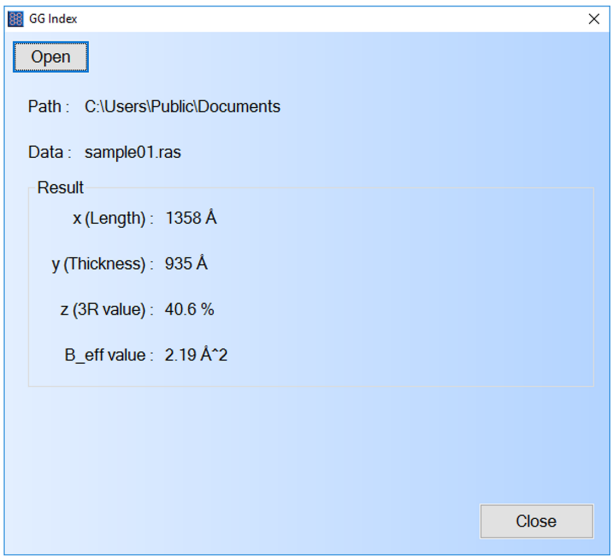
Graphite/graphene analytical index calculator

GG Index



1. Introduction

The discovery of graphite and its industrial use dates back to the 16th century, more than 200 years before the first industrial revolution, which took place from the middle of the 18th to the 19th century. The first industrial use of graphite was as pencil lead and fire-retardant materials. It is now used in a variety of high-tech fields, including nuclear energy. More than 1.2 million tons of graphite is produced each year, with an upward trend foreseen in future demand.

Graphite is inexpensive and distributed throughout the world. Sufficient reserves exist to meet demand for hundreds of years, according to verifiable sources. The existing supply of graphite is almost infinite.

Once a flake of graphite is peeled off, it becomes a fascinating material called "graphene," a stunning discovery that did not occur until 2004. Graphene is 1,000 times stronger than iron steel, exhibits more than 10 times higher electrical and thermal conductivity than metals, and is the thinnest and lightest flexible material known today. In 2010, the Nobel Prize in Physics was awarded for its discovery.

Innovative materials and products can potentially be created in various fields using graphene. Therefore, research institutes and companies all over the world conduct research and development into practical application of graphene in almost every industrial field. In the years since its discovery, products such as electronic items, acoustic products, daily commodities, tires, golf balls, sportswear and shoes have been developed, making use of graphene for improved impact strength, conductivity characteristics, and so forth.

However, reasonably accurate measurement methods, analytical methods, definitions, standard references etc. have not been developed to identify graphite or graphene qualitatively or quantitatively. Graphite and graphene are currently evaluated in a limited, subjective, speculative way by shape observation using an electron microscope, surface analysis using Raman spectroscopy, a specific surface area measurement by gas absorption and so forth. The purpose of the Graphite/Graphene Analytical Index presented here is to exhaustively identify and characterize graphite, graphite-based graphene intermediates and bulk graphene, and to significantly enhance the efficiency of research and development related to these materials. Furthermore, we hope this index accelerates the development of breakthrough products based on graphite and graphene.

2. What is the "GG Index"?

The goal of the Graphite/Graphene Index (referred to hereafter as the GG Index) is to elucidate the following items in association with future research.

(1) Characterization and identification of graphite as raw materials
(2) Characterization and identification of graphite, graphene intermediates, and graphene in general
(3) Determination of the specifications of graphite, graphene intermediates, and graphene as products
(4) Characterization and identification of denaturation products of graphite, graphene intermediates and graphene denaturation processed by heat treatment, grinding, chemical treatment, or plasma

Table 1. Four parameters of GG Index.

X: Crystallite size (unit: Å)	Lateral size of graphite crystallites in the planar direction calculated based on the 100 diffraction peak shape
Y: Crystallite thickness (unit: Å)	Thickness of graphite crystallites in the stacking direction calculated based on the 004 diffraction peak shape
Z: Graphenization parameter (unit: %)	The ratio of rhombohedral graphite crystals to the sum of hexagonal and rhombohedral graphite crystals
M: Collapse parameter of graphite crystals (unit: Å^2)	A value related to the structural strain of graphite crystals It indicates the amount of displacement of the carbon atoms from the regular positions in graphite crystals.

treatment as refining processes

(5) Selection of raw graphite and optimization of treatment processes for required graphite or graphene as products based on the four items above

As a reference for these analyses, the GG Index consists of the following four parameters calculated based on the X-ray diffraction patterns of graphite/graphene powder samples.

2.1. X and Y: Crystallite size and thickness (unit: Å)

The fundamental parameters (FP) approach is used here. The theoretical diffraction peak shape f_s^{LN} (k; D_0, σ) obtained from the following equation is fitted to experimentally obtained 100 and 004 diffraction peak shapes to obtain D_0 as X and Y, respectively.

$$f_s^{LN}(k;D_0,\sigma)=\int_0^\infty f_s(k;D)\,f_{LN}(D;D_0,\sigma)\,dD$$

k : Scattering vector
D_0 : Volume-weighted size
D : Crystallite size
σ : Standard deviation
f_s : Peak profile from one crystallite
f_{LN} : Lognormal distribution
f_s^{LN} : Peak profile from particles

(1) "Crystallite" here is the part regarded as a single crystal.

(2) A single crystal is one crystalline particle where atoms are arranged with three-dimensional regularity. Even if defects exist (where some 6-membered rings turn to 5- or 7-membered rings or some carbons have an sp^3 hybridized orbital due to addition reactions of hydrogens or hydroxy groups), the part where the atoms are arranged with a roughly three-dimensional regularity can be regarded as a single crystal.

(3) The thickness of the crystallite is the number of layers stacked.

(4) The crystallite size calculated based on the hkl diffraction peak shape is the single crystal size along the hkl direction. In the case of graphite, the ⟨100⟩ direction means the planar direction, and the ⟨001⟩ direction (calculated based on the 004 diffraction peak shape) means the stacking direction.

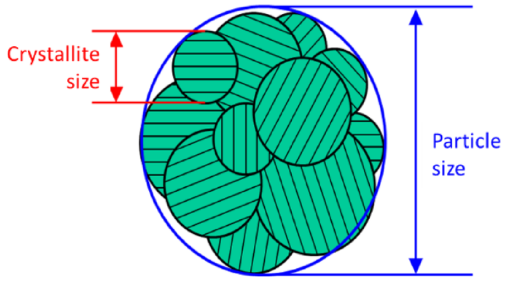


Fig. 1. Difference between a particle and a crystallite.

(5) Normally, one recognizable particle in a powder consists of several crystallites (see Fig. 1.). For example, the ⟨001⟩ direction of one of the adjacent two crystallites differs from that of the other.

(6) Although the crystallite sizes and thicknesses of a real sample have size distributions, the GG Index software calculates the volume-weighted average values.

(7) According to the accuracy of the XRD peak shape analysis, the analyzable maximum size is now around 1,000 Å. The possibility and benefit of obtaining crystallite sizes larger than 1,000 Å should be discussed in the future.

2.2. Z(R): Graphenization parameter (unit: %)

According to the following formula[1], the ratio of rhombohedral graphite contained in the graphite crystalline sample is calculated based on the integrated intensities of 101 diffraction peaks of hexagonal graphite 2H and rhombohedral graphite 3Rh. The obtained ratio is what we call the "graphenization parameter".

$$R=\frac{I_{3Rh_{101}}}{I_{2H_{101}}+I_{3Rh_{101}}}$$

The stacking behavior of hexagonal crystallites is different from that of rhombohedral crystallites. The larger the ratio of rhombohedral graphite, the easier the layers are peeled off; in some cases, exfoliation may have already begun[2]. In general, graphene, graphene intermediates, and some graphite show a high trend in terms of R values.

2.3. M(B_{eff}): Collapse parameter of graphite crystals (unit: Å^2)

The effective Debye parameter B_{eff} calculated based

Table 2. The crystalline state of graphite based on the M value.

M	< 1.0	Crystalline state of graphite is maintained in a very good condition.
	1.0–3.0	Crystalline state of graphite is maintained.
	> 4.0	Crystalline state is largely destroyed.

on the following formula is affected by the amount of displacement of the carbon atoms—which are supposed to be arranged with 3-dimensional regularity—from their regular positions in graphite crystals[3].

$$\ln\left(\frac{I_{obs}}{I_{calc}}\right) = \ln k - 2B_{eff} \cdot \left(\frac{\sin\theta}{\lambda}\right)^2$$

B_{eff} : Effective Debye Parameter
I_{obs} : Observation Intensity
I_{calc} : Calculated Intensity

B_{eff} is almost zero for ideal crystals; however, atomic positions in real crystals are displaced slightly from their regular positions due to thermal vibrations and lattice defects. The larger B_{eff} is, the larger the thermal vibrations and the amount of lattice defects are. In other words, B_{eff} can be regarded as the degree of crystal collapse.

The target material is graphite only; therefore, the thermal atomic vibrations are the same regardless of sample if the temperature is the same. The difference between obtained B_{eff} values can be attributed to the difference in the amount of lattice defects; i.e., to the structural strain.

3. GG Index software

The GG Index software calculates the GG Index (X, Y, Z, M) based on the X-ray diffraction patterns of graphite/graphene powder samples measured using the SmartLab automated multipurpose X-ray diffractometer.

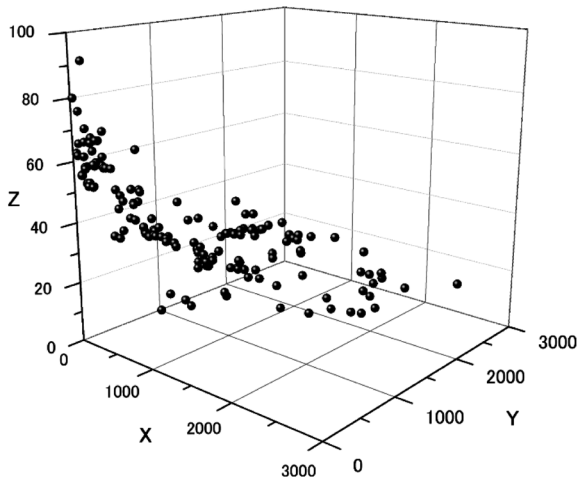


Fig. 2. GG Index from graphite based carbon materials (X, Y, Z only).

Shown below is an example of the GG Index results from about 100 samples of carbon materials obtained from representative manufacturers around the world.

The GG Index has the potential to find a correlation between the indices obtained from a number of graphite/graphene samples, as well as to simply analyze one graphite/graphene sample, and to generate a unified analytical method for graphite and graphene. It is hoped that the GG Index will contribute to the creation of requirements or specifications of graphite, graphene intermediates, and graphene required for a variety of products, and to select and optimize various refining processes of graphite and graphene in the future.

References

(1) M. Inagaki, H. Mugishima and K. Hosokawa: *Tanso*, (1973), Issue 73, 76–82 (in Japanese).
(2) US Patent: US9428393, UK Patent: GB2528381.
(3) M. Inagaki and S. Naka: *Zairyo*, **27** (1978), 604–609 (in Japanese).