GROWTH MECHANISMS OF GRAPHITE NANOFLAKES

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Abstract

A numerical study was performed to further comprehend the growth mechanisms of gas pockets formed within the graphite structure during exfoliated graphite processing. This model adopts a control-volume-based technique that was implemented to convert the governing integral equations into algebraic equations that can be solved numerically. A parametric study was carried out to analyze the main influences on the extent of expansion of a single gas pocket. Some of the key parameters that influence the gas pockets final size are heat flux into the system, and initial geometry of the gas pocket. The results of this study have shown that higher gas pocket pressures before breakaway of the graphite planes during the exfoliation process produce greater expansions. It was shown that smaller gas pocket volumes produce higher breakaway pressures, and thus greater percentage change in initial volumes, particularly variations in the *a* direction of the geometry of the gas pocket has the greatest effect on volume change during thermal shock. If the summation of the total volume of gas pockets is the same throughout a graphite particle, smaller defect sizes rather than larger ones, will result in greater levels of expansion.

1. Introduction

Exfoliated graphite (EG) is a low density, high aspect ratio material which has important applications for flow field plates for fuel cells, EMI shielding, gaskets, flame retardant, etc [4]. EG is an attractive additive into polymers due to its ability to strengthen the matrix while maintaining its light-weight properties [2]. The exfoliation of graphite produces a material, which has outstanding homogeneity and large surface area, it is therefore a superlative candidate for adsorption studies [5,7].

The insertion of a foreign species into the crystalline structure of graphite forms what is known as a graphite intercalation compound or GIC [5,3]. The most widely used heating source to induce expansion has been the flame. When graphite intercalation compounds are processed, the intercalate gas will diffuse through regions of the graphite structure. It was suggested by Hooley [8] that certain structural defects seal the edges of the graphite planes together, thus creating small gas-tight pockets in which the intercalate is trapped. Martin and Brocklehurst [10] postulated that gas bubbles are formed in regions where the gas is trapped by defects blocking the diffusion paths.

The dependency of expansion lies in the vaporization of the intercalate. Heating a graphite intercalation compound initiates the vaporization of the residual intercalated species and water molecules inserted into the graphite lattice. Several theories describing graphite layer expansion have been proposed. Martin and Brocklehurst's [10] model suggested that gaseous bromine bubbles within the lamellar structure of the graphite crystal are considered to be analogous to Griffith cracks. The crack diameter increases when the tensile stress in the *c* direction surpasses the fracture strength. The gas pockets, and consequently the graphite layers, will stop expanding when the gas within the individual layers reach equilibrium according to the ideal gas law or if the gas is able to escape the gas pockets through new diffusion paths that have been opened as a result of the lattice transformation.

There have been quite a few proposed mechanisms for expansion of graphite intercalation compounds [1,2,10-13]. Despite the amount of research regarding exfoliated graphite, there has not been extensive work performed studying the influences on pore growth during exfoliated graphite processing. The two most sophisticated models were proposed by Martin and Brocklehurst [10] and Mysyk et al. [11]. Martin and Brocklehurst's proposed a model to explain the breakaway expansion and the effect of externally applied stress on the thermal expansion behavior of graphite-bromine residue compounds. This model is significant because it gives the minimum force for which the graphite layers will begin to break apart. It goes on to relate this force to the equivalent pressure within the gas bubble that could break apart adjacent graphite layers. This model also uses experimental data to extrapolate values for the radius at breakaway of the bubble parallel to the planes, the pressure at breakaway, and the number of molecules in

the bubble. However, this model assumes 1D expansion, even though realistically the expansion would take place in three dimensions. Also, the bubble radius perpendicular to the planes is assumed to be restricted by the average distance separating two planes (7.05 Å), even though the bubble may be a number of different shapes and sizes depending upon the magnitude of defects present within the lattice.

Mysyk et al. introduced a technique that allows the mass and volume of GIC's to be simultaneously followed during the thermal transformation into expanded graphite. This enabled them to elucidate the mechanism for thermal expansion of GIC's and formulate a quantitative model for that process. Advantages of this model are that it adapts previous models to the third dimension and predicts the mass and volume loss as a function of temperature. However, the pressure inside the gas bubble is only approximated by the Griffith crack and only predicts results for one specific case, and no parametric study is performed to optimize the effects on growth.

In the present work, a numerical simulation, utilizing a finite volume method is introduced for the growth of a gas pocket during the expansion process of exfoliated graphite. The expansions of single gas pockets, which form from the coalescence of intercalated molecules, is the reason for the separation of the graphite layers and the development of the resultant microstructure of exfoliated graphite. Proposed is a new approach that utilizes concepts developed in models from Martin and Brocklehurst [10] and Mysyk et al. [11]. This new approach solves for the gas pockets pressure directly by using the energy equation, rather than approximating it using the Griffith crack or deriving it from experimental data. This allows for a more accurate and realistic solution. Some of the key parameters that influence the gas pockets final size are the heat flux into the system, and variations in the initial geometry of the gas pocket. Quantifying these factors to solve for the internal pressure within the gas pockets before breakaway, allows for the determination of how they affect the final pore size. From this, a parametric study is performed to optimize these mechanisms responsible for growth of the single gas pocket. This study quantifies the energy through the solution of several simultaneous non-linear differential equations using a finite volume method. The numerical method will be explained in further detail.
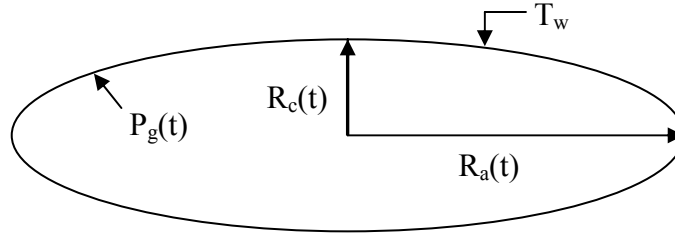

Figure 1. Schematic of model

2. Modeling Procedure

2.1 Assumptions

Islands of intercalate which form from the diffusion and trapping of gas in the graphite planes, as suggested by Daumas and Herold [6], are likely the source of the gas pockets responsible for expansion. This assumption suggests that the gas within the system can be modeled as a closed, discrete entity of intercalate gas. After the diffusion of gas through the matrix, the defects inherently present in the graphite lattice trap the gas, forming "islands of intercalate" as proposed by Daumas and Herold. A schematic representation for such a phenomena can be represented as in Figure 1. The model has been developed under the following assumptions. As shown by Inagaki [9], the gas pocket in exfoliated graphite looks like a body of rotation whose form closely resembles an ellipsoid. An ellipsoid is a three dimensional body containing three radii, R_a, R_b, and R_c. These two radii in the plane parallel to the graphite layers are assumed to be equal to one another, so

$$R_b = R_a \tag{1}$$

The assumption is made that the ratio β of the major radius R_a to the minor radius R_c of this gas pocket remains unchanged during thermal expansion. Therefore, the ellipsoid will expand equally in all three radial directions shown as

$$\frac{R_a}{R_c} = \beta = const \tag{2}$$

Therefore this discrete volume of gas within the pockets can be assumed to follow the ideal gas law.

$$P_g V = nkT \tag{3}$$

where P_g is the pressure within the gas pocket, n is the number of molecules of intercalate initially in the pocket, and k is Boltzmann's constant. The volume of the gas pocket can be defined as

$$V = \frac{4\pi}{3} R_c R_a^2 \tag{4}$$

The heat source adding energy into the cavity is set by applying an isothermal boundary condition around the outer wall of the gas pocket. In the following sections, the numerical procedure is further discussed as to how the expansion process persists.

2.2 Numerical procedure

The expansion of a gas pocket during the exfoliation of graphite can be idealized by a three step thermal transformation process. In the first step, the pocket undergoes rapid heating due to the isothermal temperature constraint imposed on the border. However, thermal expansion is initially constrained by the bonding forces between the individual graphite layers enclosing the gas pocket by Van der Waals bonds. As heating continues, the pressure within the gas pocket increases until it equals the sum of the bonding force from the planes and atmospheric pressure. This leads to the second step in which the pressure overcomes the opposing forces and expansion is allowed to occur due to the large pressure build up. In the third and final step the accumulated pressure is finally exhausted. The majority of the gas escapes from the edges due to expansion. Therefore there is negligible volume change and it can be assumed that expansion will no longer occur.

2.2.3 Energy equation

For the implementation of heat transfer, an energy equation must be applied. The energy equation takes the following form

$$\frac{\partial}{\partial t}(\rho E) + \nabla \cdot (\vec{v}(\rho E + p)) = \nabla \cdot \left(-\sum_j h_j \vec{J}_j \right) \tag{5}$$

2.2.6 Breakaway Temperature

As a graphite intercalation compound is heated the Van der Waals forces between adjacent graphite layers are initially greater than the pressure of the intercalate in the bubble. Therefore it takes a significant rise in temperature before these forces will be overcome by the pressure forces within the bubble. The temperature at which expansion first occurs due to thermal heating can be called the "breakaway temperature", T_B [10]. The summation of forces on a single gas pocket is shown in Figure 2 and can be given as
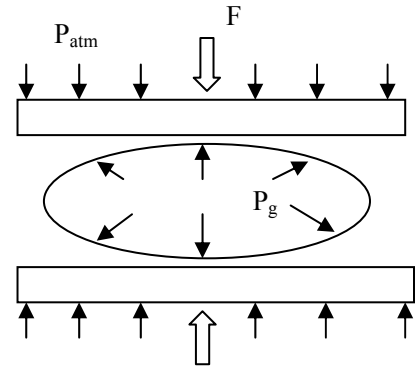

Figure 2. Summation of forces

$$P_g = P_{atm} + F \tag{6}$$

The bonding force between the layers, as described by Martin and Brocklehurst, is said to be

$$F = \left[\pi \gamma G / 2\left(1 - \sigma^2\right) R_a \right]^{1/2} \tag{7}$$

where γ is the 'effective' surface energy per unit area of the gas pocket, σ is Poisson's ratio of graphite, G is the shear modulus of the graphite crystal. Recalling that the gas pocket is assumed to follow the ideal gas law, the pressure can be computed as

$$P_g = \frac{3nkT}{4\pi R_c R_a^2} \tag{8}$$

where n is the number of molecules of the gas in the bubble, T is the absolute temperature of the gas, and k is Boltzmann's constant. Solving for T from equations (7) and (8) gives the breakaway temperature.

$$T_b = 4\pi R_c R_a^2 \frac{\left[\pi \gamma G / 2\left(1 - \sigma^2\right) R_a \right]^{1/2}}{3nk} + \frac{4P_{atm}\pi R_c R_a^2}{3nk} \tag{9}$$

2.3 Numerical Solution

Computational fluid dynamics software, Fluent was chosen to simulate this phenomenon. Due to the uniqueness of this particular phenomenon, an additional code, or user defined function (UDF), was written into the Fluent software in order to fully predict this scientific process. The purpose of the UDF created for this problem was to control the rate and extent of expansion of a gas pocket based on the several equations solved for earlier.

The major radius, R_a, was varied between 50-700μm and the minor radius, R_c, was varied between 0.1-20μm. The resolution for each grid was 1794 cells. The grid resolution was maximized while still considering its important limitations such as CPU time and computer resource limitations.

Table 1. Constant values used for solution

Parameter	Symbol	Value
Shear modulus of graphite	G	3.0×10^9 Pa
Effective surface energy	γ	0.12 J/m^2
Poisson's ratio of graphite	σ	0.3
Boltzmann's constant	k	1.38×10^{-23} J/K
Atmospheric pressure	P_{atm}	1.01325×10^5 Pa
Molecular weight of sulfur dioxide	M_w	64.06 g/mol
Density of sulfur dioxide	ρ	2.77 kg/m^3

2. Results

The significance of this study lies in its ability to predict the volume change of a gaseous pocket trapped between adjacent layers of graphite during actual exfoliated graphite processing allowing for a better process control. The processing of exfoliated graphite can be modified based on the requirements of the desired application. A parametric study is forth taken with the intent to study various changes to the model and the influence they have on changing the gas pockets volume. Therefore, the results from this study are shown to be qualitative in nature rather than quantitative. The parameters that have been chosen to be analyzed for this particular case includes the isothermal boundary condition, the size of the pocket, and the aspect ratio of the pocket described by Eq. 2 (keeping either the a-axis or c-axis radii constant). For the solution of this model, the initial conditions listed in Table 1 [10,14] were used and all of the parametric studies were performed with sulfur dioxide as the intercalated gas.

To confirm the accuracy of the proposed model, it was compared to experimental data performed Mysyk et al. [11]. Their experimental set-up allowed them to simultaneously measure the volume and mass loss of a graphite sample during an applied constant heating rate of 2K/min throughout the thermal transformation process. In the proposed model, the initial parameters including gas pocket size and the

wall temperature, which determine the heat flux into the system, were adjusted until they were in agreement with the experimental data. Figure 3 shows the comparison between the experimental data and the model proposed for the gas pocket growth, the results have been normalized. The curves depict the volume change of the system as a function of the systems temperature. The proposed model seems to be in good agreement with the experimental data on the thermal expansion of the graphite particles. These results confirm the validity of the model.
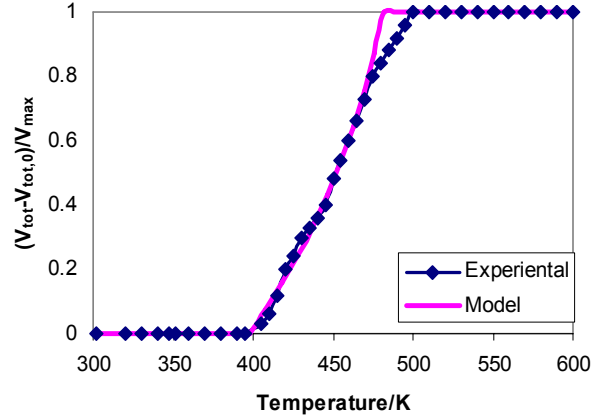

Figure 3. Comparison between the experimental data and proposed model

3.1 Wall temperature

To simulate the affects of varying the amount of heat added to the system, the isothermal boundary condition on the boundary of the gas pocket has been varied to range from 500°K to 1300°K. All of the other variables were kept constant in this particular study. Since the breakaway temperature from Eq. 10 depends upon the radii of the ellipsoid among other constants, it will also be constant. Therefore the sole influence on the amount of expansion will depend upon the maximum pressure achieved from the various wall temperatures. The higher the wall temperature, the larger the heats flux into the gas pocket. The greater amount of heat added to the system before the gas pocket reaches its breakaway temperature will increase the pressure at the point of breakaway. The pressure in the gas pocket at the instant before breakaway determines the magnitude of expansion. The results from the simulation have shown to follow this particular trend. The dimensionless variable θ has been made to quantify the amount of expansion that occurs and can be represented as

$$\theta = \frac{\%\Delta Rc}{\%\Delta Rc_{max}}$$ (10)

where $\%\Delta Rc$ is the percent change of the *c*-axis radius, and $\%\Delta Rc_{max}$ is the maximum percent change of the *c*-axis radius achieved after expansion from the solution set. Since the graphite flake is limited to growth in the *c* direction only, due to its layered structure, any growth in the *c* direction of the gas pocket will represent the extent of expansion expected for the overall system. The effects of changing the magnitude of heat flux into the system as a function of the dimensional expansion coefficient θ can be seen in Figure 4. As expected, the amount of expansion increased with increasing temperatures.
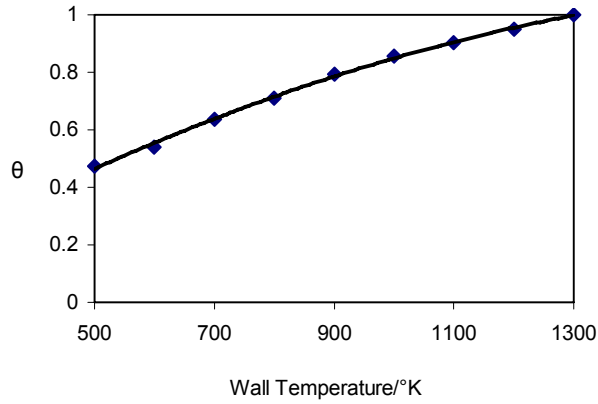
Figure 4. Radial growth as a function of wall temperature

3.2 Gas pocket size

       The size of the gas pocket trapped within the crystalline structure of graphite may vary depending on the presence and size of the defects present in the lattice. For this reason, an investigation on the effect of various sized gas pockets needs to be addressed. For clarification, various "sized" gas pockets have the same aspect ratio. The *a* and *c* axis are varied at the same ratio. The isothermal boundary condition is constant for this study. For this particular case, the breakaway temperature is dependent upon the size of the gas pocket, as the volume decreases, the breakaway temperature increases. The reasoning behind this result is due to the fact that the number of molecules *n* within the gas pocket, is defined by the volume of that particular pocket. Therefore these two volume terms in both the numerator and denominator will cancel each other out, leaving only one geometrical variable left in the equation, R_a in the denominator of the portion of the breakaway temperature equation that represents the force between the graphite layers. Then, changing the size of the bubble will change the radius R_a, and as was just shown since the single R_a term is in the denominator, as R_a decreases, the breakaway temperature will increase. The higher the breakaway temperature, the more pressure will build leading to greater expansions. The dimensionless parameter *V** will be introduced and is given as

$$V* = \frac{Vin}{Vin_{max}} \tag{11}$$

where *Vin* is the initial volume of the gas pocket, and *Vin_{max}* is the initial maximum volume from the solution set. Figure 5 shows the behavior of the dimensionless expansion coefficient as a function of the change to the dimensionless initial volume of the intercalated gas cavity. This trend suggests that as the initial volume of the gas pocket decreases, the overall percentage change in the *c* direction increases. The percent volume change will be greater for smaller pockets compared to larger ones. However, the final overall volume of an initially smaller gas pocket will not exceed that of an initially larger one. The trend observed from the results is apparent for two reasons. First, this increase is caused from the increase in the breakaway temperature as the volume decreases. The breakaway temperature is a function of the geometry of the gas pocket at hand. Higher breakaway temperatures will allow for more pressure to build up in the gas pocket before it is released. Second, lower volumes will result in greater pressure build up, according to the ideal gas law under constant temperature. As would be imagined, higher pressures right before the breakaway point will lead to greater expansion.
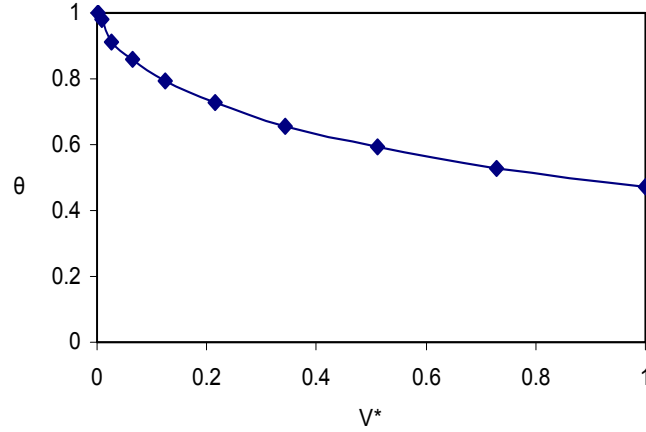
Figure 5. Radial growth as a function of initial volume at constant aspect ratio

3.3 Aspect ratio

It is important to study the effects of changing the aspect ratio of the gas pocket. Not only can the gas pocket change in volume, it can also be found in a wide gamut of aspect ratios. This can again be the cause of various sized defects, but this time the geometry of the defects is considered. Gas pockets can also be trapped within the individual layers of the graphite crystal and the aspect ratio depends upon how far the pocket is dispersed along the *a* direction of the lattice. The dimensionless variables *Ra** and *Rc** can be defined as

$$Ra^* = \frac{Ra}{Ra_{max}} \tag{12}$$

$$Rc^* = \frac{Rc}{Rc_{max}} \tag{13}$$

Varying the aspect ratio was performed by holding one radius of the gas pocket constant while changing the other. The dimensionless expansion coefficients as a function of the variations to the aspect ratio can be seen in Figure 6 and 7. Figure 6 shows the variation in the minor radius or *c* direction of the gas pocket while holding the initial *a* direction radius constant. Changing the *c* direction radius has no effect on the breakaway temperature since the *c* direction radius cancels itself out since it can be found in both the numerator and denominator. Therefore the breakaway temperature is constant for this case. The only effect on the internal gas pocket pressure at breakaway, and as a result the extent of expansion, is the change of the gas pocket volume due to changing the radius value. As the *c* axis radius decreases, the gas pocket volume decreases as well. Smaller volumes produce larger pressures as the same wall temperature. The variation in the *a* direction of the gas pocket, while holding the *c* direction radius constant, is shown in Fig. 7. Variation in the *a* direction has the same effect on expansion due to the volume change as the *c* direction did. However, the *a* axis radius does not get completely cancelled in the breakaway temperature equation. There is still influence in the portion of the equation that accounts from the tensile stress *F* that holds the graphite layers together. This will account for increasing breakaway temperatures with increasing *a* axis radius, and for the same reasons that have been seen before, increased expansion. Thus, fluctuations in the *a* direction of the gas pocket should have a stronger influence on the expansion than the *c* direction.
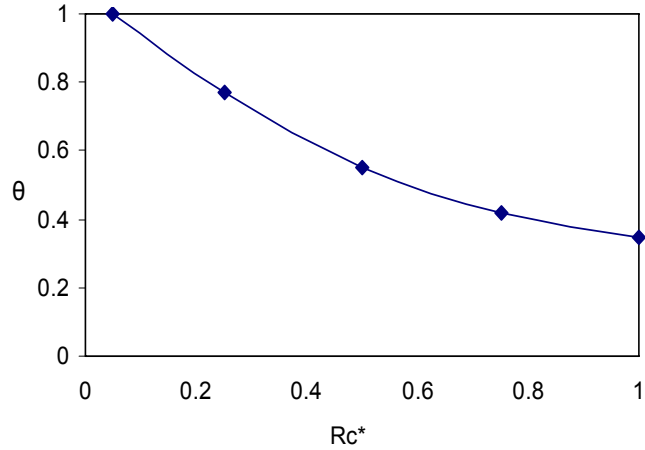
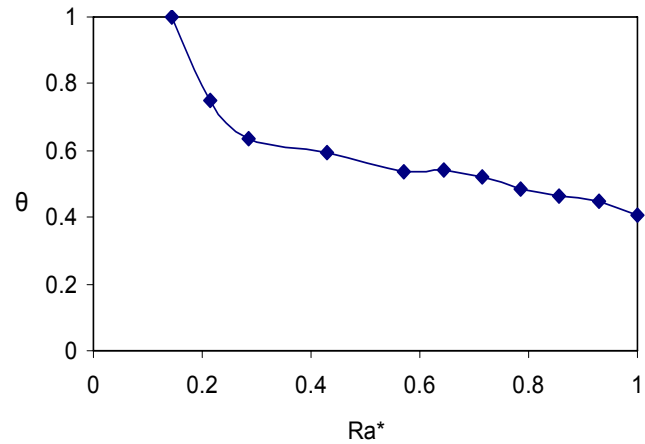**Figure 6.** Radial growth as a function of initial *c* axis radius

Figure 7. Radial growth as a function of initial *a* axis radius

4. Conclusions

A numerical model to study the growth mechanisms during the exfoliation of graphite was proposed. The expansions of single gas pockets, which form from the coalescence of intercalated molecules, are the major contributors to the separation of the graphite layers and the development of the resultant microstructure. This model is a control-volume-based technique that was implemented to convert the governing integral equations into algebraic equations that can be solved numerically. A parametric study was carried out to analyze the main influences on the extent of expansion of a single gas pocket. Some of the key parameters that influence the gas pockets final size are the heat flux into the system and initial geometry of the gas pocket. From the finding of this study it has been seen that higher gas pocket pressures before breakaway lead to larger expansions. Various changes on the system can affect the gas pocket pressure before breakaway as was evident from the parametric study. The cause of higher pressure in the gas pocket at breakaway include, but are not limited to, the magnitude of the isothermal boundary condition, and various sized volumes caused by change in the geometry. A variety of gas pocket dimensions and sizes can be possible by defects found within the crystalline structure of graphite. Therefore, all geometries were studied to verify their effect on expansion. It was seen that smaller volumes produce greater percentage change in initial volumes. Considering a graphite flake on the macro level, if the same concentration of gas is kept constant but the individual gas pocket sizes are reduced, greater expansion will occur for the overall sample. Graphite particles that most closely resemble a perfect graphitic structure, with smaller defect sizes, will result in greater levels of expansion. Also, since the force equation for the bonding of the graphite planes has been determined to only depend on R_a and not R_c, only

variations in R_a will affect the breakaway temperature providing another route for higher pressures. It can be postulated then that variations in the *a* direction of gas pockets has more influence on expansion than variations in the *c* direction, since the R_c radius gets eliminated from the breakaway temperature equation, only R_a is left to influence the breakaway temperature. As discussed earlier, decreasing R_a will increase the breakaway temperature giving a higher resultant breakaway pressure. The particular species used for intercalation plays an important role in the final expansion. Materials with superior heat transfer properties will allow more heat into the system resulting in higher pressures before breakaway. The predicted results provide insight on the exfoliated graphite formation. It demonstrates where the major influences for expansion are developed.

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