide range of applications, for example, in thermal coating of airships [1,2], bony prostheses [3], heart valves [4-6], molecular sieves [7], hydrogenation catalyst supports [8], among others. Besides, RVC has a low density and high electrical conductivity [9] that is very attractive for electrochemical applications as three-dimensional electrode [10]. Electric conductivity variation is a determinant parameter for using RVC electrodes in many electrochemical applications. The proportional increase of conjugated carbon in the sp^2 state during pyrolysis would change the material progressively from an insulator to a good conductor in the remarkable range of 19 orders of magnitude. The electrical properties will afford, therefore, a sensitive measure of various stages of pyrolysis and provide information on the structure of the final carbon [6].

RVC samples are usually produced from thermosetting resins used to impregnate polyurethane foams. The resin on the foam is hardened through curing reaction and can be carbonized at different heat treatment temperature (HTT).

The goal of this work is to describe systematically morphological and structural properties of RVC three dimensional samples, produced from furfurylic resin at different HTT. The discussions will report the importance of thermal treatment related to its strong dependence for the microstructural properties of this material, as pilling up width of layers (L_{002}), interlayer distance (d_{002}), from x-ray diffraction measurements (XRD) [11-13]. In addition, the relative intensity of D and G bands associated with their ratio and FWHM analyses from Raman spectra have corroborated the XRD results.

II. EXPERIMENTAL

RVC was obtained from polyurethane (PU) foam based on polyether impregnated with furfuryl resin. The resin curing process needs to use p-toluenosulfonic acid as catalyst, at 3% w/w. The complete curing occurred after two hours at 360 and 400 K, assuring mechanical resistance to material. Each sample is submitted to a heat treatment process for obtaining RVC. They are heated at $1\text{ K}\cdot\text{min}^{-1}$, under inert atmosphere with nitrogen flow of $1\text{ L}\cdot\text{h}^{-1}$, reaching the maximum temperature of 1000, 1300, 1600, 1800, 2100 and 2300 K, holding at this maximum temperature during 30 min and then cooling down to room temperature. The furfuryl resin used in this work is a national polymer and promotes denser final carbonized foam due to lower losses in volatiles cure and carbonization processes. This resin produces a material more electrically conductive and resistant to flexion than RVC obtained from phenolic resin [14].

A LEO 440 scanning electron microscope was used to observe RVC morphology and a Renishaw Microscope system 2000 in backscattering configuration at room temperature employing 514.5 nm argon-ion laser to obtain micro-Raman spectra. This powerful and sensible technique permits an analysis of impurities and defects, especially the ones associated to graphitic phases. XRD measurements were performed from a diffractometer Phillips, PW 1210/W/380/80.

III. RESULTS AND DISCUSSION

Images obtained by scanning electron microscopy (SEM) do not reveal large differences among struts for samples at different HTT. SEM images with magnification of 40 times are shown in Fig. 1. This image permits to estimate the pores diameter as the way to quantify such pores per inch (ppi) on RVC samples. Pores with average diameter of $300\text{ }\mu\text{m}$ were

formed, corresponding to 70 ppi. This value is important to estimate the specific geometric surface area. Friedrich *et al* [9] have measured the strut areas of such pores by SEM and found a linear relation between the quantity of ppi and the specific surface area. By using this relation, it was evaluated for 70 ppi, a volumetric specific area of around $45 \text{ cm}^2 \text{ cm}^{-3}$.

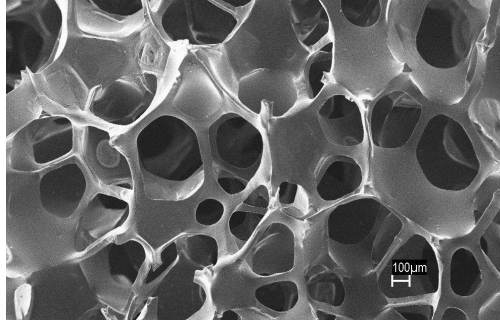


FIG. 1: SEM image of RVC sample treated at 1300 K.

For discussing the microstructural properties of RVC samples it is very important a systematic interpretation of XRD and Raman measurements in the whole range of studied temperatures. After carbonization process, RVC is a low volume disordered glassy porous carbon with a continuous skeletal structure, low resistance and some crystallographic order associated to its graphitization index [9]. RVC structures, also called turbostratic carbon (TC), have their microstructure formed by disordered, no planar and confluent graphitic ribbons. Figure 2 shows the pilling up width (L_{002}) and interplanar distance (d_{002}) as a function of HTT for RVC samples, as already studied by other authors [11,13,15]. Hydrogen and oxygen (heteroatoms) presence originated from precursor represents a contribution in surface interaction process [16], mainly for lower HTT [12]. This behavior justifies the intense decrease of d_{002} at range of 1000 - 1300 K, accomplished by increase of L_{002} due to the heteroatoms release.

In deed, this process concerns to the liberation of relatively large atoms as oxygen or nitrogen originated from precursor. This liberation occurs up to 1300 K where a significant decrease of intralamellar distance appears. The more important contributions concerning to the TC organization was observed for HTT higher than 1500 K [17]. It is possible to observe this process in x-ray response at HTT higher than 1300 K, with L_{002} increase and d_{002} decrease. Additional contribution for L_{002} increase is attributed to lamella estrangement.

Micro-Raman spectra for RVC substrate produced at 2300 K are shown in Fig. 3. RVC curve has a typical two bands spectrum of disordered polycrystalline and noncrystalline graphitic carbons [18]. The first one, at approximately 1360 cm^{-1} , exists only in defective carbons and is called “D-band”, associated to disorder and edges of these crystals. The band at 1600 cm^{-1} can always be presented in vitreous carbon as a superposition of two components: G (1580 cm^{-1}) and D’

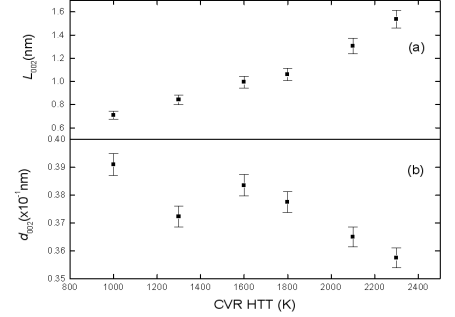


FIG. 2: (a) Pilling up width (L_{002}) and (b) interplanar distance (d_{002}) evaluated from XRD on RVC samples as a function of HTT.

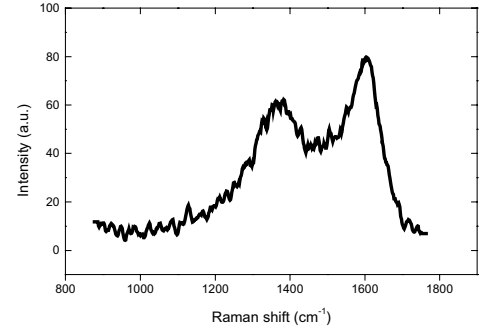


FIG. 3: Raman spectra of: (a) RVC sample treated at 1400 K.

(1620 cm^{-1}) [13]. The G-band is called “graphitic” and attributed to the graphite basal plane. On the other hand, the D’ band is attributed to second first order zone boundary phonon [18].

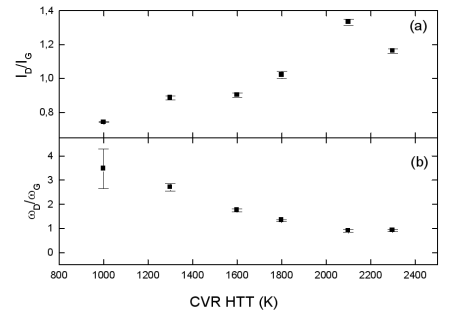


FIG. 4: (a) Relative intensity (I_D/I_G) and (b) relative FWHM (ω_D/ω_G) between D and G bands observed in the RVC Raman spectra as a function of HTT.

Figure 4 shows the ratio of D and G bands intensity and FWHM (I_D/I_G and ω_D/ω_G , respectively) from RVC Raman

spectra as a function of HTT, to observe carbon disorder degree [19,20]. It is important to note that these results were not related with carbon crystallinity, since results obtained by first order Raman spectroscopy have restrictions to evaluate the crystalline changes [21].

However, mainly G-band FWHM is a strong indicative of the better ordering of the graphite basal plane that forms TC structure. In the temperature range between 1000 and 1300 K, the I_D/I_G increase may be related to structural defects attributed to heteroatoms release process living imperfect sites in their locations. Between 1300 and 1600 K, there are not heteroatoms, and the I_D/I_G increase is asymptotic, revealing an accommodation of lamellas in a structure with high graphitic character. Practically, this ratio does not vary until 1600 K. In this temperature, warrant itself that there are not heteroatoms in the carbonous structure. Relative intensity of D-band continues increasing for HTT higher than 1300 K, but between 1600 and 2100 K it is registered a significant increase. This contribution is mainly attributed to an additional process on stacking and approaching of lamellar surfaces, associated to TC confluence of such material. In addition, the I_D/I_G decrease, observed above 2100 K, may be associated to the initial stage of anisotropic structure formation process. The ω_D/ω_G values present D-band FWHM decrease, also indicating disorder degree increase with HTT increase up to 2100 K. These analyses agree with crystallinity results from XRD and indicate the contribution of heteroatoms until 1300 K and the predominance of TC formation above 1600 K. In spite of to be studied in the literature the ratio ω_D/ω_G observe the graphitization quality [18], for this work the intensities evolution associated with D-band shift are more relevant.

This behavior is attributed to the formation of large reactivity sites [22].

It is important to highlight that XRD measurements are not necessarily related to Raman measurements. XRD offers data inherent to interlamellar structure, while Raman spectroscopy results relate aspects of intralamellar structure, observing phonon behavior. Thus, the narrowing of interlamellar distance, that indicates an ordering increase, is accomplished by defective sites appearance, as HTT increases. Thermodynamically, this is expected, since all entropy decrease in a system is accomplished by neighborhood entropy increase. It is, therefore, notable that the entropy decrease, at interlamellar system and revealed by d_{002} behavior, compensated the entropy enhancement at intralamellar level, revealed by I_D/I_G behavior.

IV. CONCLUSION

Structural properties of RVC as a function of HTT were studied by Raman and XRD analysis. In this range of carbonization temperature (1000-2300 K) studied, different contributions are important to define L_{002} and d_{002} behaviors, which are in good correlation with D and G bands behaviors analyzed from Raman spectra. For HTT lower than 1500 K, heteroatoms presence represents a dominant contribution in surface interaction process while the more important contributions concerning to the TC organization was observed for HTT higher than 1500 K.

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