Contributed Papers from Materials Science and Technology 2019 (MS&T19)
September 29–October 3, 2019, Oregon Convention Center, Portland, Oregon, USA
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DOI 10.7449/2019/MST_2019_40_45

SURFACE AREA AS A POWDER MORPHOLOGY PROBE

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Keywords: powder characterization, surface area, BET, adsorption, morphology

Abstract

The specific surface area of a powder sample measured by gas adsorption (the so-called BET method) is a well-established method within conventional powder metallurgy, ceramics, pharmaceuticals and geology. As a true measurement (based on gas pressure), within a given particle size range, the specific surface area provides quantitative information on particle morphology. When applied to lower surface area materials, the use of krypton gas a probe molecule improves resolution of the BET method by approximately 300× over nitrogen gas. The relationship between BET surface area, particle size and particle morphology has been established for a wide range of materials using techniques such as x-ray diffractometry and electron microscopy. When applied to powders used in additive manufacturing processes, the bulk morphology information obtained can be connected to powder characteristics such defect content, retained fines and contamination.

Particle Morphology in Additive Manufacturing

The morphological characteristics of particles in a bulk powder affects a wide range of behaviors. In powder-based additive manufacturing (AM) processes, particle shape and morphology can impact powder flow and spreading, laser absorption, sintering and densification. In addition, the reactivity of particles towards, for example, residual moisture can affect the final alloy composition (oxygen content, etc.). Recently, Meier and co-workers studied cohesion in Ti-6Al-4V powders for AM, noting that the low surface energies in powders are affected by properties like surface roughness and surface oxidation [1]. Similarly, researchers at McGill University examined the impacts of moisture and particle morphology on AlSi7Mg powders, and indicated that AM process optimization should include factors including particle morphology [2].

Compared to conventional water-atomized metal powders, gas- and plasma-atomized metal powders used in AM generally exhibit more uniform particle shape and texture, and therefore often have lower surface areas [3, 4]. While this uniformity aids in powder flow and packing, these powders can cost 10× more than water-atomized powders [4]. In addition, higher particle surface area improves sintering and densification. As AM process costs continue to decline, powder raw material costs are becoming more critical and higher surface area water-atomized powders are being adapted for use in certain AM processes [5].

Particle Morphology Parameters

Among various particle morphology conventions, the International Standards Organization (ISO) provides a fairly comprehensive summary of nomenclature for quantitative description of particle shape and morphology. As shown in Table I, parameters obtained from a variety of potential techniques can be categorized into four shape parameter groups or one surface (roughness) parameter.

Table I. ISO Particle Shape Parameters (ISO 9276-6:2008)

Shape Parameters				Roughness Parameter
Macroshape		Mesoshape	Combination	
Geometric	Proportion			
Ellipse of Inertia Feret Length Geodesic Length	Ellipse Ratio Aspect Ratio Elongation Straightness Irregularity Compactness Extent Box Ratio	Sphericity Solidity Convexity Concavity Concavity Index Robustness	Concavity/ Robustness Ratio	Fractal Dimension

However, obtaining particle morphology information that is both representative and useful has long been a challenge in powder technology. Existing techniques, including static and dynamic imaging, optical and electron microscopy, tomography and laser scattering, have three major limitations:

1. Limited sample size (small sample population)
2. Representation of complex shapes by comparison to equivalent ideal geometries
3. A basis in two-dimensional geometries or measurements (imaging)

Table II summarizes some of the parametric bases for particle shape and surface texture parameters along with typical techniques employed to derive them. Microscopic techniques provide the most limited sample sizes, often fewer than 100 particles. While dynamic image analysis techniques continue to improve and probe larger sample sizes, they are still restricted to two-dimensional imaging and the use of subsequent simplified shape comparisons. These are analogous to the way laser scattering particle size data is fit to equivalent spherical diameters.

As an alternative to these techniques, measurement of the specific surface area of a powder provides a way to quantify multiple scales of parameters.

Table II. Particle Scale Morphology Parameter Characteristics and Techniques

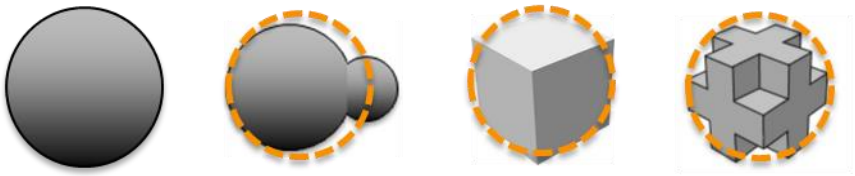
Scale	Particle Scale		Surface Scale	**Particle & Surface Scale**
	Macroshape	Mesoshape		
Descriptors	Sphericity, Elongation, etc.	Circularity, Angularity, etc.	Roughness, Surface Fractal	**Surface Area**
Nature	3D	2D	2D	**3D**
Basis	Equivalent dimensions or volume	Equivalent area or perimeter Comparative geometries	Geometric analysis (ratios, etc.)	**Pressure measurement**
Techniques	Dynamic or Static Digital Imaging, Optical or Electron Microscopy, Tomography, Laser Scattering			**Gas Adsorption (BET)**
Sample Representation	Microscopy (Static Imaging): ≈100 of particles Laser or Dynamic Imaging: 10,000's of particles			**10,000's of particles**

Specific Surface Area

The use of gas adsorption techniques provides a way to probe the particle morphology of a bulk powder sample (1,000's to 100,000's of particles). The well-known BET (Brunauer–Emmett–Teller) method uses condensation of krypton or nitrogen gas on a powder surface at cryogenic conditions. The resulting change in gas pressure is measured to quantify the exposed surface area of powder. Long used in powder metallurgy [6, 7], the method is also used extensively in ceramics, pharmaceuticals, glass and geology to characterize particle morphology [8-12]. The specific surface area is reflective of the particle size, shape, texture and porosity.

Figure 1 exemplifies how various ideal shapes with identical projected areas can show dramatic differences in specific surface area, owing to differences in the surface area-to-volume ratio for each. In this figure, the average cross-sectional area was calculated for all possible orientations, from which a characteristic particle dimension was derived by setting the area of each equal to the equivalent projected area of a 30-micron sphere. An arbitrary specific area of 1 m^2/g was then defined to the spherical case. As can be seen, these various geometries can hypothetically produce up to a 70% increase in specific surface area for the same equivalent particle size. Similarly, the BET method can also serve as a way to monitor surface contamination via either the surface area value itself or the associated C constant [13].

Many studies relating BET surface area to particle morphology have been published. Faroongsarng and Peck utilized laser scattering and BET adsorption to generate a Surface Irregularity Index to quantify the surface roughness of powder particles, which were subsequently confirmed by microscopic analyses [8]. XRD crystallography of bulk powder samples has been used to calculate Morphology Indices that provide strong quantitative correlation the contribution of particle size and morphology toward measured specific surface area. [9, 12]. Mills and Rose provide extensive comparisons of particle shape and surface area by employing scanning electron microscopy, 2D shape measurements and gas adsorption [11].



Equivalent Spherical Diameter (μm)	30	30	30	30
Characteristic Dimension (μm)	30	28	25	25
Surface Area to Volume (m^{-1})	0.20	0.27	0.24	0.34
Specific Surface Area (m^2/g)	**1.00**	**1.37**	**1.20**	**1.71**

Figure 1. Hypothetical Impact of Morphology on Specific Surface Area

Woodward *et al.* reported good agreement between BET surface area measurements and the morphology of fine particles characterized by atomic force microscopy to determine three-dimensional shape and surface roughness parameters [14].

Table III shows the impact of particle morphology on the surface area of metal powders produced by either water- or gas-atomization.

Table III. Variations in Metal Particle Surface Area Due to Morphology

Material	Particle Morphology	Particle Size, d_{50} (μm)	Surface Area (m^2/g)	Reference
SS 316L	Irregular	15.1	0.573	Jamaludin [15]
	Spherical	19.5	0.144	
	Irregular	35.5	0.087	Hedberg [16]
	Spherical	21.4	0.069	
17-4PH	Irregular	19.3	0.22	Hausnerova [3]
	Spherical	20.0	0.15	

For routine analyses, gas adsorption is therefore an excellent way to conduct true three-dimensional, bulk morphological analysis much more efficiently and precisely than other methods. When investigating specific morphology issues, it is then useful to couple this with microscopic analyses.

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