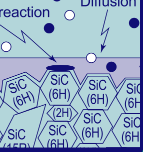

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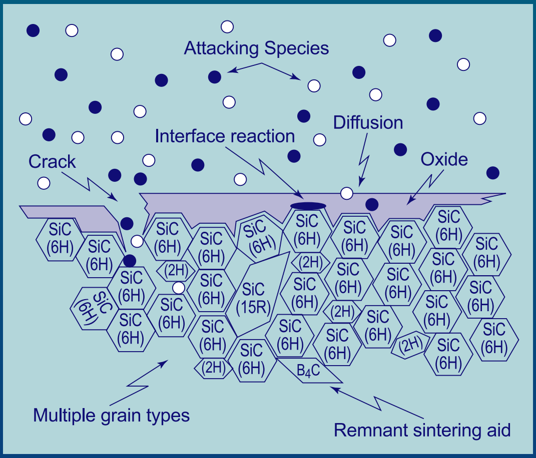

Ronald G. Munro

National Institute of Standards and Technology
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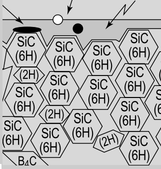
960-11

On the Cover:

Schematic of a silicon carbide ceramic in an active atmosphere. Data evaluation must account for the complexity of polycrystalline materials and the resulting dependence of material properties on chemical composition, physical microstructure, and environmental conditions.



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Data Evaluation Theory and Practice for Materials Properties

Ronald G. Munro

Materials Science and
Engineering Laboratory

June 2003

U.S. Department of Commerce
Donald L. Evans, Secretary

Technology Administration
Phillip J. Bond, Under Secretary for Technology

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FOREWORD

Data evaluation is the process by which collections of data are assessed with respect to reliability, completeness, and consistency. The present work addresses data evaluation for materials properties as a scientific discipline that evolves from the formal underpinnings of materials metrology. A theoretical foundation for data evaluation is developed and then illustrated in a practical application to the development of an operational protocol for materials property data. An extensive collection of examples is used to examine, in succession, the issues of accessibility, reproducibility, consistency, and predictability. Distinctions are made among definitive relations, correlations, derived and semiempirical relations, heuristic theories, and value estimates. Subtopics include the use of properties as parameters in models, the interpretation of *ad hoc* parameters, and the treatments of procedural properties, response dependent properties, and system dependent data.

More information on the SP 960 series can be found on the Internet at **http://www.nist.gov/practiceguides**. This website includes a complete list of NIST Practice Guides and ordering information.

ACKNOWLEDGMENTS

The collective understanding of the importance of data evaluation, particularly with respect to the use of materials property relations, has evolved significantly during the last decade. The author is especially mindful of the benefits derived during that time from numerous interactions with colleagues at NIST. A true list of the names of all the individuals who have been kind to me in this effort would, perhaps, comprise a veritable staff directory. At the risk of being accused of a certain lack of perspicacity, I would like to acknowledge explicitly a few of those people whose shared wisdom has been repeatedly useful to me: S. Block, S. Dapkunas, S. Freiman, S. Hsu, G. Piermarini, G. Quinn, J. Rumble, Jr., L. Smith, and J. Wachtman, Jr.

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SYMBOLS AND NOTATIONS

α_L	linear coefficient of thermal expansion
$\alpha_{c,L}$	cumulative linear coefficient of thermal expansion
α_V	volumetric coefficient of thermal expansion
$\alpha_{c,V}$	cumulative volumetric coefficient of thermal expansion
a	lattice parameter
A	fitting parameter

b	lattice parameter
B	bulk modulus
B_o	bulk modulus at zero porosity
B_T	isothermal bulk modulus

c	lattice parameter
c_x	crack extension, length
C_P	specific heat, at constant pressure [J kg^{-1} K^{-1}]
C_V	specific heat, at constant volume [J kg^{-1} K^{-1}]
$C^{(\mathrm{M})}{}_P$	molar heat capacity, at constant pressure [J mol^{-1} K^{-1}]

d	linear dimension of indenter's impression
D	thermal diffusivity
D_s	sliding distance

ϵ	strain, fractional elongation
E	elastic modulus, Young's modulus
E_R	Reuss approximation for the elastic modulus
E_V	Voigt approximation for the elastic modulus

$\boldsymbol{f}_\mathrm{indent}$	force vector for indentation
F	normal force, load
$\mathfrak{F}$	general purpose function

γ	shear strain
g	grain size
G	shear modulus
$\hbar$	Planck's constant divided by 2π, $1.05457266(63) \times 10^{-34}$ J s
H	hardness
κ	thermal conductivity
k_B	Boltzmann's constant, $1.380658(12) \times 10^{-23}$ J K^{-1}
K_{Ic}	critical stress intensity factor, fracture toughness
K_W	wear coefficient
$\varkappa$	Palmqvist crack coefficient, 0.018 ± 0.004
Λ_1, Λ_2	general purpose constants, fitting parameters
L	length
μ_i	mass fraction of component i, $\mu_i = m_i/M$
m	Norton model, grain size exponent
m	Weibull model, Weibull modulus
m_i	mass of component or particle number i
M	mass or total mass, $M = m_1 + m_2 + \ldots$
M_W	molar mass, *e.g.*, 100 g/mol
η	Meyer law exponent
ν	Poisson's ratio
n	fitting parameter, stress exponent, Norton model
$n(\mathbf{r})$	flaw density
N_a	number of atoms
N_A	Avogadro's number, $6.0221367(36) \times 10^{23}$ mol^{-1}
N_f	number of flaw sites

π	ratio of the circumference of a circle to the diameter of the circle, 3.141592653...
p	exponent, attractive term of Φ_{ij}
P	pressure
$\mathcal{P}$	probability function
q	exponent, repulsive term of Φ_{ij}
Q	apparent activation energy
ρ	density
ρ_{theo}	maximum theoretical density
r_{ij}	distance between ion number i and ion number j
R	molar gas constant, 8.31451(7) J mol^{-1} K^{-1}
σ	stress, force per unit area
$\overline{\sigma}$	mean fracture strength
σ_o	Weibull characteristic strength
Θ	Debye temperature
τ	shear stress
t	time
T	absolute temperature [K]
T_c	critical temperature
ϕ	volume fraction of porosity
Φ	total potential energy function
Φ_{ij}	pairwise potential energy function
$\Phi(\sigma)$	unimodal probability stress function, $\Phi(\sigma) = \ln(1 - \mathcal{P})$

$\mho_i$	volume fraction of component number i; $\mho_i = V_i/V$
v_L	velocity of sound, longitudinal mode
v_m	velocity of sound, mean, $([v_L^{-3} + 2v_S^{-3}]/3)^{-1/3}$
v_S	velocity of sound, shear mode
V	volume
V_o	volume at zero porosity
V_p	volume of pores
ω_D	Debye cutoff frequency
W	work, energy
χ	renormalization scale factor
ψ	cavitation model stress coefficient
ψ_1, ψ_2	coefficients, attractive and repulsive terms of Φ_{ij}
Y	linear fracture mechanics coefficient (dimensionless numeric factor)
ζ	Meyer law coefficient
z	number of formula units in a unit cell
ς	median crack coefficient, 0.016 ± 0.004

1. INTRODUCTION

The departure of a physical property from its expected behavior can be a cause for scientific discovery if the departure occurs in a research exercise. The same departure occurring in an engineering design can be ruinous. In the former case, the departure is a novelty that may be the result of a previous lack of comprehension or a previous insufficiency in the available data. In the latter case, the departure is a failure that may be the result of a lack of reliability or a lack of sufficient investigation of the data. In each case, the pivotal issue underlying the conclusion is an assessment of the data.

Ascertaining the credibility of data is the function of data evaluation.

Whether the application is scientific discovery or engineering design, what we know about the data has a direct influence on our perception of the results and the interpretation of the data. In every case, the determining issue is one of confidence. An extraordinary observation must be reconciled with our previous experience, while routine observations may need to be brought into conformity with common knowledge and known constraints, such as a trend that should be followed by the data. In both application domains, whether explicitly or implicitly, data evaluation is fundamental to our acceptance of observations and technical designs.

The same conclusion follows if we consider this issue in the context of theory and experiment. For theory, the challenge is to mold principles into conformity with observations. If the observations are deficient or lacking in any manner, the efforts to develop theoretical models may be highly frustrated. Conversely, for experiment, the challenge is to make observations accurately and without bias. If the measurement principles are unfounded, efforts to elucidate the understanding of material behavior may be highly illusive. More subtly, if measurements are undertaken to confirm a theory, the resulting observations may be prejudicial *a priori*.

Data evaluation, as a discipline, uses the fundamental principles of theory and the practical observations of experiment as complementary exercises to ensure that data compilations reflect the best understanding currently available for the given subject matter. The end result of this discipline is an assurance of the harmonization of theory and experiment, and, by extension, of science and engineering.

1.1 A National Priority

Early recognition of the national importance of materials property data began to emerge from studies[1–3] on the availability of property data for metallic systems and on the economic effects resulting from the corrosion of metallic structures. Subsequently, national attention to the broader issues of materials property data acquired a sharper focus when the National Materials Advisory Board of the National Academy of Science issued a report[4] tailored to that purpose. That report cited materials information as a critical national need. Further studies on the economic effects of fracture[5] and the status of materials property databases[6] emphasized how pervasive the need for property data had become. Recognition of the growing urgency of this need was echoed[7] by the Director of the National Bureau of Standards who cited the need for materials data as a national priority. It was not long thereafter that several national and international studies on the status, issues, and concerns regarding materials property databases followed.[8–13] Among those studies were numerous discussions on the logical design of databases[14] and their practical development.[15–21] So thorough were those discussions that the mechanical aspects of constructing a database need not be discussed further in the present work. Indeed, ample discussion of that task has been well documented by the American Society for Testing and Materials (ASTM). During the years from 1986 to 2000, ASTM Committee E-49 conducted extensive deliberations and held five international conferences[15–19] to debate and resolve the issues specifically associated with the computerization of materials databases. Much of that work was summarized in two documents, one being a collection of ASTM standards[20] and the other being a manual[21] about constructing a database. Especially noteworthy in the present context is a review[22] of the nomenclature and contextual significance often associated with data evaluation.

1.2 Overview and Scope

The complexities of advanced materials and their designed applications pose a difficult problem for practitioners of science and engineering alike. The degree of specialization required to comprehend every measurement nuance pertaining to a reported property value often exceeds the breadth of knowledge of the general practitioner. Consequently, the practitioner must rely on recommended values or must apply other assessment guidelines.

This treatise is directed towards the vast segment of technology whose scientists and engineers must use materials property data, at least on occasion, without the benefit of direct measurement or other assessment experience. The intent is to provide a thoughtful and systematic approach towards establishing confidence in numeric materials properties. Throughout the work, it will be found that this particular interest is addressed in a manner that evolves into one basic theme. Stated with perhaps some oversimplification, it is that our confidence is high when the data are sensible.

In spite of the pervasive significance of reliable data, there are relatively few dedicated and sustained efforts to compile and disseminate fully evaluated materials property data. The scope of such an undertaking is usually too broad for commercial enterprises that necessarily are focused on the requirements of their products and too diffuse for national programs whose priorities must be focused on transient critical issues. Most database efforts, therefore, tend to be necessarily delimited to a small, but well-defined, scope. Superficially, these delimited efforts may appear to be quite unrelated. Yet, as diverse as these efforts might be, all of the efforts are confronted with numerous common issues that must be addressed in the course of their respective developments. This treatise takes the view that the solutions to the common issues derive from a small number of underlying principles that may be developed generically and applied systematically.

It will be seen that among these unifying principles are concepts that largely have been ignored or unrecognized in the progressive evolution of materials science. A greater understanding of the mutual relations among properties, or of the controversies surrounding the lack of expected relations, is gained by acknowledging these principles.

Consequently, two chapters are devoted to formal considerations: one on materials metrology in general, and one on data evaluation *per se*. Subsequent chapters illustrate the principles by means of practical applications, each chosen to represent a different aspect of data evaluation. In each chapter, the discussion is presented in a manner that reflects a logical evolution of the concepts, proceeding from the clearest, most well-defined conditions and progressing to conditions that are less well defined.

All of the examples in this work are taken from actual exercises in materials property data evaluation. These examples are meant to be merely illustrative. In an undertaking as vast as data evaluation, no pretense to an exhaustive dissertation would be supportable. It is hoped, however, that the principles and practices set forth in this work will guide and sustain a productive application of data evaluation across many disciplines wherein considerations of numeric property data are crucial to the interpretation and application of quantitative observations.

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2. Formal Materials Metrology[1]

It is, perhaps, profoundly obvious that measurement processes have been an integral part of every civilization, whether primitive or advanced, and, thus, that every civilization has, in some way, felt the impact of metrology. If we understand "materials metrology" to mean the science of measurement applied to the characterization, understanding, and development of materials, then this derivative of metrology will be seen to be nearly as ancient as metrology itself. Yet, upon careful examination and in spite of their common ancestry, it will be found that there remains an intellectual chasm separating these two disciplines. We explore that issue in the present section and present a resolution of the last intellectual disparity between conventional metrology and materials metrology.

It is easy to imagine our earliest ancestors marveling at the shapes and colors of rocks, assessing the advantages of their sizes and weights, or recognizing that softer materials could be used for different purposes than harder materials. Modern materials metrology differs in essence from those crude beginnings by the deliberate attempt to understand the nature of the materials and to use that understanding to improve their characteristics or to develop entirely new materials.

We may also note that the rapid pace of technological innovation and the sometimes alarming rate of consumption of natural resources create unprecedented demands to use materials more wisely, more effectively, and more strategically. Concurrently, while the world remains divided into distinct geographical areas, each with its own sovereignty, there is a *de facto* unity among nations resulting from instantaneous communications, short transit times, and global economies. Because of that technological unity, there is a common need and an obligation to pursue advances in materials metrology in a coordinated international effort.

Fortunately, there has been a natural evolution of just such an international effort propelled principally by standards organizations. While each country must acknowledge responsibility for its own standards, economies and the well beings of nations suffer when those standards are not compatible with

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[1] This chapter is based on an internal study, "Taxonomy of Materials Metrology," prepared by the author at the request of Dr. Leslie Smith, Director, Materials Science and Engineering Laboratory, as part of a strategic planning exercise for MSEL. As such, the author has had the benefit of comments from L. Smith, D. Hall, K. Jewett, S. Freiman, E. Amis, C. Handwerker, F. Fickett, M. Rowe, S. Dapkunas, J. Tesk, G. Quinn, T. Siewert, C. Ehrlich, and B. Taylor.

the prevailing markets. Consequently, numerous international organizations have been established specifically to promote the harmonization of standards, and there already exists a rich history of standardization activities.

The most significant agreement promoting international standards was the *Convention du Mètre*[1] which was signed in 1875. This treaty established the *Conférence Générale des Poids et Mesures* (CGPM), composed of representatives from the member states, to provide general oversight for the international efforts. The CGPM, meeting approximately every four years, elects the members of the *Comité International des Poids et Mesures* (CIPM) which, in its turn, provides supervision for the *Bureau International des Poids et Mesures* (BIPM).[2] Together, these interrelated organizations diligently coordinate the development and maintenance of the basic units of weights and measures, which form what we may refer to as conventional metrology. An additional organization, the *International Organization for Standardization* (ISO),[3] aggressively promotes the harmonization of measurement standards relating to all facets of physics, chemistry, and materials. Other organizations, such as the *International Union of Pure and Applied Chemistry* (IUPAC)[4] and the *International Union of Pure and Applied Physics* (IUPAP),[5] also support and promote standardization. In addition to those efforts, the *Versailles Project on Advanced Materials and Standards* (VAMAS)[6] actively conducts prestandardization research, in the form of international round robins, as a preliminary step towards the subsequent development of new standards in support of advanced materials and related high technology products.

Central to the success of all of these efforts is agreement on the meanings of basic terms commonly used in all aspects of measurement science. This important issue was addressed by seven independent international organizations including BIPM, IEC (*International Electrotechnical Commission*), IFCC (*International Federation of Clinical Chemistry*), ISO, IUPAC, IUPAP, and OIML (*Organisation Internationale de Métrologie Légale*). The product of this cooperative venture was the *Vocabulaire International des Termes Fondamentaux and Généraux de Métrologie* (VIM).[7]

Remarkably, it appears that no organization has undertaken the task of formally applying and extending the VIM to materials metrology. We address this task in the present work and, in the process, develop a taxonomy for materials metrology that is consistent and compatible with the VIM.

2.1 Fundamentals

Metrology, like all scientific endeavors, is a paradigm that is built upon a foundation of concise definitions of basic terms and rational relations among derived quantities. The specialization to materials metrology should be no less concise, and of course, much of what is required is achieved instantly by adopting the VIM in its entirety. Consequently, we need to focus only on those terms not treated by conventional metrology, *i.e.*, not currently addressed in the VIM.

It is most appropriate that we begin with a definition of materials metrology since no speciation of metrology is considered in the VIM. The rules of English language simply imply that materials metrology means metrology with respect to materials. However, this interpretation is not very enlightening. We suggest the following two terms to provide a more appropriate definition of the scope of this discipline.

> *Material*: An assemblage of matter delimited in space.
>
> *Materials Metrology*: The science of measurement applied to the characterization, understanding, and development of materials.

The latter definition acknowledges not only the role of measurement science, but also that measurements on materials may be subservient to specific purposes. The role of "purpose" is therefore very important for materials and implies that the intended purpose may influence the specification of the measurement standard.

The notion that measurements may be used to characterize a material is critical to materials metrology and leads to the equally critical definition of a material property.

> *Material Property*: A quantifiable response of a material to an externally applied stimulus.

This definition recognizes that the role of a property is to gauge how a material interacts with its environment and implies that there is some process by which a number can be assigned to the response that the material makes to the external stimulus. It is the process of assigning a number that begins to form the link between materials metrology and conventional metrology. It should be noticed most particularly that the definition of a material property is distinct from the definition of a measurable quantity.[2]

> (*Measurable*) *Quantity*: [VIM 1.1] An attribute of a phenomenon, body, or substance that may be distinguished qualitatively and determined quantitatively.

The critical aspect of this definition is that a measurable quantity is an attribute of the body. The dilemma that this definition poses for materials metrology is that there are important materials properties that are not attributes of the body. For example, one may recognize qualitatively that some materials are harder than others, but the technical material property called hardness is defined only when a procedure is specified, *i.e*., the process by which the number is assigned defines the property. Thus, Knoop hardness, Vickers hardness, and Rockwell hardness are different quantities. This situation may be contrasted with the measurement of a quantity called length. Different procedures for measuring a length may produce differing degrees of uncertainty in the value[8,9] assigned to the quantity, but the identity of the quantity is unchanged by the particular procedure. As a result of this conceptual difference, important material properties such as hardness, fracture toughness, three-point bend strength, four-point bend strength, and creep are inadmissible as measurable quantities!

To resolve this logical and practical dilemma, we must introduce a new term.

> *Procedural Quantity*: A quantity whose identity is determined concurrently as an attribute of a phenomenon, body, or substance and an attribute of a measurement procedure, and that may be distinguished qualitatively and determined quantitatively.

---

[2] Revision of the VIM is under consideration. It has been proposed that the term "measurable quantity" be replaced by a broader term, "quantity," which would accommodate any attribute to which more than one value (numeric or non-numeric) could be assigned. The revised term would be supplemented by an additional term, "kind of quantity," which would distinguish four types of quantities: nominal (*e.g*., non-numeric values such as gender = male or female), ordinal (distinguishable by order of magnitude), difference (*e.g*., gravitational potential), and ratio (*e.g*., relative atomic mass, formerly known as atomic weight). While this generalization is more inclusive than the current term, it does not resolve the logical dilemma encountered in materials metrology.

This new term preserves the scope of conventional metrology while encompassing all of the material properties that would otherwise be excluded from the formal realm of measurement science. Upon this term and those preceding it, we may build a formal taxonomy of materials metrology.

2.2 Taxonomy of Materials Metrology

It is clear from the preceding subsection that materials metrology may be divided into two parts consisting of measurable quantities and procedural quantities. The measurable quantities of conventional metrology obviously belong to the former part, while some material properties will be of the former type, and some of the latter. It will be convenient to introduce two additional terms to distinguish the material properties that belong to the two parts.

> *Inherent Material Property*: A material property that is a measurable quantity.
>
> *Procedural Material Property*: A material property that is a procedural quantity.

It will be convenient also to distinguish a special class of measurable quantities, called structures, that are of considerable importance to materials metrology. For example, an ideal, monatomic crystal consists of an assemblage of identical atoms whose equilibrium positions in space are distributed on a periodic lattice in which the positions are related by a well-defined group of symmetry operations. The volume of such a lattice may be subdivided into smaller volumes of identical shapes, called cells, any one of which may be used as a generator of the entire volume through the use of symmetry operations. The cell selected as the generator is called the unit cell, and the smallest such cell is called a primitive cell. The lengths of the principal axes of the unit cell, commonly denoted by the symbols a, b, and c, are measurable quantities. The set of lengths and the set of angles between the axes collectively comprise the lattice parameters. Further, the positions of the atoms within the unit cell may be determined and expressed relative to a, b, and c. The symmetry group, the lattice parameters, and the relative atomic coordinates of the atoms are taken together as the specification of the crystal structure. Thus crystal structure is a special construct used to characterize materials, and it is desirable, for both compatibility and convenience, to retain this special construct as a special class of measurable quantities.

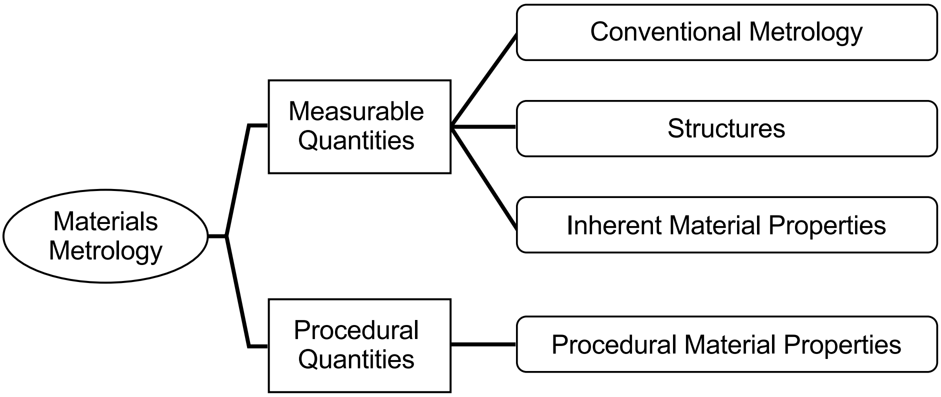

Figure 2.1. *Schematic of the taxonomy of materials metrology.*

The basic taxonomic scheme for materials metrology that evolves from these considerations is depicted graphically in Figure 2.1. This schema may be readily expanded into a full classification of all the measurements pertinent to materials metrology. Tables 2.1–2.4 illustrate how such a classification scheme can be developed from the taxonomy. In the present exercise, approximately 130 measurable and procedural quantities pertinent to materials science and engineering have been classified within the context of this new taxonomy for materials metrology.

Table 2.1: **Examples of Measurable Quantities of Conventional Metrology**

Category	**Quantities**
Base Quantities	length, mass, time, electrical current, temperature, amount of substance, luminous intensity
Derived Quantities	strain, area, volume, concentration, velocity, acceleration, force, pressure, stress, voltage, charge, capacitance, current density, resistance

Table 2.2: **Examples of Measurable Quantities of Structures in Materials Metrology**

Category	**Subcategory**	**Quantities**
Unit Structures	Crystallography	lattice parameters, atomic coordinates
	Noncrystallinity	radial distribution function
Microstructure	Grains and Pores	size distribution, mean size, aspect ratio, texture
	Dendrites	mean size, orientation, branch density
	Phase Equilibria	phase transition temperature, phase transition pressure, glass transition temperature, Curie temperature, Néel temperature, triple point temperature
	Interphase Region	thickness
	Magnetic Domains	mean size, aspect ratio, orientation
Surfaces	Topography	asperity mean size, aspect ratio, orientation; surface roughness; crack size, orientation, depth
	Films and Deposits	thickness
Electromagnetic	Charge Distribution	valence, ionicity, covalency, spin, space charge density

Table 2.3: **Examples of Measurable Quantities of Inherent Material Properties**

Category	**Subcategory**	**Quantities**
Mechanical	Elasticity	Young's modulus, shear modulus, bulk modulus, compressibility, Poisson's ratio, elasticity tensor, compliance tensor, sound velocity, Debye temperature
Thermal	Capacity	specific heat, Gruneisen parameter
	Transport	thermal conductivity, thermal diffusivity, emissivity, interfacial resistance
	Stability	thermal expansion, residual stress
Electromagnetic	Electricity	resistivity, conductivity, thermoelectric power, Hall coefficient, critical current density
	Magnetism	susceptibility, coercivity, critical field strength
	Optics	dielectric strength, index of refraction, permitivity, transmisivity, reflectivity, absorptivity

Table 2.4: **Examples of Procedural Quantities of Procedural Material Properties**

Category	Subcategory	Quantities
Mechanical	Plasticity	ductility, brittle to ductile transition point, hardness, creep rate, creep activation energy, creep stress exponent
	Strength	yield strength, proportional limit, tensile strength, flexural strength, shear strength, compressive strength, ultimate strength, fracture toughness, fracture energy, fatigue strength, Weibull modulus, Weibull characteristic strength
Thermal	Stability	flammability
Durability	Thermomechanical	thermal shock resistance
	Adhesion	adhesive strength
	Tribology	friction coefficient, wear rate, wear coefficient, lubricity, machining rate
Chemical Aging	Corrosion	corrosion rate, activation energy
	Hydration	hydration rate
	Interdiffusion	diffusion rate
Physical Aging	Delamination	delamination rate

There is a certain useful insight regarding measurement technology that evolves from this taxonomic view of materials metrology. In all applications of measurement science, the reproducibility of a measurement is unexceeded in importance by any other consideration and is accorded, therefore, the highest priority for measurement technology. This basic importance often leads to a vigorous effort to standardize the measurement procedure. It is not unusual in such efforts to consider alternate procedures or to compare different measures of the same quantity. When it happens that two measures of a quantity are significantly different, fairly intense discussions of the relative merits of the two measurements may ensue to excess.

Recognizing the distinction between measurable quantities and procedural quantities may help to alleviate some of the unproductive aspects of such debate. When the measures in question effectively pertain to procedural materials properties, the quantitative results may be significantly different, even though the individual measurements are highly reproducible with small measurement uncertainty. For procedural materials properties, it is not necessarily possible, even in principle, to resolve the differences of two such measurements, and expending resources trying to do so would be an unproductive and futile exercise.

In summary, it is important to remember that materials metrology is an extension, not a subset, of conventional metrology. The fundamentals of conventional metrology provide the essential basis on which is built the rational extension of measurement science that is tailored to the intricacies and technological necessities of materials science and engineering. Materials metrology extends that basis by including measurement aspects not immediately compatible with conventional metrology. The introduction of the notion of a procedural quantity as an element of measurement science, however, resolves the disparity and permits the discipline of materials metrology to be formally and logically consistent and compatible with conventional metrology.

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3. Formal Considerations in Data Evaluation

Data evaluation implies an imposition of criteria. The criteria set forth the conditions under which the data may be deemed "accepted." Obviously, the criteria depend on the purpose or function to be served by the data. Consequently, it should be understood readily that some circumstances require more stringent conditions than do others, and we should anticipate, therefore, an evaluation scheme that allows multiple acceptance categories with differing acceptance criteria.

Regardless of the number of acceptance categories, the end result of data evaluation is that a set of data is either accepted or it is not accepted. Data that are not accepted fail to satisfy the criteria of any allowed acceptance category. All such data may be placed together in an additional category labeled simply "unacceptable."

The classification "unacceptable" is conclusive and is meant to result in the immediate exclusion of the data from the database. In this case, the criteria must reveal a significant deficiency in the data or its associated metadata to such an extent that there is no perceived application of the data, in the context of the given database, for which this data would be useful. In this respect, note that "unacceptable" does not convey a connotation of "wrong."

> *Example*: Suppose a paper contains a report on the hardness of two materials and that the report consists only of the statement, "The hardness value of material A was 31, and for material B it was 17, each with an extended measurement uncertainty of 1 using a coverage factor, $k = 2$." We might well understand from these values that material A was harder than material B, and if that circumstance is relevant to our purpose, we might wish to include this information as supplementary metadata. However, from this report, we do not know what measure of hardness was used, and we do not know what unit was associated with the numeric value. Consequently, the reported values would be considered "unacceptable" as independent entries in the database because they are independently uninterpretable.

Data that are not "unacceptable" are syntactically "acceptable;" *i.e.*, the data satisfy the criteria of some allowed acceptance category. As a practical matter, if we use a label to identify the separately allowed categories, then we may interpret the label as a data quality indicator. In the present work, we call that indicator the data evaluation level.

For the purposes of this discussion, we shall assume that there are multiple (two or more) acceptance categories and that no two categories are identical. While the categories are required to be distinct, we may anticipate that there will be both similarities and differences between any two sets of criteria from any two acceptance categories; *i.e.*, some of the criteria may be the same, while at least one criterion must be different. To consider how these similarities and differences are manifest in the decision process, let us focus on the application of a single criterion.

When any individual criterion is applied to the data set, the result is that the criterion is either satisfied or it is not satisfied. Consequently, we may represent any criterion as a mathematical operator which returns one of two allowed outcomes when it is applied to the data set. It is convenient to represent the allowed outcomes by the numeric values 1 and 0. We may choose 1 as the outcome when the criterion is satisfied, and 0 as the outcome otherwise. If we now form an ordered collection of all distinct criteria from all of the acceptance categories, then each acceptance category may be represented as an ordered n-tuple of 1s and 0s. By construction, no two of the category n-tuples are identical. Application of the ordered collection of distinct criteria to a given set of data then yields a response, the data evaluation n-tuple, which may be compared to the category n-tuples. A matching category n-tuple uniquely determines the data evaluation category for that set. If there is no matching category n-tuple, the data set is unacceptable.

Automation of this evaluation scheme might not be possible for all types of criteria because it is sometimes very useful to have criteria that are subjective and require judgmental responses. In such cases, it may be advantageous to consider an equivalent alternative approach in the form of a deductive, hierarchal protocol. We have seen in the preceding formal considerations that each criterion has only two responses and, thus, may be viewed as a simple binary filter. In this view, the admission of a set of data to a particular acceptance category can be viewed as the successful passage of the data through a sequence of these filters. If at any filter the criterion is not satisfied, the data set would be passed to a different filtering sequence. Thus, the evaluation protocol would appear as a collection of linear chains of filters interconnected *via* branches to alternate chains. This collection of branching chains is a classical model for a decision tree.

To construct a decision tree representing the evaluation process, we need to consider the nature of the individual filters. With respect to the qualitative outcomes of the filters, there must be a set of allowed terminal outcomes, *i.e.*, decisions which cause the decision process to terminate. If a filter operation yields any other outcome, the decision process continues. Topologically, therefore, we need to consider only three types of binary filters: decisive (doubly terminating), semi-decisive (singly terminating), and branching (non-terminating). When a filter has a decisive outcome, the decision process is complete. Thus, a decisive filter terminates the chain no matter which outcome of that filter occurs. A semi-decisive filter may either terminate the chain or extend the chain to another filter. A branching filter represents a bifurcation point in the tree and causes the initial chain to divide and extend into two different branches.

Using only these three types of filters, it is possible to attain a complete implementation of a decision tree for data evaluation. In the following two sections, we will develop a rationale for the criteria that may be used in the design of such filters, and then we will construct a practical illustration of a decision tree for materials properties.

4. Data Evaluation Levels for Materials Properties

There is no fundamental necessity to have more than one acceptance category for data evaluation. However, convenience and the desire for a logical, orderly classification scheme often dictate or, at least, favor the decision to use multiple categories. Once that somewhat arbitrary choice is accepted, an equally arbitrary task, choosing what categories should be used, follows. Although this subsequent task is also arbitrary, we can cast it into a fairly reasonable approach if we let the categories be determined by the objectives served by the data system. We explore that approach in this section by explicitly constructing a rational set of acceptance categories for a materials property database used as a general reference system.[1]

We must begin by detailing a working model of the reference system. For the present purposes, we assume that the reference system consists of data extracted from published technical papers. In this case, the heritage of the data, from laboratory to database, may be relevant to the context in which we accept the data. In most cases, the relevant history begins with the production or procurement of a material and the measurement apparatus. Subsequently, specimens for testing are prepared, instrumental and environmental parameters are set, and measurements are made. After collecting and processing or analyzing the raw data, a report is written describing the measurements and the results. The report may be sent to a project sponsor, a conference, or a journal, and after being reviewed, the paper is published in the appropriate medium.

Several natural considerations evolve from this basic scenario. Perhaps the most insightful cursory observation regards the nature of the project. Was the project conducted as a normal or regular research effort, or was the project distinguished in some manner? For example, a project in an established standards setting laboratory whose goal is to provide a reference material for material property measurements might well be considered special. The rigorous requirements established for such efforts are usually fully described and documented, and the property values usually are certified in some explicit manner by the measuring laboratory.[2] Given the important role of reference materials in measurement calibration, ***certified*** values have a *de facto* acceptance in the user community and warrant a special category.

A project may also be distinguished by measurements at the forefront of the technology. In this case, the material or experiment may represent an innovative achievement that is being reported for the first time. The results might even be considered preliminary or tentative, but the desirability of the results imparts sufficient urgency to their announcement that including those values in the database would be welcomed. We might generally think of such works as ***research in progress***. A category by this name might serve to alert the user to both the currency of the results and the possibly tentative nature of the values.

A third category that follows rather naturally from the circumstances of the measurements is that of ***commercial*** data. It is usually in the best interest of materials producers to inform their clientele about their products. Consequently, commercial manufacturers of materials usually take great care to provide property data on the principal characteristics. The view often taken is that these data serve as a guide to the useful application of the material. In this respect, the manufacturer may indicate that the reported values are typical of results obtained using specimens from several production batches of the material. As such, the manufacturer may present the property values in a tabular format providing nominal information about the measurement conditions. It is not unusual for those values to be propagated into the technical literature by users who report the values in subsequent publications, usually without further discussion or assessment.

The largest sustained effort to report materials properties arises collectively from the broad spectrum of independent materials research programs that are dedicated to characterizing, understanding, and improving materials of all types. The laboratory conducting the measurements usually has invested a considerable amount of its resources to acquire, develop, or refine the measurement apparatus, and the personnel in these efforts often have acquired a notable amount of experience and expertise in the measurement technique. These efforts, consequently, tend to focus on the one or two characteristics or properties of the material that pertain to the laboratory’s area of capability and expertise. Reports issued by such programs tend to follow what might be called the classical research protocol. After a general introduction describing the background and current objectives for the work, both the material and the measurement technique are discussed in rather precise detail. The guideline commonly used in this portion of the report is that enough detail should be reported that any other reasonably experienced research team, comparably equipped, could reproduce the experiment. Only when this degree of detail and qualification has been achieved can the reader proceed to knowledgeably address the results, analysis, and discussion of the measurements. Research conducted and reported in this manner serves as the figurative bedrock of evaluated databases. In recognition of that fundamental role, data confirmed to be of this type might well be categorized as ***qualified*** data.

An important characteristic of the category of qualified data is that results from many laboratories are determined and reported independently. However, it is sometimes desirable to have an overview of how a property varies over a range of conditions or over a range of materials. A common method used to construct the overview is to review the literature for similar studies and to combine the results. In this manner, ranges of observed values, differentiated by general material or measurement conditions, can be identified. It is often possible to designate a value that is typical of the material or property in the context of some noted condition. ***Typical*** values derived from literature surveys are generally only representative of the trend of observed values and are not necessarily appropriate for any particular specimen. The utility of typical values is, firstly, that useful order of magnitude estimates typical of a material class sometimes can be made and, secondly, that functional trends, such as power laws or dependance on a type of chemical dopant, may be identified.

Table 4.1: **Data Evaluation Levels**

Designation	**Comment**
Certified	Standard reference values, specific to known production batches
Validated	Confirmed via correlations and models
Qualified	Basic acceptance criteria satisfied
Commercial	Manufacturer’s data for specific commercial materials
Typical	Derived from surveys of nominally similar materials
Research	Preliminary values from work in progress
Unevaluated	All other data

Collections of both qualified data and literature surveys also form the basis of more in-depth analyses leading to the establishment of reliable models or correlations among properties. Subsequently, these models and correlations may be applied to determine optimized or refined estimates of property values for specific materials, thereby enhancing the reliability of evaluated data. Data ***validated*** in this manner are distinguished by their mutual consistency with other properties for the same material.

Other data, that cannot be validated, qualified, or otherwise documented with respect to the measurements that were conducted, can still serve a useful and desirable purpose as supplementary information providing a relevant context for other properties. For example, it is not unusual for density to be reported with no indication of how the density was measured or even with no indication of the origin of the reported value. In this case, the data are not amenable to any useful assessment. Nevertheless, these data often are essential for understanding the context of other property measurements contained in the same report. Consequently, it is desirable to have a category for ***unevaluated*** data to permit the recording of contextual information while clearly indicating that the reported values cannot be assessed in any manner.

Clearly, other categories may be defined according to the special interests served by the database. The present reasoning, by design, considers relatively generic categories and allows the data contained in a materials property database to be organized or classified into seven distinct categories, summarized in Table 4.1. The derivation of this classification scheme, again by design, uses only generic considerations to distinguish the data entries and does not depend on any restriction to a particular material class. Hence, the classification scheme of Table 4.1 is applicable to any type of material, whether the general class be ceramic, metallic, polymeric, or biomaterial.

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5. Operational Protocol

Compilations of data always are plagued by one overriding concern: are the values credible? This concern most commonly is focused on whether or not the values may be used reliably. This particular focus emphasizes the intrinsic worth of data evaluation and argues for an evaluation procedure that is conducted with the utmost care and consistency. More emphatically, the critical role of data in advanced technologies demands that the quality of the data be of the highest caliber.

The foremost consequence of such considerations is that reliability must be accorded the highest priority in the assessment criteria applied to the data.

However, it must be recognized that data comprise a remarkably expensive commodity. The costs incurred by the need for suitable equipment, measurement standards, materials, and expertise extend far beyond the immediate funds expended to measure a particular set of data, and the latter expenditure can be significant by itself. The evaluation process, therefore, should consider all data as being potentially useful and should discard data only with the greatest reluctance.

Consequently, at the base of the data evaluation paradigm, there are two counterbalancing mandates: (1) ensure the reliability of the data; and (2) do not reject data without cause.

These mandates can be made an integral part of the decision logic applied to the evaluation of data. Using the data evaluation levels discussed in the preceding chapter, we present here a suitable protocol for assessing materials property data.

5.1 General Considerations

Perhaps the most widely observed and practiced method of demonstrating the credibility of experimental data is to establish reproducible results, *i.e.* the mutual agreement among independent studies. We may think of this notion of reproducibility as a one-dimensional assessment of the data because it focuses on the replication of a single observation.

Higher-dimensional assessments, yielding correspondingly higher levels of confidence, may be constructed using correlations with other measurements and theoretical models. In this approach, multiple independent observations of related properties are used together to assess the reliability of any one of them. Since each property represents a different measurement perspective, a higher level of confidence may be ascribed to these data collectively, owing to the consistency of the observations across the multiple properties, than could be ascribed to any one of the properties individually.

Such considerations illustrate the general themes of independence, replication, and multiplicity that form the underpinnings of data evaluation. These themes are also fundamental to the development of a data evaluation protocol.

5.2 A Protocol for Materials Property Data

The evaluation protocol[1] developed for the NIST Structural Ceramics Database (SCD)[2] and the High Temperature Superconductors (HTS)[3] database is shown schematically in Figures 5.1 to 5.4. This protocol adheres to the procedure discussed in Chapter 3 and uses the data evaluation levels listed in Table 4.1 in Chapter 4. In the present section, a brief commentary is given to illustrate how each node in the decision process contributes to the assessment of the data.

5.2.1 Material Specification

Question: *Is the material specification or identification sufficient for the purpose?*

The first consideration stems from the understanding that materials properties are of no value without some identification of the material. It follows rather simply from this observation that we should establish what is known about the material at the very beginning of the hierarchy of evaluation criteria.

Specific guidelines for identifying materials and for determining the adequacy of the identification have been discussed extensively by the ASTM.[4] The ASTM scheme recommends the use of seven distinct categories of identification information plus a general category for supplementary information. These categories distinguish among primary identifiers (*e.g.*, material class), widely recognized specification codes (*e.g.*, M-52 steel), characterization of the material (*e.g.*, in terms of its chemical composition), the source of the material and its processing history, geometrical details for the specimens used in the measurements, and any fabrication treatments (*e.g.*, heat treatments) and service history experienced by the specimen used in the measurements.

However, we need to recognize that the adequacy of the material identification can be interpreted either broadly or narrowly, depending on the purpose of the data. For most property data, a basic objective of

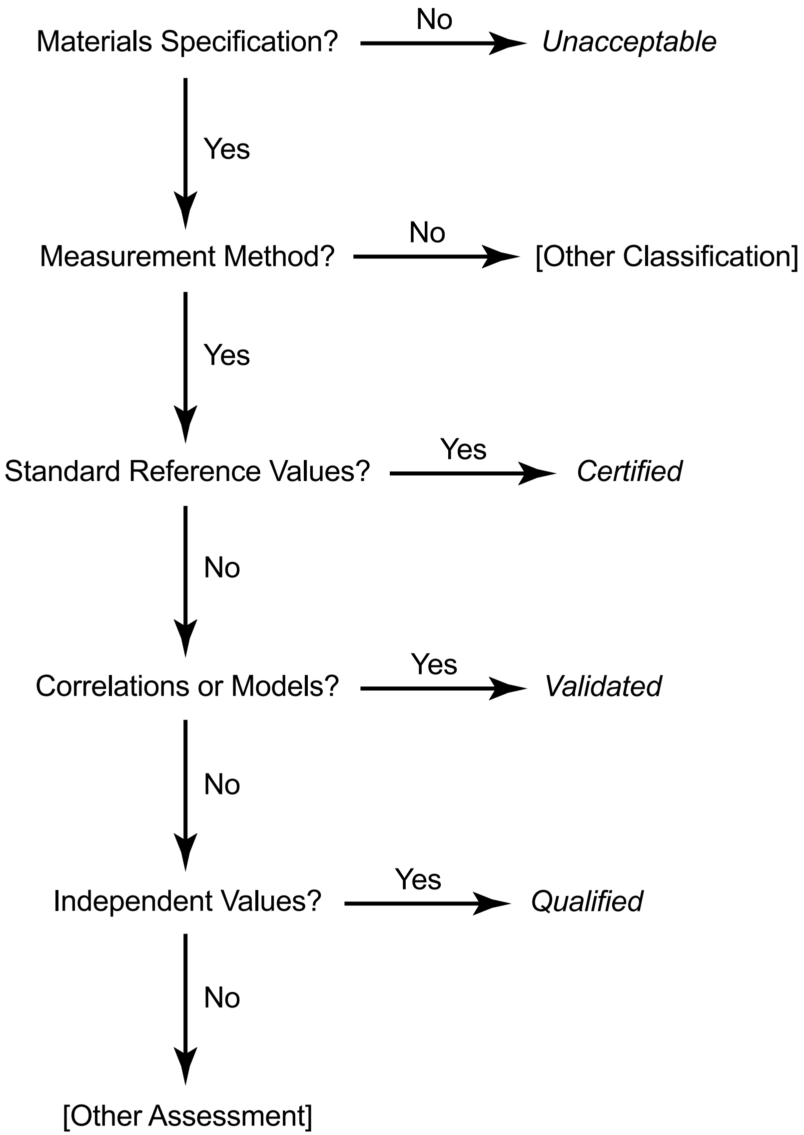

Figure 5.1. *Schematic of the basic data evaluation procedure. The node labeled [Other Assessment] is expanded in Figures 5.2 and 5.3; [Other Classification] is expanded in Figure 5.4. The data evaluation levels given in the italic font are described in Table 4.1.*

material identification is to present sufficient information that someone working independently of the original research would be able to prepare or obtain a similar specimen. However, not all sets of data are meant to pertain to specific materials. Surveys, for example, commonly present only typical values or ranges of typical values; merely identifying a class or subclass of material might be adequate for that purpose.

Consequently, the first question in the protocol, while simple and direct, should be addressed in the context of both the purpose of the data set and the extent to which identifying information has been provided. In all cases, a negative answer to this first question obviates any need for further consideration.

5.2.2 Measurement Method

Question: *Is the description of the measurement method sufficient?*

A basic objective in describing a measurement method is to present sufficient information that someone working independently would be able to conduct a comparable measurement. For purposes of comparability, it must be noted that all measurement techniques have associated measurement uncertainties, and all techniques have limited ranges within which they may be usefully applied. It is possible for a measurement technique to be developed for a particular class or subclass of material, sometimes exploiting a characteristic that is not available in other material classes. Further, the measured values of procedural properties (see Chapter 2) depend (often explicitly) on the specific procedures that are followed in conducting the measurement.

A case in point is the difference between a Vickers hardness and a Knoop hardness. The two methods provide measures of hardness that are fairly similar in the mechanical steps. Each method uses an indenter under normal loading to create an impression in the surface of the material. The ratio of the applied force and the area of the remnant impression yields a measure of the hardness of the material. These two measures of hardness, however, are necessarily different because: (1) the indenters used by the two methods have different shapes; and (2) one technique uses the actual surface area of the impression, while the other uses the projected surface area.

There is rarely, if ever, a good excuse for not identifying a measurement technique, but such is often the case when supplementary data are reported. It is not uncommon, for example, for the density of a specimen to be reported only summarily, such as: “The density was 3.21 g/cm^3.”

Such supplementary data may be critical to understanding or using other property data in the same report. Consequently, lack of information about the measurement procedure is not automatically sufficient to cause a set of data to be unacceptable. This assessment protocol considers other data evaluation levels when the measurement method is not described sufficiently.

5.2.3 Certified Reference Values

Question: *Does the set of data consist of certified reference values?*

Certified reference values generally are established by a recognized national standards measurement laboratory.[5] A certified reference value usually is a property value for a specific batch of a material. The material usually is designated as a standard reference material on which homogeneity and other quality assurance tests have been conducted. Commonly, more than one measurement method is used to determine the property value. The certified value is determined statistically and reported with an analysis of the associated measurement uncertainty.

5.2.4 Correlations or Models

Question: *Are the reported values consistent with or confirmed by correlations with other properties or model calculations?*

A material property may be known to be well described by a model or may have well-established relations with other properties. For example, the oxygen content in the high temperature superconductor Y:123 in the orthorhombic crystal structure is known to be correlated to the c-axis lattice parameter. In such cases, it may be possible to confirm the measured values by means of the correlations, if the correlated property data also are available, or by means of the established model calculations.

5.2.5 Independent Values

Question: *Do the current values agree with other values reported independently for the same property and material?*

Reproducibility is perhaps the most reassuring evidence that a proper value has been determined for a property. Values are considered reproducible when independent measurements are conducted and the resulting measured values are found to agree within a reasonable measurement uncertainty.

5.2.6 Related Properties (with adequate measurement information)

Question: *Are the current values consistent with values estimated independently using known related properties of the same material?*

It often happens that a material property has a theoretical relation to one or more other properties that can be determined independently. For example, the elastic (Young's) modulus, the shear modulus, the bulk modulus, and Poisson's ratio are often used to characterize the elasticity of isotropic materials. However, for isotropic materials, only two of these quantities are independent. Given any two of the elastic properties, the others may be calculated. Consequently, if the elastic modulus is reported in one paper, the shear modulus in a second paper, and Poisson's ratio in a third paper, it is possible theoretically to verify the mutual consistency of these values within the bounds of the appropriate measurement uncertainty.

5.2.7 Peer Review

Question: *Was the report published under independent peer review?*

Journals and other publications usually take great care to ensure that papers undergo independent review by at least one person who is considered knowledgeable in the subject area. In such cases, it is assumed that the reported values are reasonable within the experience of the reviewer. The specific rationale used by the reviewer usually is unknown. However, it may be assumed that no substantial objection to the paper was established and, more importantly, that at least some merit was found to support its publication.

5.2.8 Incompatible Properties

Question: *Is there any apparent conflict between the present data and other properties or trends that have been reported for this material?*

When no direct confirmation of a property value is available, it is desirable to verify that the present result is not incompatible with the general knowledge base for this material or this type of material. This assessment includes the possibility that there are independent measurements of this property that disagree with the present data in some significant manner. Heuristics or "rules of thumb" also might be applicable to this consideration. For example, it is a common observation that if the hardness of a bulk material increases, the elastic modulus of the bulk material increases also. Contradictory observations would indicate a need to reassess the apparently conflicting reports.

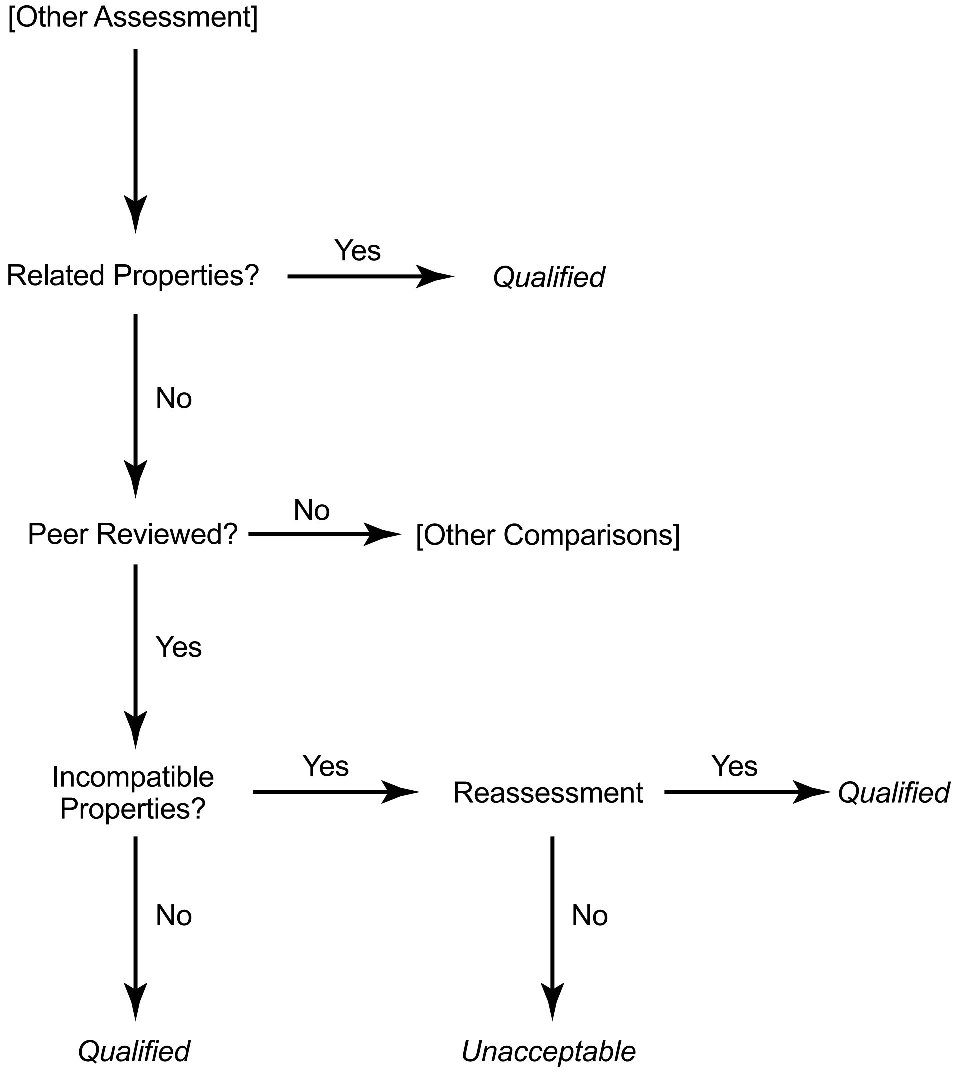

Figure 5.2. *Expansion of the data evaluation branch introduced in Figure 5.1 as [Other Assessment]. The node labeled [Other Comparisons] is expanded in Figure 5.3.*

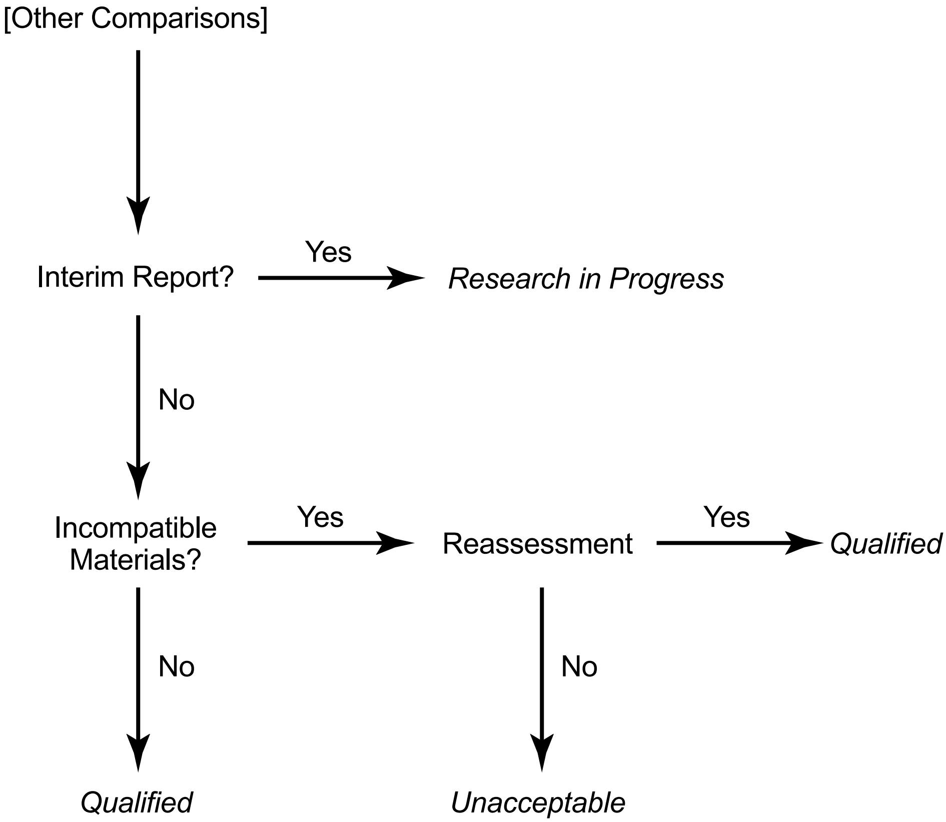

Figure 5.3. *Expansion of the data evaluation branch introduced in Figure 5.2 as [Other Comparisons].*

5.2.9 Manufacturer's Data

Question: *Is the data set provided by the commercial manufacturer or supplier of the material?*

Commercial manufacturers and suppliers of materials usually take great care to provide property data to their customers or as general information about their products. Often the values are reported with only a nominal or a brief indication of the measurement details. The data also may be presented as being typical of results obtained using specimens from several production batches of the material. These values are sometimes reported subsequently in published works without further discussion or assessment.

5.2.10 Survey Data

Question: *Is the data set provided as a literature survey or an overview?*

It is sometimes desirable to have an overview of how a property varies over a range of conditions or over a range of materials. A common method used to construct the overview is to review the literature for similar studies and to combine the results. Values derived from such surveys generally are representative of the trend of observed values but are not necessarily appropriate for any particular specimen. Typical values are useful for making order of magnitude estimates and for illustrating a functional trend such as a power law dependence on temperature.

5.2.11 Subsidiary Data

Question: *Is the data set provided as supplementary information?*

It is not unusual for a paper to focus rather sharply on one property, providing considerable details about its measurement, while other properties are mentioned only briefly. These additional data often are intended collectively as supplementary information that helps to define the context of the principal measurement. Subsidiary data of this nature often are reported without discussion of the measurement details. Density is very often reported in this manner.

5.2.12 Related Properties (without adequate measurement information)

Question: *Are the current values consistent with independent reports of this property or related properties for this material or a similar material?*

It sometimes happens that independent studies have been made on the same property or on related properties for the same material or for similar materials. Independent measurements of the same property may be compared for mutual consistency. It also may be possible to estimate a value for the current property from known values of related properties. Such estimates provide a reasonable validity check on the reported value but cannot be said to confirm the reported value because of the lack of information on the measurement technique or because of differences in the experimental specimens.

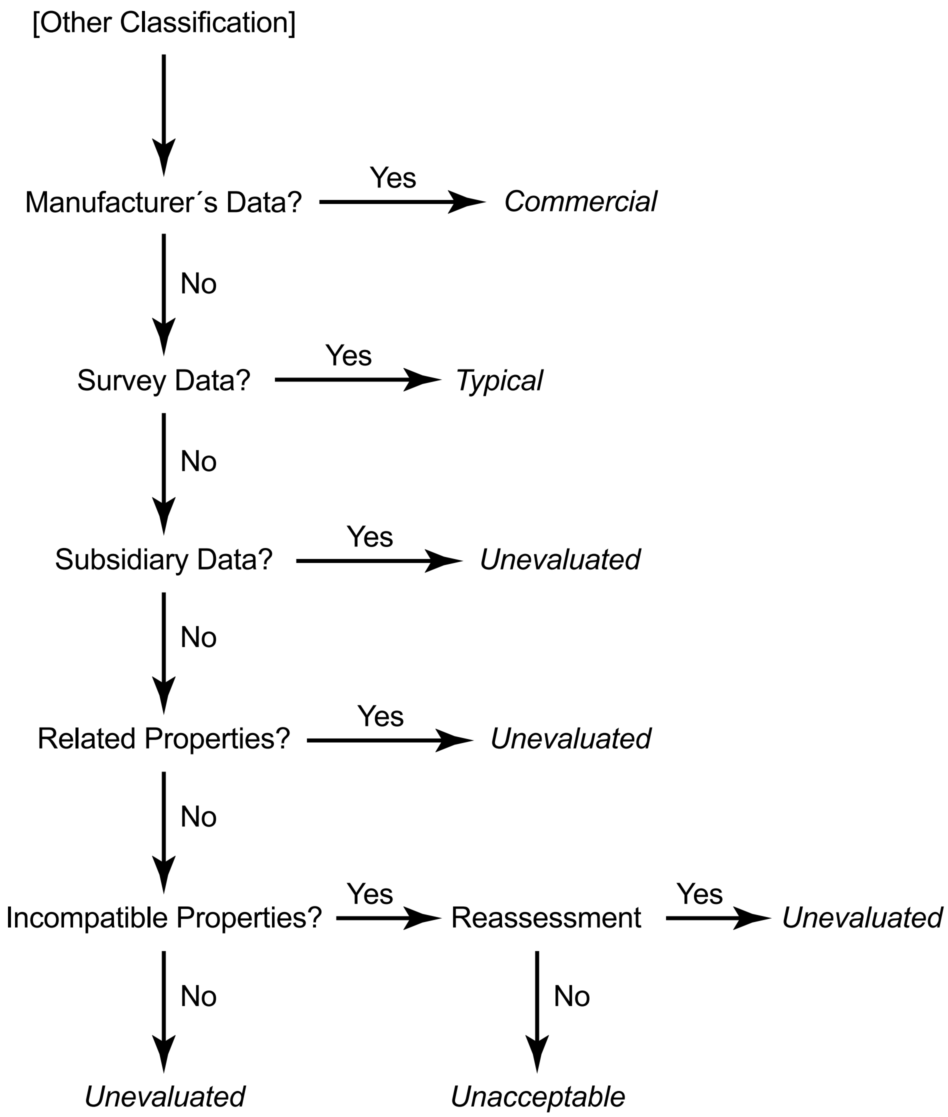

Figure 5.4. *Expansion of the data evaluation branch introduced in Figure 5.1 as [Other Classification].*

5.2.13 Interim Report

Question: *Are the reported values considered preliminary data?*

Preliminary results are sometimes reported in conference proceedings, interim reports to sponsors, or other status reports. Results that are the first of their kind might also be reported as a brief communication prior to the completion of the study. In such cases, it is tacitly understood that the reported values are subject to further study and may be different in the final report of the work. The timeliness and interest in the current status, however, warrant the reporting of the preliminary values.

5.2.14 Reassessment

Question: *If an apparent conflict was identified between the present data and other results, was the conflict resolved favorably for the present data?*

Many apparent discrepancies among material properties have rational explanations and are not true discrepancies. For example, two specimens of polycrystalline sintered ceramics having identical chemical compositions might be reported as the same material. However, if the sintered specimens have different densities, porosities, or grain sizes, the two measured property values could be significantly different, with both values being correct. Differences in measurement techniques can also result in apparent discrepancies. For example, the flexural strength of a ceramic material measured in three-point bending is generally different from the flexural strength measured in four-point bending because the two methods sample different volumes of the statistically distributed flaw sites.

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6. Issues and Practices in Data Evaluation

It is virtually impossible to undertake the deliberate collection of property data without some form of data evaluation be it primitive or highly refined. The very act of designating the kind of data to be accumulated is discriminatory and therefore constitutes a degree of evaluation. For design purposes, for materials science, and for the development of measurement standards, it is usually desirable to have a much higher degree of evaluation than is provided by a primitive discrimination applied to the nature of the data. Designers need to have values that pertain to the materials that will be used in their products. Materials scientists need values that can be used to distinguish the roles of underlying independent variables and to deduce relations and correlations among properties. Measurement standards require data of the highest attainable reliability. Between the basic needs of a primitive classification and the advanced status of a fully refined uncertainty analysis may be found a wealth of requirements that are suitable for diverse intermediate purposes. Accordingly, it may be useful to consider the deliberate evaluation of data in a series of progressively refined stages of discrimination and analysis.

6.1 Stage I: Data Collection (Issue: Accessibility)

All design and analytical applications of property data are predicated on the existence of a significant collection of values. Even cursory applications using order of magnitude estimates require data collections that are sufficient to establish ranges of typical values. The task of amassing data, therefore, is fundamental to all efforts requiring data, whether the requirement is for data of maximal reliability or for data of minimal reliability.

Perhaps the most daunting obstacle impeding data collection, and the most worrisome, is the immediate need to identify suitable sources of data. With the advent of computerized information systems, this task has been reduced in many cases to the development of an appropriate search strategy.

Computerized information systems used for literature searches are similar, with respect to content, to their printed ancestors. The computerized versions, however, differ from the printed versions in two important respects. First, computerization reduces both the time needed to conduct the search and the tedium that must be endured during the process. Second, most of today’s computerized routines allow searches to be constructed from words commonly used in the subject area.

In the past, the practical and economic incentives to keep the printed search documents as small as possible often led to the use of cryptic abbreviations or code sequences. The user had to expend additional time deciphering those codes and abbreviations to determine which search results were relevant. In contrast, today's computerized search results usually contain the full title of the paper, along with the names of the authors and the complete journal citation. Frequently, keywords and an abstract of the paper are provided also. This information usually is sufficient to determine whether or not a paper is relevant to your particular interests.

Regardless of the available tools, the success of a search depends on the logistical aspects of the strategy that is used to conduct the search. For the NIST databases, it has been found that comprehensive focused searches can be achieved using a strategy that evolves in three phases.

The first phase is to construct a "random sampling" of the literature by using basic keyword searches to probe the appropriate subset of the literature. For example, if you were searching for data on the elastic modulus of alumina, you might begin by specifying "alumina" as a keyword. One such keyword search of the open literature found 29866 papers involving that keyword. The papers in this subset addressed a great many topics other than the elastic modulus. Fortunately, most search routines allow you to specify compound searches consisting of multiple terms. To find only those papers pertaining to the elastic modulus of alumina, you might specify "alumina AND elastic AND modulus" as the search condition. This compound condition applied to the same bibliographic database reduced the number of potentially relevant papers to 202. Further specialization to "alumina AND elastic AND modulus AND porosity" reduced the count to 24, a readily manageable number of papers.

The second phase of the search strategy expands the reference set using a technique that might be called "progressive branching." In this phase, the papers found in the first phase serve as seed references (because the reference set will grow from them). Progressive branching makes use of the observation that an essential aspect of technical writing is the proper accreditation of prior research. This characteristic of technical writing allows you to anticipate that some of the papers that you have identified in the first phase of your search have also been used as references in research reported by other authors. This circumstance leads quite naturally to a technique known as the "cited reference" search. In this technique, you search for all the papers that have cited a particular paper. Because these papers necessarily were presented after the cited work, they represent a branching forward in time from the cited paper.

The third phase of the search strategy consists of following the reference trails of the papers already identified, a technique that might be called “regressive branching.” Quite simply, each paper that you have collected for your reference set has its own list of references, some of which may differ from your current collection and are therefore candidates for expanding your set. Because those references necessarily preceded the current paper, they represent a branching backward in time.

Upon reflection, it should be clear that each new reference that is collected may be used for both progressive branching and regressive branching. Consequently, the iterative application of these two search techniques has the potential of generating a collection of references that encompasses all of the mutually related papers that are documented in the bibliographic database.

6.2 Stage II: Basic Evaluation (Issue: Reproducibility)

The underlying criteria for Stage I: Data Collection are existence and availability. The purpose of Stage II: Basic Evaluation is to augment these criteria with conditions that address the central issue of credible data, *i.e.*, reproducibility. The underlying criteria added in Stage II are identification, description, and comparability. These criteria were applied in Chapter 5 in developing an operational protocol for data evaluation. Their roles are discussed under the headings of Material Specification (section 5.2.1), Measurement Method (section 5.2.2), and several of the decision nodes relating to the issue of reproducibility and the comparison of values from independent studies.

A special case of twofold interest to Stage II analysis is the round robin technique applied to measurement science. Round robin studies commonly address two concerns: the relative reliability of the measurement methods and the quantitative reliability of the measurement results.

6.2.1 Illustrative Example: Particle Size Measurement

When multiple techniques can be used for alternative measurements of the same property, the data evaluator needs to be aware of the limitations of the different techniques. Those limitations sometimes can be subtle. A round robin study provides an opportunity to examine those limitations under controlled conditions. A case in point is the measurement of the mean particle size of a ceramic powder.[1]

The processing procedure that produces a polycrystalline ceramic generally begins with a powder and proceeds through a series of mixing, compaction, sintering, and other heat treatment processes.[2] The mechanical, thermal, and electrical properties of the finished material often depend on the resulting microstructure and, most particularly, the grain size and porosity of the material. Characterization of the starting powder is critical to both understanding the process and ensuring the reproducibility of the process.

To address numerous issues in powder characterization, the International Energy Association (IEA) organized a series of round robin studies. These studies were exploratory in nature, and their primary purpose was to provide a basis for discovering and resolving potential problems that could affect international measurement standards. Among the issues addressed was the determination of the mean particle size of a starting powder.

The participants in the IEA studies voluntarily conducted a variety of measurements for characterizing ceramic powders.[3] Twenty-five laboratories from Germany, Sweden, and the United States participated in this study, designated Annex II in the IEA program structure. Each laboratory was supplied a set of five powders carefully derived from a master supply that had been developed specifically for this purpose at the National Institute of Standards and Technology (NIST). Previous efforts on ceramic powder characterization had established the critical importance of the sampling procedures used to prepare these sets of powders.[4] As a result, in Annex II, the master supply for each powder was subjected to extensive rifling, handling, and packaging procedures to ensure that the samples were homogeneous in content. The laboratories were requested to follow their usual procedures in preparing their test specimens from the materials that were supplied to them, and each laboratory was to conduct measurements according to the methods and procedures normally used in its own work.

Included in the results[1] were two sedigraph techniques, two light scattering methods, and two electron microscopy procedures. All of these methods were expected to have size detection limits that would be adequate for the powders used in the study. However, specimen preparation procedures could and did vary significantly among the methods and within a given method. The greatest concern in specimen preparation was with respect to the dispersion and deagglomeration of the particles. Deagglomeration can be affected strongly by such factors as the choice of dispersant, the power level of the sonic waves used to disrupt the agglomerates, and the duration of sonication.

Table 6.1: **Results for the mean particle size of the yttria-stabilized zirconia powder (YSZ) in IEA Annex II, as determined by the indicated methods.[5]**

Test Method*	Number of Laboratories	Mean Value [μm]	Standard Deviation [μm]
GS	6	0.21	0.03
CS	4	1.32	0.52
FMLS	5	2.33	1.29
PCLS	2	0.19	0.01
SEM(WD)	1	2.02	—
SEM(MD)	1	1.65	—

* The method abbreviations are:

GS = Gravitational Sedimentation
CS = Centrifugal Sedimentation
FMLS = Fraunhofer-Mie Light Scattering
PCLS = Photon Correlation Light Scattering
SEM(WD) = Scanning Electron Microscopy (Waddel Diameter)
SEM(MD) = Scanning Electron Microscopy (Maximum Diameter)

Results[5] for the zirconia powder, Table 6.1, were quite dramatic. The two sedigraph techniques differed by a factor of six, and the two light scattering methods produced results differing by more than a factor of ten. The microscopy results were of the same order of magnitude, but the agreement was not especially good. Using Student's t-test at a confidence level of 99 %, the gravitational sedimentation (GS) and photon correlation light scattering (PCLS) methods easily were found to be distinctly different from the other four methods, while the differences among the centrifugal sedimentation (CS), Fraunhofer–Mie light scattering (FMLS), and the two scanning electron microscopy (SEM) methods, SEM(WD) and SEM(MD), could not be judged to be significant.

It might be conjectured that if the only results showing an extraordinary difference were the results from the two laboratories using the PCLS method, then there would have been a strong inclination to declare those results to be of a spurious nature. The concurrence of the GS method and the consistency of the six laboratories using that method clearly showed that the results should not be dismissed as spurious.

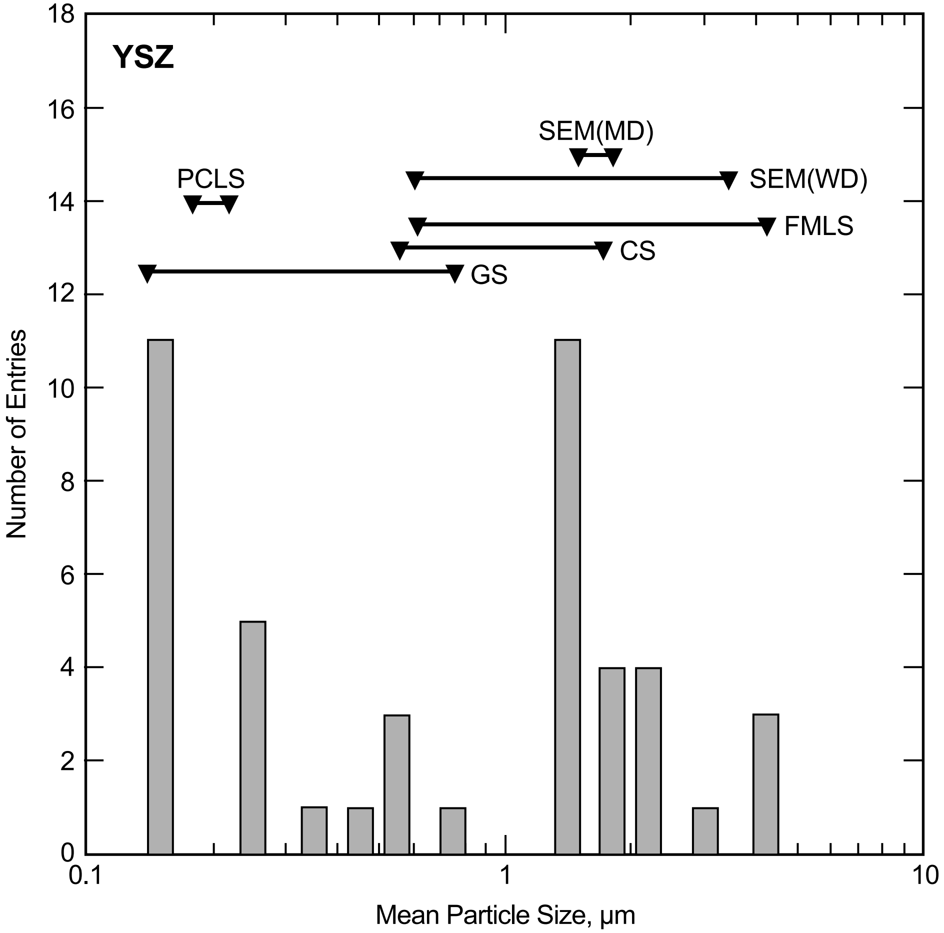


Figure 6.1. *Histogram of particle size distribution for the yttria-stabilized zirconia powder studied in IEA Annex II.*[6] *The horizontal bars identify the actual ranges of values reported by the different methods. CS: centrifugal sedimentation. GS: gravitational sedimentation. FMLS: Fraunhofer-Mie light scattering. PCLS: photon correlation light scattering. SEM(MD): scanning electron microscopy (maximum diameter). SEM(WD): scanning electron microscopy (Waddel diameter).*

Some insight into this puzzle may be gleaned from Figure 6.1, a histogram constructed[6] from all of the individually reported observations of the mean particle size for the zirconia material. This figure reveals that the material had a bimodal particle size distribution. The horizontal bars superimposed on the histogram show the ranges of sizes actually reported by each measurement method. Apparently, the various methods reported quite different results because the methods sampled quite different portions of the bimodal distribution. Given that all of the methods had theoretical detection limits that were much wider than the observed intervals, it had to be concluded that the discrepancies were consequences of the specimen preparation procedures. Thus, the procedures used with the devices had to be considered, in addition to the detection limits of the devices, in determining the limitations of the measurements.

Observations of this nature illustrate how the depth of detail of a measurement procedure can influence both the interpretation of the results and the conclusions drawn from them regarding the general applicability of a measurement method. Clearly, both of these issues need to be examined critically in applied data evaluation efforts.

6.3 Stage III: Relational Analysis (Issue: Consistency)

In the preceding section, Stage II: Data Evaluation, the given data set was examined in the one-dimensional context of reproducibility. In Stage III, the data set is viewed through its relations to other data, particularly through trends, correlations, and known material property relations. The central focus of Stage III is on consistency.

6.3.1 Definitive and Derived Relations

Technical expressions often depend on semantics to ensure clarity of meaning. An underlying requirement of proper semantics is the use of basic definitions. In data evaluation, these basic definitions and the rudimentary relations derived from them often can be used directly to assess the consistency of independently reported measurement results. In the technical literature, however, some terms are in such common usage that there is sometimes a confusion regarding which terms are definitive and which are derived. The basic importance of definitive relations and the potential for confusion in the literature warrant a brief review of some of these terms.

6.3.1.1 Mass Fraction, Mole Fraction, Volume Fraction

Elemental, molecular, phase, and microstructural compositions often need to be described in the reporting of technical results. The mixture of initial powders; the addition of stabilizers or sintering aids; the assessment of the composition of a material after processing, heat treatment, or environmental reaction; and the quantitative measure of a material's microstructure represent some of the more common situations requiring a quantitative expression of a composition. The prescription for such expressions has been provided as part of the International System of Units (SI),[7–9] which currently represents the agreement of 51 member states and 9 associates to the General Conference.[10] The prescription is quite simple. For example, if a substance has *n* components whose masses are denoted by m_i for i = 1 to *n*, resulting in a total mass $M = m_1+m_2+...+m_n$, then the mass fraction, μ_i, of the ith component in *M* is simply

$$\mu_i = \frac{m_i}{M} \tag{1}$$

where clearly, $(\mu_1 + \mu_2 + ... + \mu_n) = 1$. Similar definitions apply to mole fraction and volume fraction.

Mass fractions are frequently reported using the fraction's unit, %. For example, if the mass fraction of powder A in a mixture is $\mu_A = 0.98$, the value might be reported as 98 % A. There is a long standing, very widespread practice in the literature of condensing the identification of the quantity (mass fraction of A) and its value (98 %) into an abbreviated expression (98 wt % A). Similar condensed expressions occur for mole fraction (mol %) and volume fraction (vol %). While this practice is discouraged by the SI, the condensed expressions are still favored by many journals, even by some journals that have expressly endorsed the SI.

One consequence of this common practice is a relatively rare occurrence of confusion between the proper SI term, mass fraction, and another commonly used term, fractional density. When a polycrystalline material is processed, the density of the end product is often compared to the maximum density that could be achieved by an ideal single crystal of the same material. The ratio of the actual density to the maximum density is the fractional density, also known as the relative density. The popular jargon, percent theoretical density, is also found in the literature. The two terms, mass fraction and fractional density, are clearly distinct. Mass fraction relates to composition while fractional density relates to the degree of compaction or consolidation. The potential for confusion apparently arises from use of the word "mass" in the term "mass fraction." Because density also is related to mass, "mass fraction" may be interpreted incorrectly as a density fraction and, hence, as "fractional density." While the correct meaning is usually clear from the context in which the two terms are used, it is useful to be alert to the possibility of confusion. Terms related to density are discussed more fully in the following section.

6.3.1.2 Density, Theoretical Density, Porosity

Among the basic physical characteristics of a solid material is its mass density, defined as the mass of the specimen divided by the volume of the specimen. Most polycrystalline materials contain void spaces between material grains resulting in a density that is less than the density that would be obtained for a perfect single crystal of the same material. The density of a perfect single crystal is the maximum attainable density for a given structural phase of the material and is quite commonly known as the theoretical density. Other terms often used for this same quantity include the crystal density and the x-ray density of the material. If the material has a molar mass M_W, computed from its chemical formula, and the unit cell of its crystal structure has volume V, computed from its measured lattice parameters, then the theoretical density, ρ_theo, of the material is

$$\rho_\mathrm{theo} = \frac{M_W z}{N_\mathrm{A} V} \tag{2}$$

where z is the number of formula units in the unit cell, and N_A is Avogadro's number ($6.0221367(36) \times 10^{23}$ mol^{-1}). The volume of the unit cell depends on the symmetry of the crystal system. Appropriate expressions[11] are given in Table 6.2 for the seven distinct crystal systems.

Table 6.2. **Unit Cell Parameters and Unit Cell Volumes for the Seven Crystal Systems[11]**

Crystal System	Cell Axes	Cell Angles	Volume
Cubic	$a = b = c$	$\alpha = \beta = \gamma = \pi/2$	$V = a^3$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = \pi/2$	$V = a^2c$
Hexagonal	$a = b \neq c$	$\alpha = \beta = \pi/2,\ \gamma = 2\pi/3$	$V = (3/4)^{1/2}\, a^2c$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma < 2\pi/3 \neq \pi/2$	$V = a^3\ \{1\text{- } 3\cos^2(\alpha) + 2\cos^3(\alpha)\}^{1/2}$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = \pi/2$	$V = abc$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = \pi/2 \neq \beta$	$V = abc\ \sin(\beta)$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	$V = abc\ \{1\text{-}\cos^2(\alpha)\text{-}\cos^2(\beta)\text{-}\cos^2(\gamma) + 2\cos(\alpha)\cos(\beta)\cos(\gamma)\}^{1/2}$

For polycrystalline materials, the measured density, ρ, is less than ρ_{theo} because the specimen's volume, V_s, is occupied, in part, by voids. If M is the total mass of the specimen, then the measured density is $\rho = M/V_s = M/(V_m+V_v) = \rho_{\text{theo}}V_m/(V_m+V_v)$, where V_m is the ideal volume, free of voids, that would be occupied by an ideal material component of mass M, and V_v is the total volume of the void space in the real specimen. It follows that the volume fraction of the material component in the specimen volume is the fractional density, ρ/ρ_{theo}. The complementary quantity, the volume fraction of void space, commonly known as the porosity, $\phi = V_v/(V_v+V_m)$, may then be computed as

$$\phi = 1 - \frac{\rho}{\rho_{\text{theo}}}\ . \qquad \textbf{(3)}$$

This expression for porosity may be extended readily to a multicomponent material. If the material consists of n material components, then

$$\phi = 1 - \left[\mu_1\left(\frac{\rho}{\rho_1}\right) + \mu_2\left(\frac{\rho}{\rho_2}\right) + \cdots + \mu_n\left(\frac{\rho}{\rho_n}\right)\right] \qquad \textbf{(4)}$$

where ρ_i is the theoretical density of the i$^{\text{th}}$ component and μ_i is the mass fraction of the i$^{\text{th}}$ component in the material.

It should be noted that the porosity computed in this manner is the total porosity including contributions from intra-granular void space as well as from inter-granular voids. When porosity is measured experimentally by immersion or pyncnometry techniques,[12] only a portion of the total void space, the "open porosity," is accessible to the diffusing species. Some of the pores are "closed," *i.e.*, inaccessible to the diffusing species, and, therefore, are not included in the void space detected by these techniques. Consequently, the measured open porosity is necessarily less than or equal to the total porosity. This distinction can be important when comparing results from independent studies or when the influence of porosity on property values is being investigated.

6.3.1.3 Thermal Expansion

For most materials, an increase in the temperature of a substance that is maintained at constant pressure is accompanied by a change in the volume occupied by the material. The fractional amount by which the dimensions of a material change per degree of temperature change is called the coefficient of thermal expansion (CTE). The volumetric CTE is defined as

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{5}$$

where the subscript on the derivative denotes constant pressure. In many practical applications, changes in linear dimensions are more relevant. The linear CTE is defined as

$$\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P \tag{6}$$

where L is any linear dimension. For isotropic polycrystalline materials such as ceramics, the magnitude of the CTE is in the range from 10^{-6} K^{-1} to 10^{-5} K^{-1}. For such small CTE values, it may be found for isotropic materials that $\alpha_V \approx 3\alpha_L$ given that V is of order L^3 and α_L is the mean linear CTE for the material.

A more common measure of expansion is the cumulative linear coefficient of thermal expansion,

$$\alpha_{c,L} = \frac{1}{L_0} \left(\frac{L - L_0}{T - T_0} \right) \tag{7}$$

in which expansion is expressed relative to a reference state of dimension L_0 at temperature T_0. The continuous and cumulative linear coefficients are related by

$$\alpha_L = \left[\frac{1 + (T - T_0) \dfrac{1}{\alpha_{c,L}} \left(\dfrac{\partial \alpha_{c,L}}{\partial T} \right)_p}{1 + (T - T_0)\alpha_{c,L}} \right] \alpha_{c,L} \tag{8}$$

All of these measures of thermal expansion are related to changes in volume, and any change in the volume of a material must produce a change in the density when the mass of the material is conserved. The definition of density requires

$$\frac{\rho(T)}{\rho(T_0)} = \frac{V(T_0)}{V(T)} \tag{9}$$

from which it is straightforward to find

$$\rho(T) = \frac{\rho(T_0)}{1 + \alpha_{c,V} \cdot (T - T_0)} \tag{10}$$

with respect to the cumulative coefficient of volumetric expansion, and

$$\rho(T) = \frac{\rho(T_0)}{[1 + \alpha_{c,L} \cdot (T - T_0)]^3} \tag{11}$$

for isotropic materials when V is of order L^3.

These relations are particularly useful for applications involving elevated temperatures. Density is commonly determined only at room temperature, while the expansion of a specimen with temperature often is reported only as the relative change in a linear dimension between room temperature and one or more higher temperatures. In such cases, the value of the density at high temperature must be calculated using these relations.

6.3.1.4 Elasticity

All solid materials will deform in response to external forces or internal thermal stresses. The extent to which a material deforms and the nature of that deformation depend on geometrical features of the microstructure of the material, interactions occurring among grains, inclusions, other secondary material phases, and the bond strengths of elemental constituents. When the deformation is recoverable, it is said to be elastic. More precisely, the deformation produced by an external force acting on a solid is said to be elastic when removing the external force returns the solid to its original undeformed state.[13]

The phenomenon of elastic deformation is a familiar one, being commonly seen in the stretching of a spring, the flexing of a beam, the bending and twisting of a cable, and the swaying of a tree in the wind. Quantitative observations made as early as the 1600s[14] found that most solids exhibit a linear response when the applied stress is not too large. The relation known as Hooke's law, $\sigma = E\epsilon$, defines a coefficient of elasticity relating the applied stress, σ (force per unit area), to the strain, ϵ (fractional elongation), produced by the stress. The coefficient, E, is known as the elastic modulus or, perhaps more commonly, as Young's modulus. A similar coefficient, G, the shear modulus, also known as Coulomb's modulus, is defined for angular or torsional deformation, γ, produced by a shear stress, τ, such that $\tau = G\gamma$.

For crystals and anisotropic materials, these definitions need to be generalized to account for the different responses of the material in different directions, and the scalar coefficients are replaced by a tensor. For isotropic materials, however, the two coefficients, E and G, are sufficient to describe the macroscopic elastic behavior completely. However, it is convenient to consider two alternate parameters, Poisson's ratio and the bulk modulus, that describe specific attributes of the elastic behavior of isotropic materials.

The bulk modulus, *B*, describes the particular circumstance when stress is applied hydrostatically rather than axially. The hydrostatic pressure, *P*, applied to an isotropic solid, causes the volume, *V*, to decrease such that,

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T \qquad \textbf{(12)}$$

where the subscript *T* denotes constant temperature.

Poisson's ratio, ν, describes the relation between axial and lateral strains. For example, when a rod of uniform circular cross section is elongated by a tensile stress along the rod axis, the cross section undergoes a decrease in diameter. The negative of the ratio of the lateral and axial strains is Poisson's ratio,

$$\nu = -\frac{\epsilon_{lateral}}{\epsilon_{axial}} \cdot \qquad \textbf{(13)}$$

It can be shown that

$$\nu = \frac{E}{2G} - 1 \qquad \textbf{(14)}$$

$$B = \frac{EG}{9G - 3E} \qquad \textbf{(15)}$$

for isotropic materials. In principle, any two of the four quantities, *E*, *G*, *B*, and ν, can be used to describe the elastic properties of an isotropic material.

The elastic and shear moduli can be determined directly from the slopes of the appropriate stress *vs*. strain curves.[15] In practice, however, the measurement of elastic properties is most commonly accomplished using sonic resonance or the propagation of ultrasonic waves in the material.[16–23] There are two independent sound wave velocities corresponding to the two independent coefficients of elasticity for isotropic materials. These velocities commonly are denoted v_S for the shear mode and v_L for the longitudinal mode. The relations between the sonic velocities and the elastic moduli may be written as

$$G = \rho v_S^2 \tag{16}$$

$$E = 3\rho v_S^2 \left[\frac{v_L^2 - (4/3)v_S^2}{v_L^2 - v_S^2} \right] \tag{17}$$

where ρ is the mass density of the material.

It should be noted that the explicit occurrence of density in these expressions does not imply a linear dependence of the elastic moduli on density. The sound velocities also vary with density, and it will be shown in Section 6.4 that the density dependence of the elastic moduli is generally nonlinear.

6.3.1.5 Heat Capacity and Specific Heat

When materials are used at elevated temperature, the presence of temperature gradients, thermally induced strains, and the rate of transport of thermal energy become special concerns. The properties of immediate interest in this context are specific heat, thermal conductivity, and thermal diffusivity. The specific heat is related to the increase of temperature when a quantity of heat energy is added to the specimen; the thermal conductivity characterizes the steady state heat flow in the material; and the thermal diffusivity is related to the transient response of the material to a heat pulse.

The heat capacity of a material specimen is the amount of energy that must be added to the specimen to raise its temperature by 1 K. It is a fairly common observation that a larger specimen requires more energy than a smaller specimen to produce the same change in temperature. To compare results from different specimens, it is necessary to normalize the measured values to a common amount of substance. There are two such normalized measures of heat capacity that are in common use. One is called the molar heat capacity, and the other is commonly called the specific heat. The molar heat capacity expresses the heat capacity per mole of the substance. The specific heat expresses the heat capacity per unit of mass of the substance. In practice, the heat capacity of a specimen is determined experimentally[24–26] under isobaric conditions, normalized to specific heat, C_P, using the known mass of the specimen, and then converted to molar heat capacity, $C^{(\mathrm{M})}{}_P$, for more convenient use in thermodynamic relations.

A subtle point in the conversion of specific heat to molar heat capacity is worthy of additional comment. The conversion relation is simply

$$C^{(\mathrm{M})}{}_P\ [\mathrm{J/mol\ K}] = \left(\frac{M_W[\mathrm{g/mol}]}{1000\,[\mathrm{g/kg}]}\right) C_P\ [\mathrm{J/kg\ K}] \tag{18}$$

where M_W is the molar mass of the substance. While the mass of an atom is a fundamental characteristic of matter, the recommended values of the atomic masses (a.k.a., atomic weights) of the elements change from time to time as the necessary experimental techniques are improved or the determinations of the values are refined. Older technical papers used values for M_W that differ from the values that would be used today. Consequently, to calculate the specific heat from a molar heat capacity reported in an older paper, the older values of M_W need be used for the calculation rather than the present values. However, if molar heat capacity is also desired, then the current value of M_W must be used to correct for the changes in atomic masses. Symbolically,

$$C_P = \left(\frac{1000}{M_{\mathrm{old}}}\right) C^{(M)}{}_P(old) \tag{19}$$

$$C^{(M)}_P\,(new) \;=\; \left(\frac{M_{new}}{M_{old}}\right) C^{(M)}_P\,(old) \tag{20}$$

where it should also be noted that the distinction of “old” and “new” is not needed for C_p because the value of C_p is derived directly from the measurements of heat, mass, and temperature and is unaffected by any change in M_W.

Laboratory measurements to determine heat capacity are usually performed under conditions of constant pressure, yielding the specific heat C_p. In theoretical models and computations, it is often more convenient to use the specific heat at constant volume, C_V. The two specifications yield slightly different values for the specific heat, the difference being given by the thermodynamic relation

$$C_P - C_V \;=\; T\rho^{-1} B_T\,\alpha_V^2 \tag{21}$$

where B_T is the isothermal bulk modulus, α_V is the volumetric coefficient of thermal expansion, T is temperature, and ρ is density. This difference often is considered negligible even at high temperature. For example, for high purity TiB_2,[27] $(C_p{-}C_V)/C_p \approx 3.7\,\%$ at 1000 °C, while for α-SiC [28] at the same temperature, the relative difference is only 1.4 %.

6.3.1.6 Thermal Transport

The capacity of a material to store heat also has an influence on the transport of heat energy through the material under nonequilibrium conditions. For isotropic materials, thermal conductivity and thermal diffusivity should be correlated through a relation involving the density (ρ) and the specific heat at constant pressure (C_p); i.e., the transport properties should be related by the expression

$$\kappa \;=\; \rho\, C_P\, D \tag{22}$$

where κ is the thermal conductivity and D is the thermal diffusivity. This simple relation is quite remarkable because it can serve as a unifying factor imposing consistency among otherwise unrelated data.

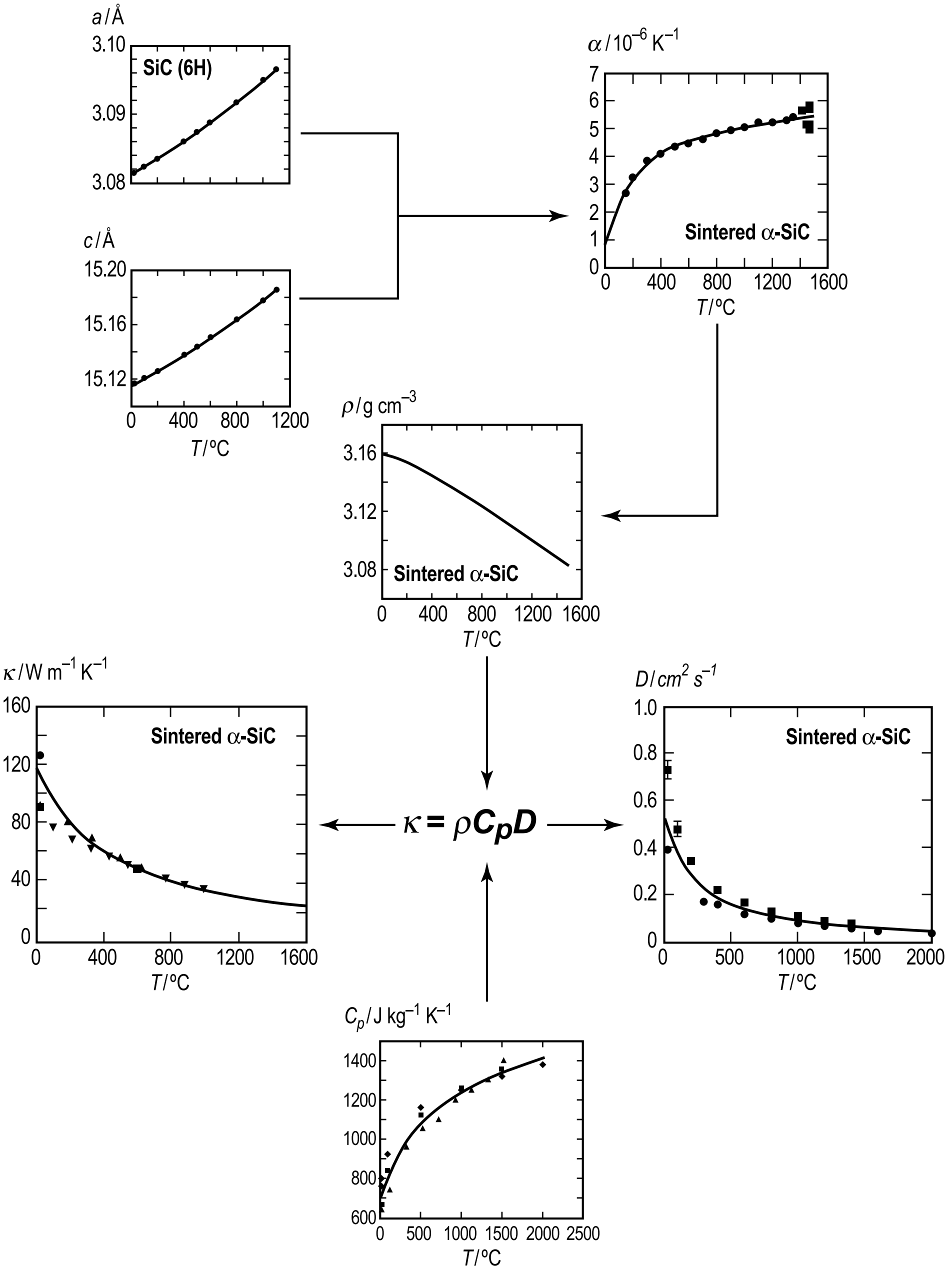


Figure 6.2. *Consistency and data optimization through property relations, illustrating the use of multiple data sets to optimize the correlation of thermal conductivity and diffusivity for sintered α-SiC.*[29]

The flow chart in Figure 6.2 illustrates how this consistency arises.[29] The temperature dependence of the density is governed by the thermal expansion of the specimen. Quantitatively, the temperature dependence of the thermal expansion coefficient may be established by means of lattice parameters and dilatometry results. These results then may be combined [see section 6.3.1.3 Thermal Expansion] with Archimedean measurements of the density at room temperature to establish the variation of density with temperature. In separate work, the temperature dependence of the specific heat may be established independently, often combining the results of several studies to obtain an optimum representation of C_p. Then (and only then), Equation (22) can be used to obtain maximum consistency among the measured transport values. In this latter step, it is very useful to have an analytic expression representing the general trend of the transport properties with temperature. In practice, both thermal conductivity and thermal diffusivity have been modeled successfully at elevated temperatures using expressions of the same form[27, 28, 30]

$$D = D_0 + \frac{D_1 \exp[-D_2 T]}{D_3 + T}, \tag{23}$$

$$\kappa = \kappa_0 + \frac{\kappa_1 \exp[-\kappa_2 T]}{\kappa_3 + T}, \tag{24}$$

where the D_i and the κ_i are adjustable parameters. In Figure 6.3, results are shown[30] for sintered α-alumina (99 % purity). The data points shown for thermal conductivity were reported separately from the points shown for thermal diffusivity. The dashed curves show the fits of the respective models when the data sets are considered separately as standalone results. The solid curves show the optimized fit when the data sets are considered simultaneously, subject to the consistency constraint provided by Equation (22). At the low temperature end of the observed range, the fully evaluated results differ by more than 30 % from the standalone results, a quantitative demonstration of the value-added benefit of data evaluation.

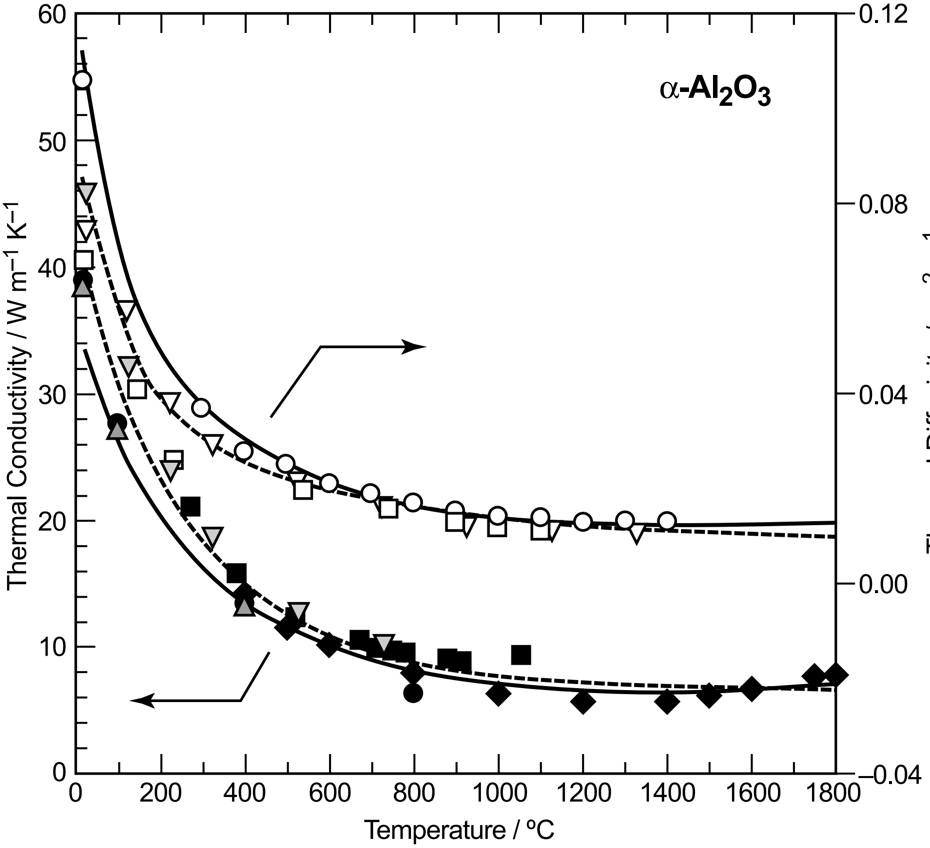


Figure 6.3. *Thermal transport data for sintered α-alumina (99% purity). The dashed curves show fits when the data sets are considered separately as standalone results, while the solid curves show optimized fits constrained for consistency in the manner of Figure 6.2.*[30] *[Data: See* Additional Source References, *Figure 6.3.]*

6.3.2 Correlations and Semiempirical Relations

Materials science is fundamentally an observational discipline, and its foremost objective is to gain from its observations an understanding of material behavior. The process of subjecting a material to a variety of stimuli and observing its responses leads naturally to the introduction of properties or characteristics as quantitative measures of the behavior of that material. The number of properties that can be introduced in this manner is limited principally by the imagination of the observer. In contrast, the effective number of degrees of freedom of a bulk specimen is relatively limited. It should be expected, therefore, that not all of the identified properties and characteristics are independent, *i.e.*, there must be subsets of properties that are interrelated.

Such relations are of considerable importance to data evaluation because they provide some of the most compelling evidence for consistency. When relations between different properties can be applied successfully to data obtained from measurements that were conducted independently, the result is a cross validation of the two results. Further, the more these relations are found to be valid and reliable, the more reasonable it becomes to use them to make estimates of property values when direct measurement results are not available.

Correlations, in general, serve numerous purposes. Perhaps their most obvious function is to provide reliable interpolation functions for estimating property values. Under limited conditions, they might also be used as a means to extrapolate the property estimates beyond the range observed experimentally. Further, when materials behave in a similar manner under similar stimuli, we may expect their properties to exhibit functionally similar correlations. Hence, the analytical forms of the correlations may serve as a means of classifying material behavior. When semiempirical models are applied as part of the correlation or analysis, the parameters of the model may be related to specific physical characteristics, or the parameters may have physically meaningful interpretations. In both cases, useful quantitative estimates may be derived from fitting the model to the observed data. Correlations and semiempirical models are also exceptionally useful in assessing procedural properties, underlying variables, and the scope of physical process mechanisms.

6.3.2.1 Estimates of Unmeasured Quantities

{***Example:*** Critical temperature, oxygen content, and crystallography}

Quantitative applications of correlations are especially useful when the mathematical concept of transitivity applies. Here, transitivity means that if a quantity A is related to a variable C by a relation $A(C)$, and a quantity B is related to C by $B(C)$, then a variation dA of A implies a variation dB of B such that an estimate of dB can be made from

$$dB = \frac{(dB/dC)}{(dA/dC)}\,dA \qquad \textbf{(25)}$$

given the value of dA. This situation is encountered, for example, in studies of oxide superconductors.

The outstanding characteristic of a superconductor is that the electrical resistance of the material vanishes when the temperature of the material becomes less than a well-defined value known as the superconducting critical temperature, T_c. In 1957, the theoretical understanding of conventional superconductors was established in what quickly became known as the BCS theory of superconductivity.[31] When superconducting oxide ceramics were discovered in 1987,[32] they were found to have characteristics distinctly different from those described by the BCS theory. An intensive research effort was launched immediately worldwide to study the properties of this new class of materials. In less than fifteen years from the date of their initial discovery, more than fifty thousand papers were published on studies of this phenomenon.

While many materials were soon found to belong to this class of unconventional superconductors, a major portion of the effort was focused on $YBa_2Cu_3O_x$ which quickly became known as Y:123 or YBCO. It was established rather quickly that the superconducting properties of Y:123 and other oxide superconductors had a strong dependence on the oxygen content of the material. For Y:123, Figure 6.4,[33] the dependence of T_c on the oxygen content was nonlinear and reproducibly exhibited plateau-like regions. An interpolation expression that mimics the plateau regions was established empirically on the interval $6.4 \leq x \leq 6.95$.

$$T_c/K = 89.5 + 4.37(x - 6.73) - \frac{30.57}{1 + \exp[331.65(x - 6.73)]} - \frac{35.79}{1 + \exp[27.84(x - 6.45)]} \qquad \textbf{(26)}$$

giving the critical temperature (the solid curve in Figure 6.4) with a combined standard uncertainty of 3 K for $x \geq 6.5$ and 5 K for $x < 6.5$.

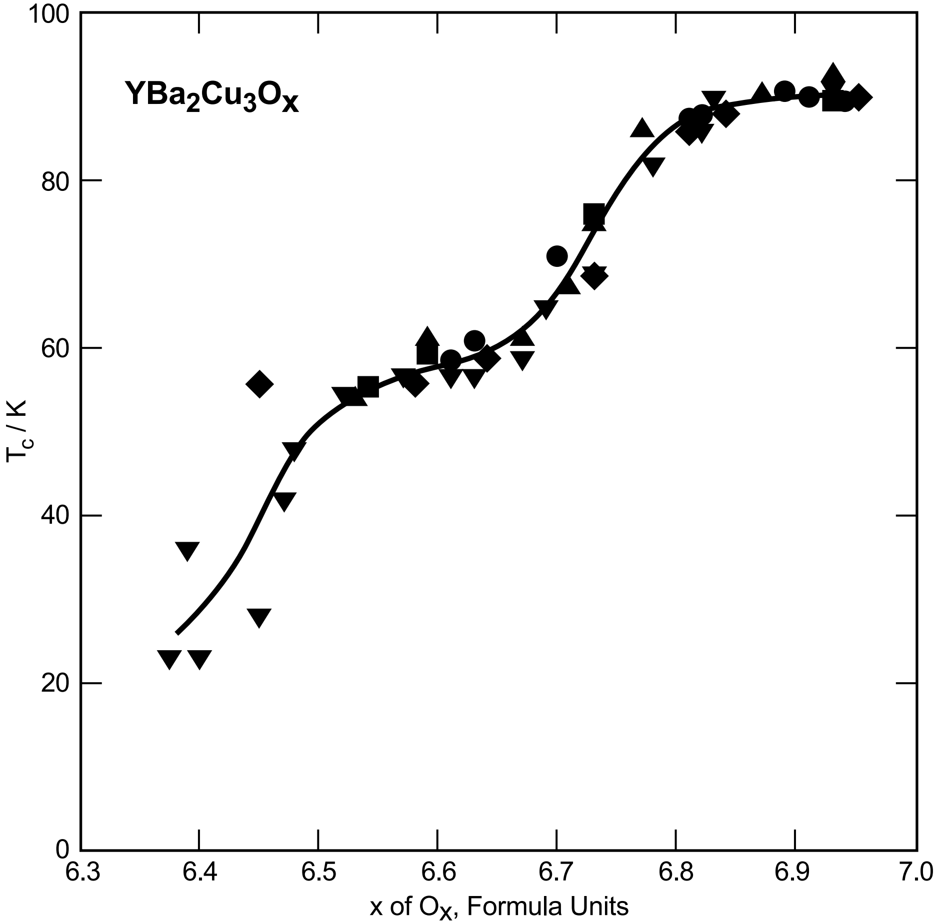


Figure 6.4. *The dependence of the superconducting critical temperature,* T$_c$*, on the oxygen content in* $YBa_2Cu_3O_x$.[33] *[Data: See* Additional Source References, *Figure 6.4.]*

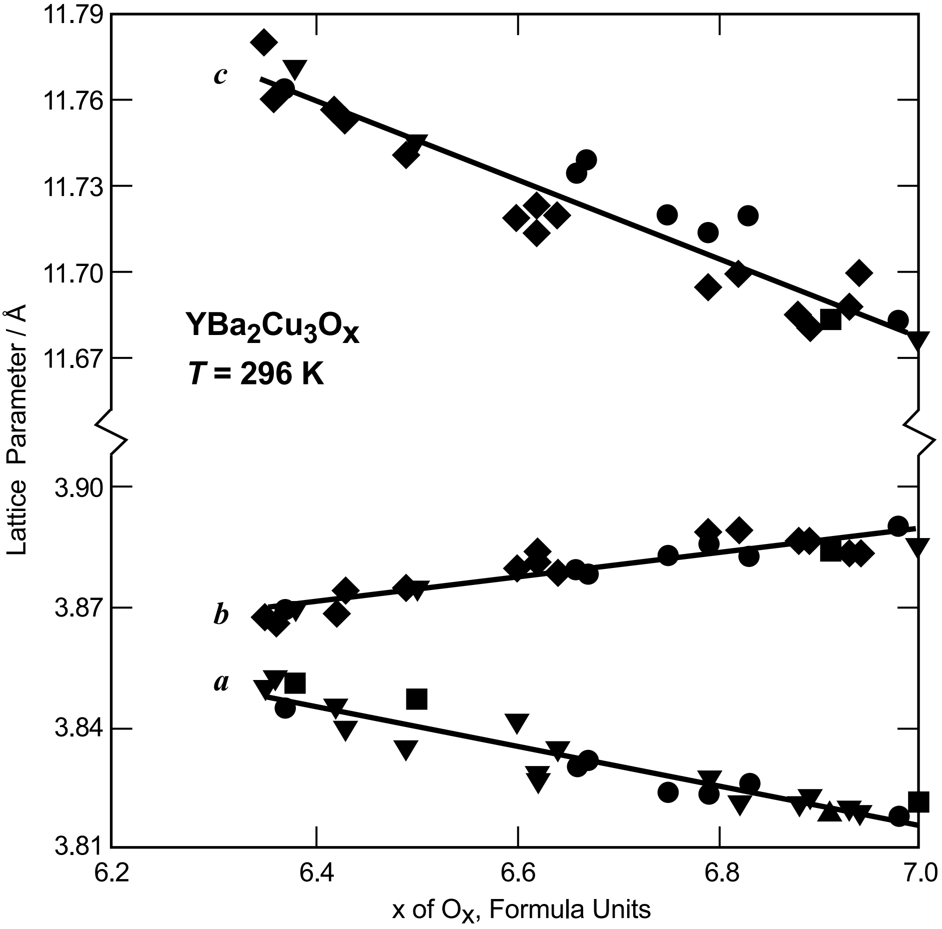


Figure 6.5. *Lattice parameters, a, b, and c, for the orthorhombic structure of $YBa_2Cu_3O_x$, varied linearly with oxygen content.*[33] *[Data: See* Additional Source References, *Figure 6.5.]*

Concurrently, crystallographic studies also had found a highly reproducible dependence on the oxygen content. On the interval $6.35 \le x \le 7.0$, the lattice parameters, a, b, and c, for the orthorhombic structure of Y:123, varied linearly, Figure 6.5,[33] with oxygen content. Simple linear least squares fitting of the data from several sources found

$$a/\text{Å} = 4.1696 - 0.0506x \quad \textbf{(27)}$$

$$b/\text{Å} = 3.6830 + 0.0294x \quad \textbf{(28)}$$

$$c/\text{Å} = 12.641 - 0.1378x \quad \textbf{(29)}$$

with relative standard uncertainties of 0.13 %, 0.15 %, and 0.16 % respectively.

Given that there is a significant dependence on the oxygen content, these empirical correlations are especially useful when comparisons of independent studies are made. For example, if one study includes a value of T_c while another reports the lattice parameters, these relations can be used to verify whether the two studies pertain to similar compositions or to significantly different compositions. The lattice parameter c, in particular, often has been used to estimate the oxygen content of a specimen of Y:123.

6.3.2.2 Properties as Parameters

{***Example:*** Isothermal equations of state}

Quantitative applications of semiempirical relations often are used to deduce the absolute values of proper material characteristics that are embedded in the relations. While this practice can be quite reliable, there are pitfalls that may need to be avoided.

Table 6.3: **Semiempirical isothermal equations of state**

Name	$\mathbf{P - P_0}$
Murnaghan	$\frac{B_o}{B_o'}\left[\left(\frac{V_o}{V}\right)^{B_o'} - 1\right]$
Tait	$\frac{B_o}{1+B_o'}\left(\exp\left[\left(1+B_o'\right)\left(1-\frac{V}{V_o}\right)\right]-1\right)$
Birch	$\frac{3}{2}B_o\left[\left(\frac{V_o}{V}\right)^{7/3} - \left(\frac{V_o}{V}\right)^{5/3}\right]$
Birch–Murnaghan	$\frac{3}{2}B_o\left[\left(\frac{V_o}{V}\right)^{7/3} - \left(\frac{V_o}{V}\right)^{5/3}\right]\left[1-\left(3-\frac{3}{4}B_o'\right)\left(\left(\frac{V_o}{V}\right)^{2/3}-1\right)\right]$
Bardeen	$\frac{3}{2}B_o\left[\left(\frac{V_o}{V}\right)^{2} - \left(\frac{V_o}{V}\right)^{4/3}\right]\left[1+\frac{3}{8}B_o\left(3B_o'-10\right)\left(\left(\frac{V_o}{V}\right)^{2/3}-1\right)\right]$
Born–Mie	$\frac{3B_o}{n-m}\left[\left(\frac{V_o}{V}\right)^{1+n/3} - \left(\frac{V_o}{V}\right)^{1+m/3}\right]$; n, m = integers
Olinger–Halleck	$\frac{B_o(1-V/V_o)}{\left[1-\frac{1}{4}(1+B_o')(1-V/V_o)\right]^2}$

Table 6.3, for example, lists seven different semiempirical expressions for the isothermal equation of state (EOS) used to described the compression of a solid while the temperature is maintained constant.[34] Each of these expressions has a well-defined material property, the bulk modulus, embedded in the expression as a parameter whose value is to be determined by fitting the expression to the observed compression data. The expressions in Table 6.3 assume that the thermodynamic relation between pressure, P, and volume, V, can be cast into the form

$$P - P_0 = \Im(V, V_0, B_0, B_0') \tag{30}$$

where

$$B_0 = -V_0 \left(\frac{\partial \Im}{\partial V}\right)_{T, V=V_0} \tag{31}$$

$$\Im(V_0, V_0, B_0, B_0') = 0 \tag{32}$$

such that B_0 yields an estimate of the bulk modulus in the reference state whose volume and pressure are respectively V_0 and P_0 at the fixed temperature T. The additional parameter, B_0', occurring in some of the expressions is the isothermal pressure derivative of the bulk modulus, $B_0' = (\partial B/\partial P)_{T,V=Vo}$. The intrinsic difficulty with this approach is that different expressions for $\Im(V)$ result in different expressions for B_0 with the end result that the various estimates must intrinsically disagree. For example, the Murnaghan EOS is equivalent to the assumption that the bulk modulus is exactly linear in the pressure,

$$B_{Murnaghan} = B_0 + B_0'(P - P_0). \tag{33}$$

In contrast, all other relations require the bulk modulus to be nonlinear in the pressure. In the Tait model, a linear term is multiplied by a pressure dependent volume,

$$B_{Tait} = \frac{V}{V_0}[B_0 + B_0'(P - P_0)], \qquad \textbf{(34)}$$

while the Birch model is made nonlinear by means of an additive term.

$$B_{Birch} = \frac{5}{3}[P - P_0] + B_0\left(\frac{V_0}{V}\right)^{7/3}. \qquad \textbf{(35)}$$

Clearly, the bulk moduli deduced from these differing models are inequivalent.

The inequivalence of these models motivated the use of a simulation study[35] to examine how reliably B_0 could be estimated under idealized conditions using the expressions in Table 6.3. That study produced several observations of interest to data evaluation. Using idealized data to which a normally distributed error component was subsequently added either to the volume or the pressure, the study concluded:

(a) The Birch EOS worked well only when the idealized data were generated by the Birch EOS. In that case, the other model expressions did well also. The converse, however, was not true. The Birch EOS performed poorly in all other cases in the study.

(b) Models other than the Birch EOS determined B_0 within 10 % of the ideal value when the volume was known within 0.9 % (*i.e.*, the lattice parameter was known within 0.3 %), or the pressure was known within 4 %.

(c) When the uncertainty in the lattice parameter was greater than 3 %, only the order of magnitude of the estimate was reliable.

Consequently, estimates of the bulk modulus obtained by means of the Birch EOS should be treated with some caution, and preference with respect to credibility should be given to the other models. In this respect, it should also be noted that the Birch–Murnaghan EOS reduces identically to the Birch EOS when the fitting parameter B_0' is constrained to be exactly 4. This constraint sometimes is applied in the literature to simplify the least squares fitting routine. In this particular case, identifying the expression as the Birch–Murnaghan EOS should be treated as a misnomer, and it should be recognized that the reliability of the result is merely that of the Birch EOS.

6.3.2.3 Interpreted Parameters

{***Example:*** Creep deformation}

Many semiempirical models describe the net outcome of a complex process in terms of a small number of the independent variables, such as temperature or pressure. At the atomic or molecular scale, a material may be undergoing numerous parallel and sequential interactions distributed inhomogeneously throughout the material. However, in many cases, the macroscopic behavior of the material may be viewed as a statistical average of the accumulated microscopic events. In such cases, a semiempirical model, with perhaps a few adjustable parameters, can form a useful representation of the average response of the material to changes in the control parameters.

When semiempirical models are used in this manner, it is not unusual that some of the adjustable parameters in the model may be interpreted as characteristics of the physical mechanisms assumed to be at work in the material. Activation energies often are used in this manner. These interpreted parameters, in turn, provide a useful means of classifying and comparing the behaviors of materials subjected to similar conditions.

Creep deformation, for example, can be described by models of this type.[36] In the absence of creep, a tensile stress, σ, applied to the end of a rod of length, L_0, will cause the rod to stretch to establish a new mechanical equilibrium length, $L(\sigma)$. Once equilibrium is established, the length remains constant if the applied stress is unchanged, *i.e.*, the strain at time, t, is $\epsilon(\sigma,t) = (L(\sigma,t) - L_0)/L_0 = \epsilon(\sigma,0)$. When creep deformation occurs, $\epsilon(\sigma,t)$ generally increases with time.

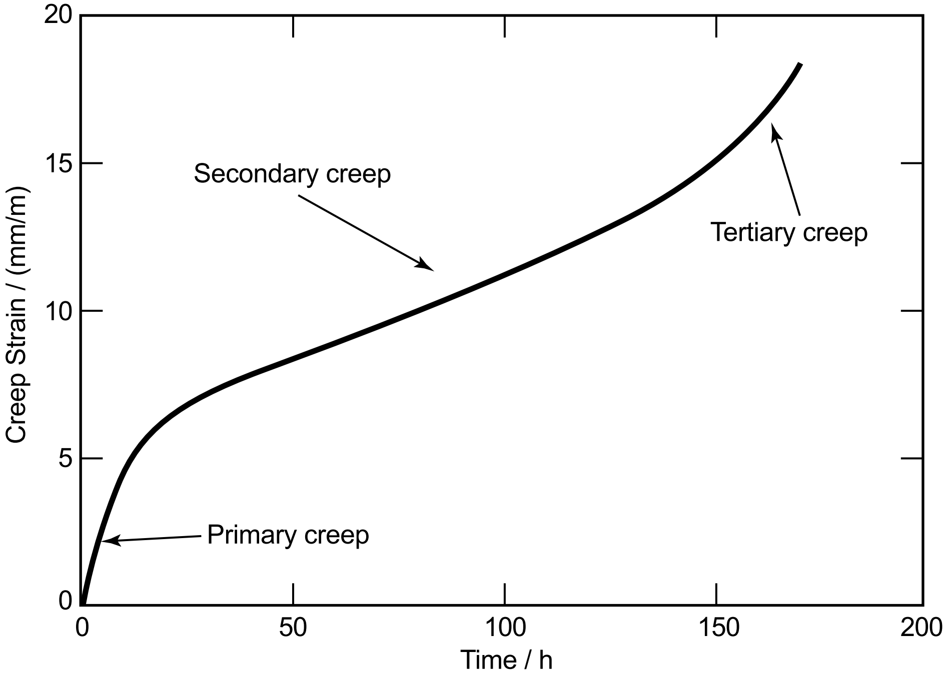


Figure 6.6. *Schematic of a typical creep curve (strain* vs. *time) showing three distinguishable regions termed, respectively, primary, secondary, and tertiary creep.*[37]

For polycrystalline materials, a graphical plot of an isobaric (constant σ) strain, $\epsilon(\sigma,t)$, as a function of time typically exhibits a nonlinear curve, Figure 6.6, consisting of three distinguishable regions termed, respectively, primary, secondary, and tertiary creep.[37] The strain rate in secondary creep (variously termed the secondary creep rate, the steady state creep rate, and the minimum creep rate) is most often the focus of attention in creep studies because the useful lifetime of a material undergoing creep deformation is related to this particular rate.

When diffusion is responsible for the creep behavior, either in the form of dislocation movement[38] or material transport along grain boundaries,[39, 40] the Norton model[41] is commonly used to described the secondary creep rate.

$$\frac{d\epsilon_{Dif}}{dt} = A\,(\sigma/\sigma_0)^n\,(g/g_0)^m\,e^{-Q/RT} \qquad \textbf{(36)}$$

where A is an amplitude factor; σ_0 and g_0 are fixed scale factors defining, respectively, the unit of stress and the unit of grain size; n is the stress exponent; g is the grain size; m is the grain size exponent; Q is the apparent activation energy; $R = 8.31451(7)$ J mol^{-1} K^{-1} is the molar gas constant; and T is the absolute temperature (*i.e.*, the temperature on the Kelvin scale). An example of the application of this expression is shown in Figure 6.7.[27] Note that when only a single batch of a material is considered, the grain size factor is effectively constant. In that case, the grain size factor is effectively absorbed into the amplitude factor, and only the dependence on temperature and applied stress are considered.

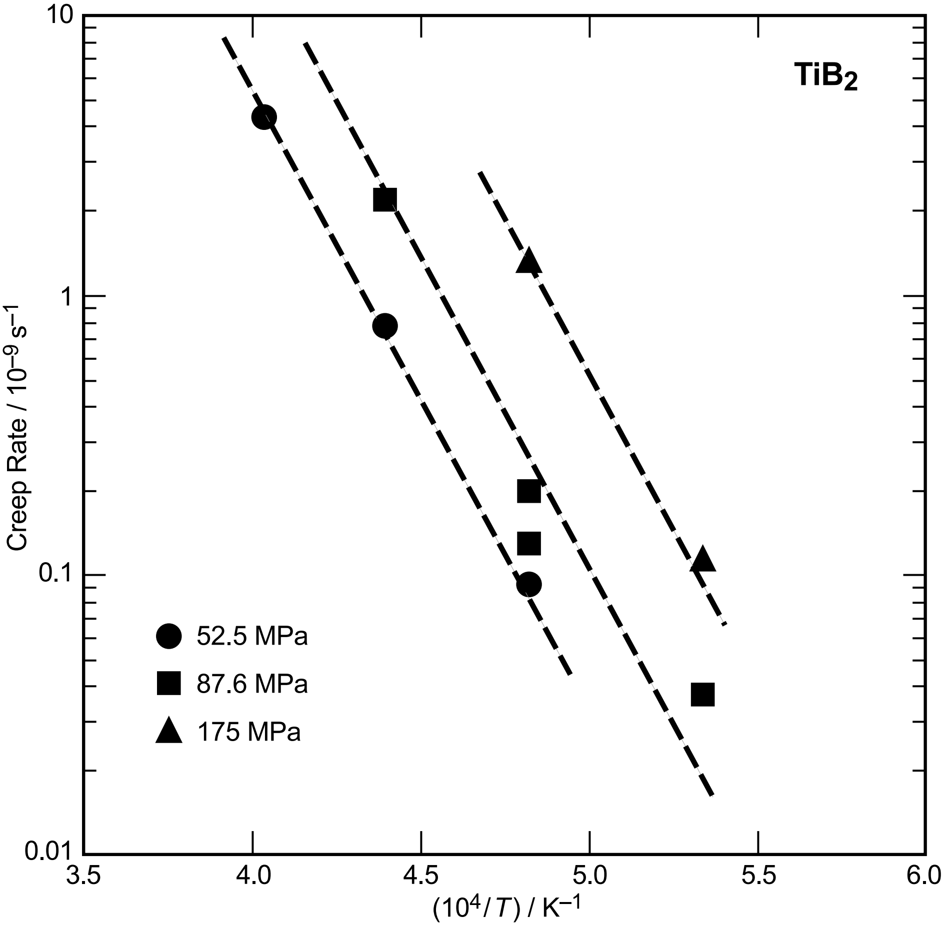
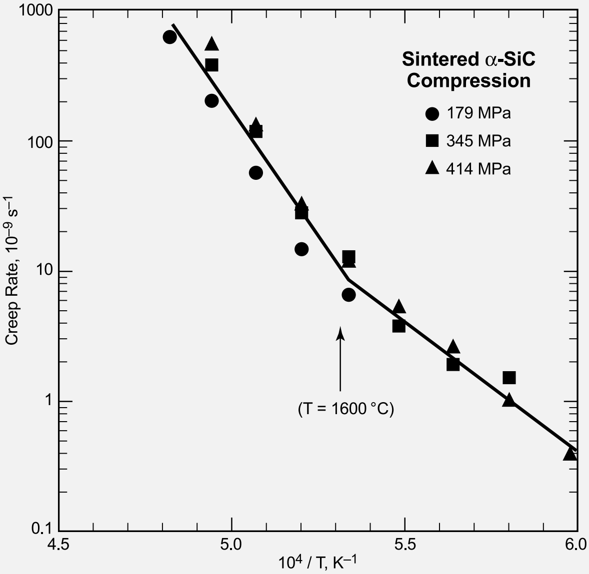


Figure 6.7. *Flexural creep rate of TiB$_2$ as a function of inverse temperature for various values of applied stress. The dashed lines show the fit of Equation (36).*[27] *[Data: See* Additional Source References, *Figure 6.7.]*

Activated Processes

Many physical phenomena have thresholds, usually with respect to temperature, denoting the perceptible onset or alteration of the phenomena. For thermally activated processes, such as creep deformation, the temperature dependence of the process rate, Þ, often can be described by a multiplicative exponential factor, $Þ \sim \exp[-\beta/T]$. In this case, a plot of log(Þ) *vs.* $(1/T)$, with all other variables held constant, exhibits a straight line whose slope determines the value of β. In the example of creep deformation, the parameter, β, is written as Q/R, where R is the molar gas constant. The quantity Q then has units of energy per mole and is usually interpreted as the activation energy for the process.



The interpretation of Q as an activation energy assumes implicitly that there is a specific mechanism or process that accounts for the observed material behavior. If there is a change in the physical mechanism, then there is likely to be a change in the associated activation energy. If the change in mechanism is sufficiently abrupt, the change will be manifest as a change in the slope of the apparent trend line in the plot of ln(Þ) *vs.* $(1/T)$. An example of this behavior is illustrated in the figure which shows creep data for a sintered α-silicon carbide. The abrupt change in slope at 1600 °C indicates that a low temperature mechanism with an activation energy of 442 kJ/mol is dominant in this material for $T \leq 1600$ °C, while a different process with a much higher activation energy, 944 kJ/mol, dominates for $T > 1600$ °C.

The temperature dependence in this expression is captured entirely in the exponential factor, $e^{-Q/RT}$, which is a very common representation for a thermally activated process. In isobaric studies for a single batch of material, a plot of the logarithm of the creep rate at various temperatures

$$\ln\left(\frac{d\epsilon_{Dif}}{dt}\right) = \ln[A\,(g/g_0)^m\,(\sigma/\sigma_0)^n] - (Q/R)\,\frac{1}{T} \tag{37}$$

will be linear in the reciprocal temperature. The activation energy, Q, clearly is determined by the slope of such a plot. However, in the practice of determining Q in this manner, there is potentially a point of confusion, a pitfall into which many studies have fallen. It is not unusual for studies of the temperature dependence to be conducted at several values of the applied stress, in which case Q might be determined for each value of the stress. When this practice is followed, it should be recognized that the model of diffusive creep given by Equation (36) is ***not*** being applied *per se*. Rather, the modified expression

$$\frac{d\epsilon_{Mod}}{dt} = A\,(\sigma/\sigma_0)^n\,(g/g_0)^m\,e^{-Q(\sigma)/RT} \tag{38}$$

is used. The significance of this distinction is that in the modified expression, the stress dependence is no longer a power law. Similarly, applying the Norton model independently to data obtained at different temperatures leads to an exponent *n(T)* rather than the constant *n*, resulting again in a stress dependence that is not a simple power law.

As it happens, the power law dependence of the isothermal strain rate on the applied stress is an important distinguishing feature of the diffusive model of creep and serves as the characteristic signature of diffusion creep. In a log–log plot of creep rate against applied stress,

$$\ln\left(\frac{d\epsilon_{Dif}}{dt}\right) = \ln[A\,(g/g_0)^m\, e^{-Q/RT}] + n\ln(\sigma/\sigma_0) \tag{39}$$

the power law dependence results in a straight line with slope n. It has been observed that for a material transport mechanism,[39, 40] $n \approx 1$, while for dislocation controlled creep,[38] n typically is in the range from 3 to 6. Consequently, the stress exponent may form a useful characteristic in classifying long-term material behavior.

Rather generally, the values of the parameters, n and Q, form a basis for the comparison of material performance under creep conditions. A larger value of the stress exponent is indicative of a material that is more susceptible to creep under an applied stress, while a higher activation energy is indicative of a material that is more resistant to creep at a given temperature. Consequently, these parameters may have useful applications in materials selection exercises.

In recent work, it has been recognized that the tensile creep rates of some materials, such as polycrystalline silicon nitride, Figure 6.8, are not well described by the diffusion model.[42] In particular, a power law dependence on stress does not appear to be appropriate for these materials, and there does not appear to be a significant dependence on grain size. Instead, the tensile creep rate is strongly correlated with the formation of discrete cavities in the material as the material deforms. These cavities typically occur at multigrain junctions where grains may more readily separate under tensile stress and where intergranular phase materials may more readily diffuse to accommodate the formation of a cavity.

When cavitation controls the creep behavior, the dependence of the strain rate on the applied stress is quite distinct from that of the diffusion model.[42]

$$\frac{d\epsilon_{Cav}}{dt} = A\,(\sigma/\sigma_0)\, e^{\psi\sigma}\, e^{-Q/RT} \tag{40}$$

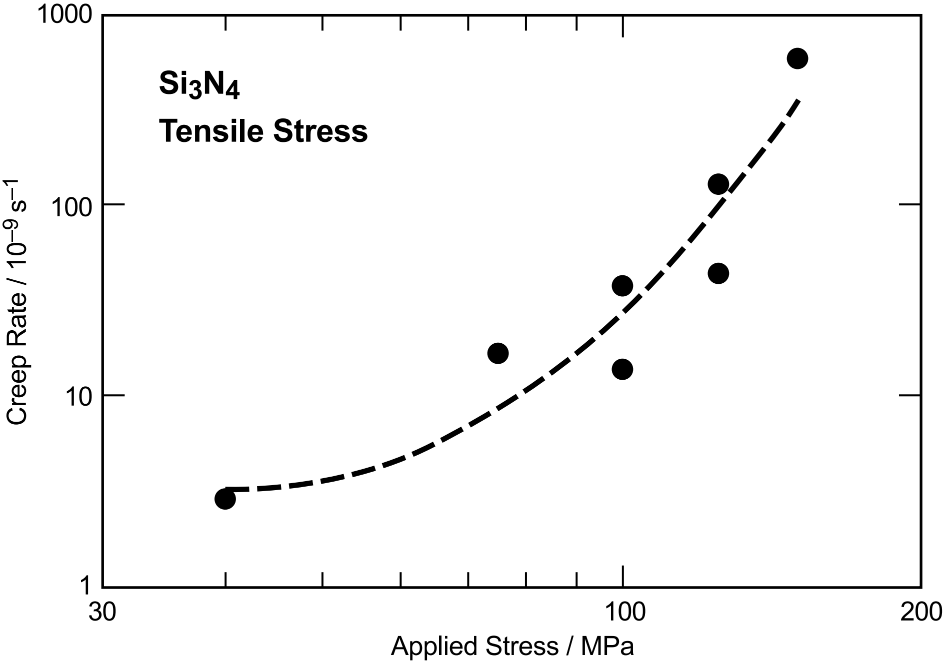


Figure 6.8. *Tensile creep of polycrystalline silicon nitride, showing a stress dependence that is not well described by the diffusion model.*[42]

The parameters, ψ and Q, for the cavitation model serve functions similar to those of the parameters, n and Q, in the diffusion model and may be useful in materials selection exercises in the same manner. Note, in particular, that a plot of the logarithm of the creep rate against the logarithm of the applied stress

$$\ln\left(\frac{d\epsilon_{Cav}}{dt}\right) = \ln(A\, e^{-Q/RT}) + \ln(\sigma/\sigma_0) + \psi\,\sigma \tag{41}$$

will exhibit a nonlinear curve when this model is appropriate, as in Figure 6.8, because the term linear in σ changes much more rapidly than the logarithmic term, $\ln(\sigma/\sigma_0)$. For that same reason, a log–linear plot, logarithm of creep rate against linear applied stress, will be approximately linear. Consequently, in the context of data evaluation, these two plots together provide a convenient means of distinguishing between the diffusion model and the cavitation model.

The distinction between these models becomes even more convincing when data over a large range of temperature and applied stress can be examined, as in Figure 6.9.[42] In this example, the diffusion model is clearly an inadequate representation of the simultaneous dependence of the creep rate on temperature and applied stress, while the three-parameter cavitation model adheres faithfully to the trends of the data over the entire range.

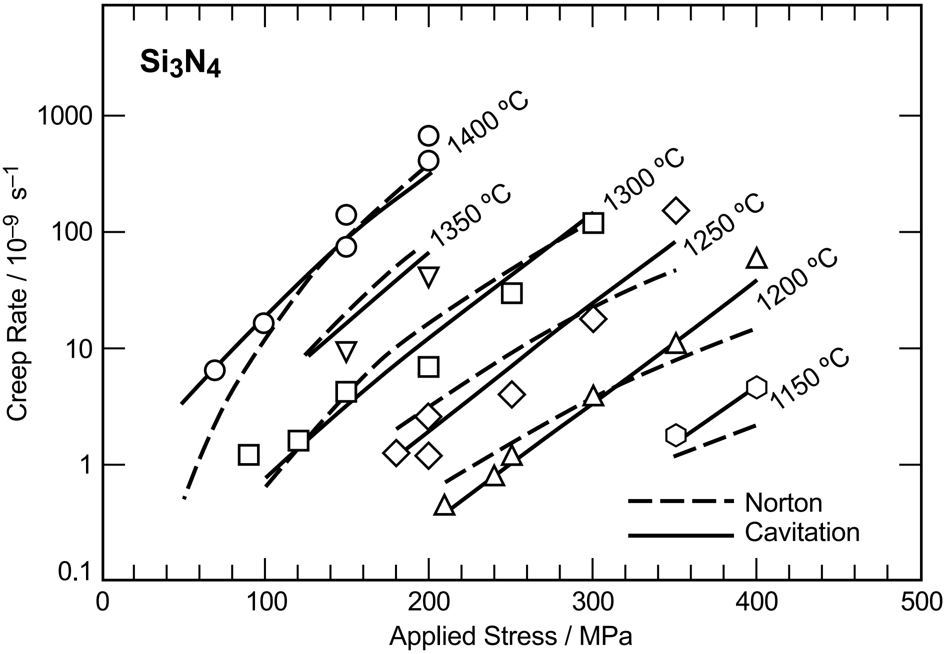


Figure 6.9. *Tensile creep of polycrystalline silicon nitride over a large range of temperature and applied stress, showing the greater suitability of the cavitation model.*[42]

6.3.2.4 Procedural properties

{***Example:*** Indentation size effect, Meyer's law}

Correlations and semiempirical relations have an especially important role to perform in understanding the measurement results for procedural properties. It will be recalled from Chapter 2 that the quantitative values obtained for procedural properties depend intrinsically on the details of the specific measurement procedures used in their determination.

The hardness of a material[43] is perhaps the most pervasive example of a procedural property. Intuitively, materials that yield less when you press against them are harder. This qualitative notion of hardness can be quantified by specifying how to press against the material and how to measure the material's response. The quantified results, in turn, can be used to verify the consistency of a material production or a heat treatment process or to rank a collection of materials according to their relative hardness values. The broad utility of hardness measurements in quality control and material characterization has led to applications ranging from cutting tool bits, dies, and seals to dental restorations, bone implants, and to a wide variety of other industrial, biomedical, and engineering uses. Accommodating this variety of applications are numerous measurement procedures. While the definitions of these procedures are relatively straightforward, their applications have several features of interest to data evaluation.

In the subclass of hardness measurements known as indentation tests, an object, called an indenter, is pressed into a locally flat, polished surface of a specimen. The load applied to the indenter is chosen to be sufficiently large that the outline or impression of the indenter remains in the surface of the specimen when the indenter is removed. The ratio, F/A, of the applied force or load, F, and a measure of the area of the residual impression, A, provides the quantitative value of the hardness.

The simplicity of this definition is not without its pitfalls. The load must be sufficiently large to produce an impression. When the load is sufficiently small, the interaction of the indenter and the specimen may be entirely elastic, and no impression will be formed. An impression will be formed only when the applied load is sufficient to cause plastic deformation in the specimen. The plastic response of the specimen, however, will depend on the shape of the indenter and the brittleness of the surface material. Indenters of different shapes applied in otherwise identical manners result in different hardness values because the force vectors, $\boldsymbol{f}_{\text{indent}}$, resolve differently with respect to the normal to the surface. Consequently, the work done by the indenter, W_{indent}, is different for indenters of different shapes.

$$W_{\text{indent}} = \int \boldsymbol{f}_{\text{indent}} \cdot d\boldsymbol{x}_{\text{indent}} = E_{\text{elast}} + W_{\text{impres}} \qquad \textbf{(42)}$$

The brittleness of the material affects the measured value because the stress intensities differ along the points of application of the indenter. If the stress intensity is sufficient to generate cracks (at an apex of the indentation, for example), then the irreversible work done by the application of the indenter is divided between the formation of the impression and the generation of cracks away from the impression.

$$W_{\text{indent}} = \int \boldsymbol{f}_{\text{indent}} \cdot d\boldsymbol{x}_{\text{indent}} = E_{\text{elast}} + W_{\text{impres}} + W_{\text{crack}} \qquad \textbf{(43)}$$

Further, different measures of the area of the impression (actual *versus* projected surface areas, for example) clearly also affect the numeric hardness values.

A more subtle concern, inherent to all procedural properties, can be expressed as follows in the case of hardness. If a load F produces an area A, does a load $2F$ produce an area $2A$? If the answer is "no," then the quantitative definition of hardness will be useful only with additional constraints or with additional understanding of the relation between A and F. Such is the case, for example, in the results shown in Figure 6.10 for a silicon nitride material.[44] This situation, often called the indentation size effect, occurs for hardness because the procedural definition involves both an independent variable, F, and a response variable, A, which is itself a function of F.

In early studies of indentations,[45] the indentation size was often found to be related to the applied load by a power law, often called the Meyer Law, such that

$$F = \zeta\,(d/d_0)^{\eta} \qquad \textbf{(44)}$$

where d is a linear dimension of the impression, d_0 is a fixed scale factor defining the unit of length, and ζ and η are fitting parameters.

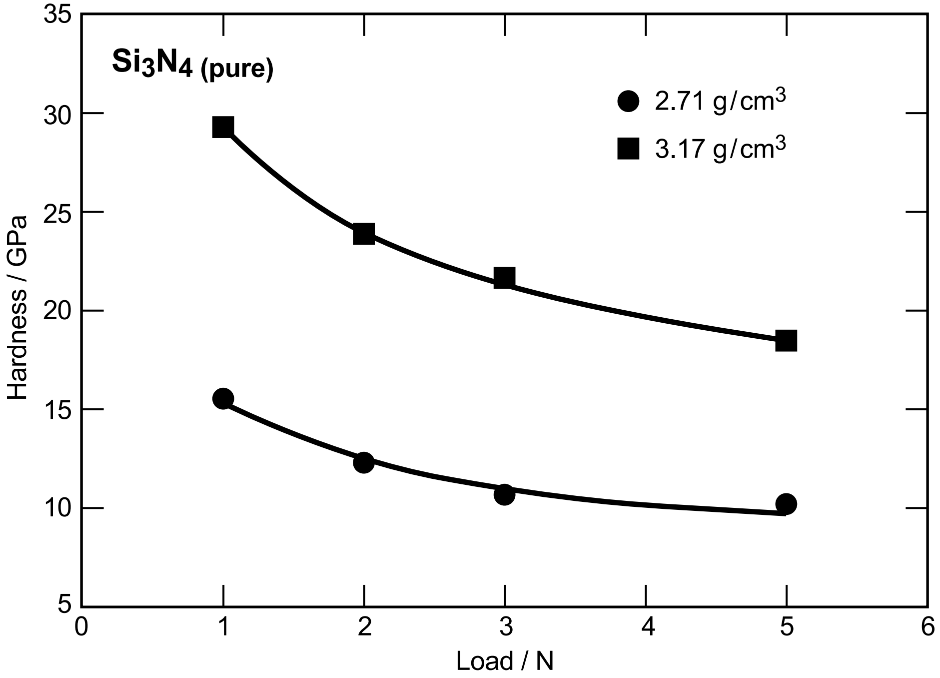


Figure 6.10. *The indentation size effect for a polycrystalline hot isostatically pressed silicon nitride.*[44]

For ceramic materials, the exponent is usually greater than one ($\eta > 1$); hence, to double the linear dimension of the impression would require more than double the load. With the latter observation, it may be anticipated that the value of the Meyer exponent may depend on the microstructure of the material, particularly the porosity. Less force should be required to produce an impression of a given size when the material has a greater porosity. This effect is seen in Figure 6.10 where the hardness is smaller when the density is lower. Consequently, the value of η should be smaller when the porosity is larger. Exactly this result has been observed, for example, in a study[46] combining the results for numerous specimens of silicon nitride, Figure 6.11.

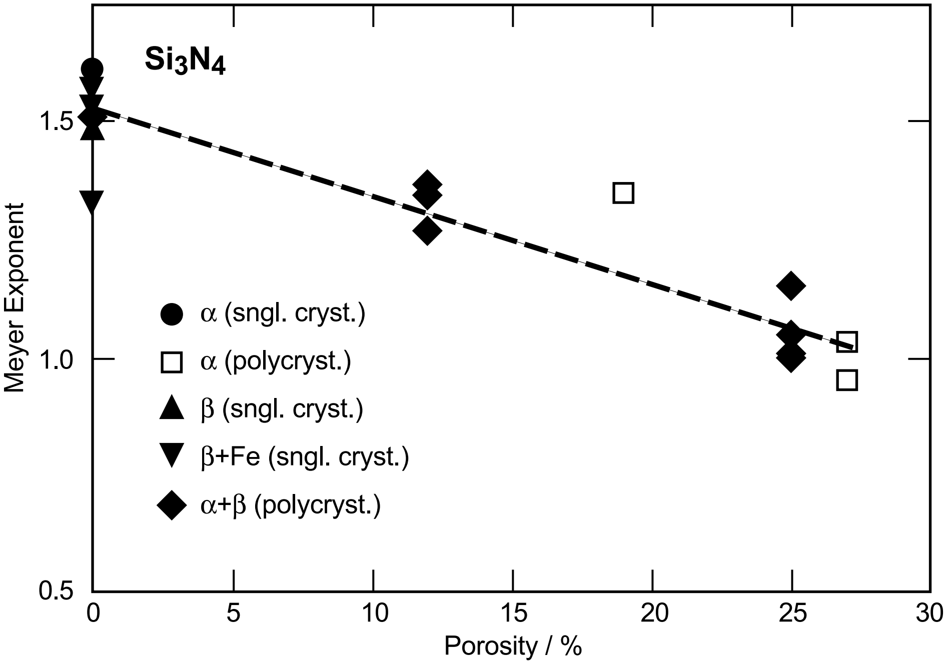


Figure 6.11. *The dependence of the Meyer exponent on specimen porosity for a collection of seventeen specimens of single crystal and polycrystalline silicon nitride.*[46]

Rather than allowing a fitting parameter to become a function of porosity, it may be advantageous to preserve the Meyer relation and to account explicitly for the dependence on the independent variables density, grain size, and temperature. If the dependence on the independent variables is amenable to the separation of variables, then a useful expression consistent with the Meyer law might be[27]

$$H = H_0 \left(\frac{\rho}{\rho_0}\right)^{h_1} \left(\frac{g}{g_0}\right)^{h_2} \left(\frac{F}{F_0}\right)^{h_3} e^{-(T-T_0)/\tau} \tag{45}$$

where H_0, T_o, τ, h_1, h_2, and h_3 are adjustable parameters, and ρ_0, g_0, and F_0 are fixed scale factors.

The utility of this model can be illustrated by its application to a study on the hardness of silicon nitride.[44] This particular study reported results for silicon nitride produced using four different starting powders, three different sintering aids, and several different processing and post-processing conditions. The specimens were viewed as two groups, one group with fractional density $\rho/\rho_o \lesssim 0.85$ and one group with $\rho/\rho_o \gtrsim 0.97$. One exception to this grouping occurred for a specimen with $\rho/\rho_o = 0.950$ which was prepared from a starting powder having a much larger grain size than the other starting powders. The study succeeded in showing, as in Figure 6.12, that the specimens in the group with higher fractional density generally had higher hardness values than the specimens in the group with lower fractional density.

Closer examination of Figure 6.12, however, raises a further issue worthy of discussion, in addition to the issue of grain size. Within each group, the quantitative differences between results for a given load are larger and more systematic than would be attributed to measurement uncertainty. Consequently, it might be expected that the ranking within each group would be similar to the ranking between groups; *i.e.*, specimens with higher fractional density should have higher hardness. In this respect, the results do not, at first, appear to be quite sensible.

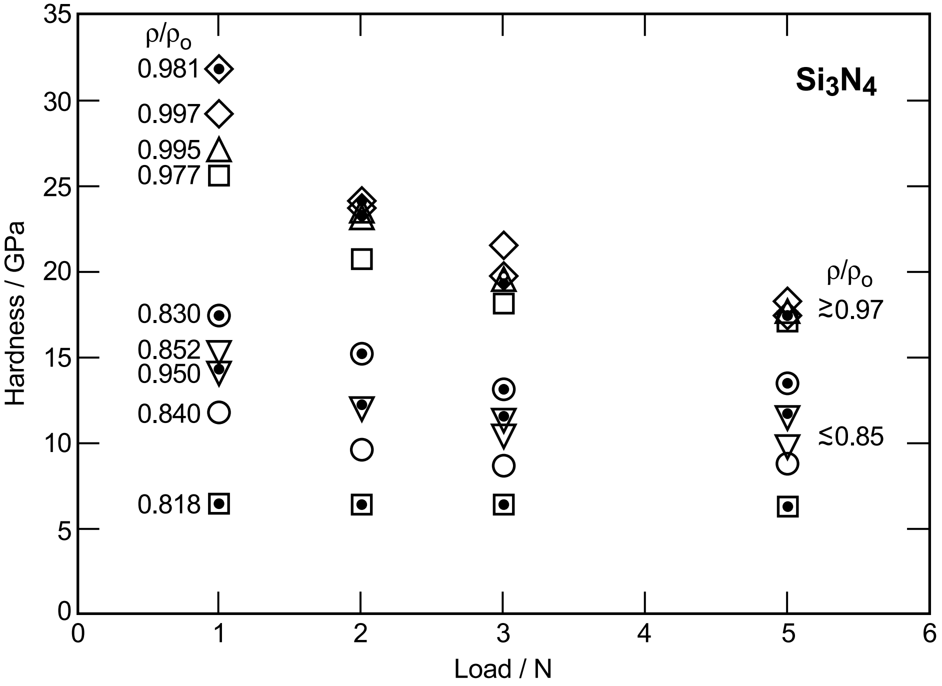


Figure 6.12. *The Vickers hardness of polycrystalline hot isostatically pressed silicon nitride varies with both indentation load and specimen density.*[44]

With reference to Equation (45), we see that there are two considerations yet to be applied. First, Equation (45) assumes that the specimens are of the same composition. There is no reason, *a priori*, to expect specimens of different composition to behave quantitatively alike. Likewise, because hardness is a measure of surface properties, post-processing oxidation of the surface can be expected to alter the quantitative results for the same specimen. Additionally, Equation (45) indicates that variation of hardness with grain size is to be expected.

While no quantitative grain size information was available in this study, the observation that the specimen with $\rho/\rho_o = 0.950$ had a larger mean grain size allows this result to be compared qualitatively with other studies. Given that the hardness for this particular case of higher density was comparable to the results for the lower density group, the implication is that the hardness may decrease with increasing grain size. This qualitative behavior has been noted for other high-hardness ceramics such as titanium diboride.[27] Consequently, this case for silicon nitride is at least consistent with results for other materials.

More convincingly, we can separate the remaining materials into subsets processed from the same starting powders and having the same mass fraction compositions. For each subset, the initial grain size distribution is, by design, a constant across all the specimens in the subset. The additional assumption required here is that the subsequent grain-size distributions, resulting from the hot isostatic pressing cycles that produced the different degrees of densification, do not differ greatly or significantly among the final specimens.

With that assumption, there remain two sets of results that can be examined in the context of Equation (45). One set consists of undoped specimens, and the other has specimens that were doped to have mass fraction compositions with 2 % Y_2O_3 and 1 % Al_2O_3. Application of Equation (45) to each set separately, with the assumption of constant grain size, produced the smooth curves in Figure 6.13. In each case, ρ_o was taken to be the theoretical density of the specified composition, accounting for the presence or absence of sintering aids. As can be seen in Figure 6.13, the results of this data evaluation exercise do, indeed, permit the rankings of the data to be understood both qualitatively and quantitatively.

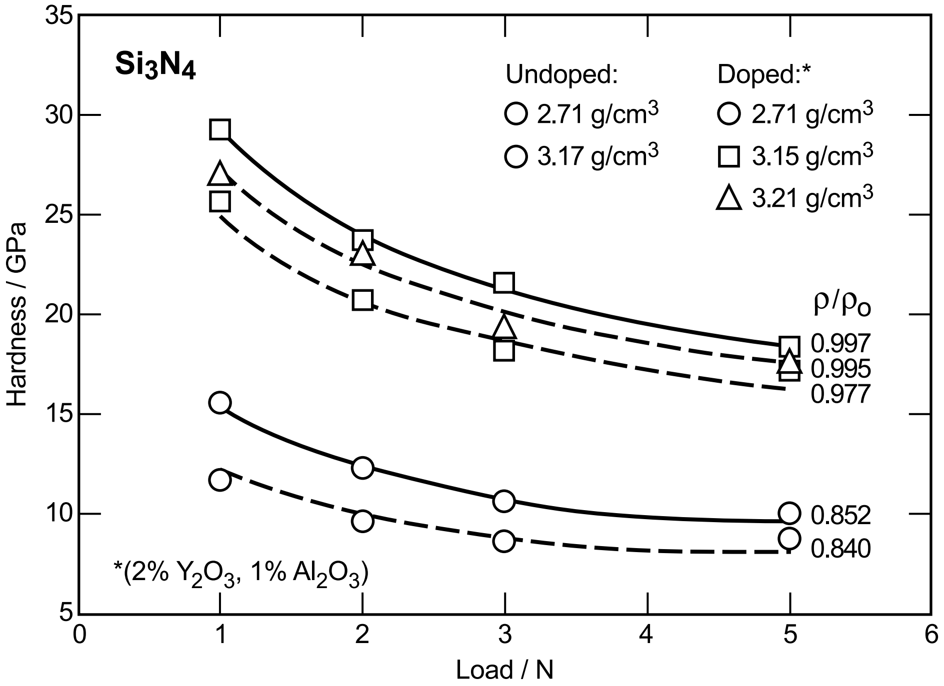


Figure 6.13. *Reduction and analysis of the data from Figure 6.12 in accordance with Equation (45).*

6.3.2.5 Response Dependent Properties

{***Example:*** Fracture toughness, Palmqvist cracks *vs*. median cracks}

Procedural properties may be subject to limitations that arise implicitly when a designated measurement procedure anticipates a particular response from the material, *i.e*., the procedure itself becomes dependent on the material’s response to the procedure. This unusual situation occurs, for example, in measurements that require the generation of a crack using an indentation technique.

Most materials can sustain the presence of a small number of minor cracks without loss of functionality. However, fracture failure may occur, particularly in brittle materials, when the extension of a crack in a solid body becomes unstable. Consequently, several procedures have been developed to measure the resistance of a material to crack extension. The material property that assesses this resistance is called fracture toughness. In principle, the work required to extend a crack should be determined by the energy required to create the necessary new surface area and, therefore, fracture toughness should be a well-defined material property. In practice, however, procedural definitions more amenable to direct application in experiments have been adopted. As a result, attention must be given to the method used in any estimate of toughness.[47,48]

To determine fracture toughness using an indentation technique, the indenter must be pressed into the material with a load sufficient to generate cracks beyond, and away from, the remnant impression of the indenter. Qualitatively, shorter cracks for a given load imply a

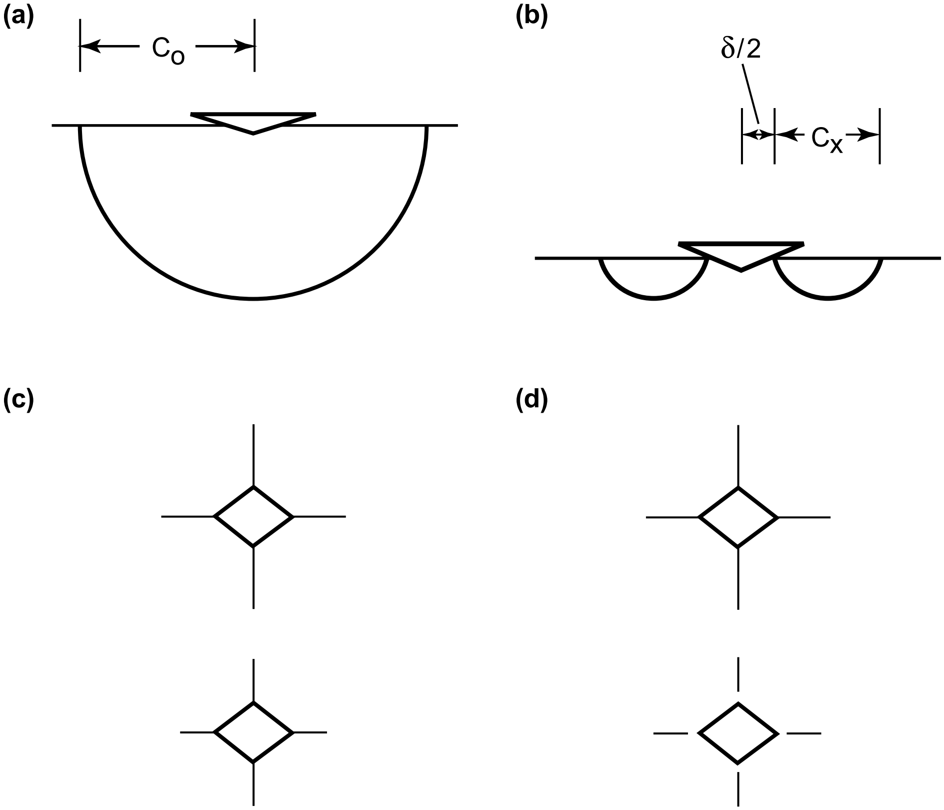


Figure 6.14. *Schematics of median and Palmqvist crack formations. Side views: (a) median, (b) Palmqvist. Top views, showing indentations as indented (upper) and after polishing (lower): (c) median, and (d) Palmqvist.*

greater toughness. However, to quantify this measure of fracture toughness, it is not sufficient to measure the size of the crack. It is also necessary to determine the type of crack that has been produced by the indentation.

There are principally two types of cracks, illustrated schematically in Figure 6.14, that need to be considered. The more common type of crack, known as a median crack, is shown in Figure 6.14(a). Median cracks form beneath the indenter along the diagonals of the impression and extend into the bulk of the material. A rather different crack formation is shown in Figure 6.14(b). These cracks extend only outward from the corners of the impression and are known as Palmqvist cracks. In both cases, a top view of the indented surface appears to indicate a crack extending from each apex of the impression. However, the two types of cracks can be distinguished experimentally by polishing the surface after indentation. After polishing, median cracks, Figure 6.14(c), are reduced in size but remain attached to the impression. In contrast, the Palmqvist cracks after polishing appear to have separated from the impression, Figure 6.14(d).

If the indentation study is done as a function of load, then the two types of cracks can be distinguished also according to the load dependence. For Palmqvist cracks, the crack extension length, c_{x}, is proportional to the load,

$$c_x \sim F \tag{46}$$

while for median cracks, the crack size, $c_0 = c_{\mathrm{x}} + \delta/2$, is proportional to the two-thirds power of the load,

$$c_0 \sim F^{2/3} \tag{47}$$

such that the slope of $\log(c_{\mathrm{x}})$ *vs.* $\log(F)$ should be 1 for Palmqvist cracks, while the slope of $\log(c_0)$ *vs.* $\log(F)$ should be 2/3 for median cracks.

Only when the type of crack has been determined can the fracture toughness be computed from the appropriate expressions for the critical stress intensity factor, K_{Ic}.

$$K_{Ic}(Median) = \varsigma \left(\frac{E}{H}\right)^{1/2} \left(\frac{F}{c_0^{3/2}}\right) \qquad \textbf{(48)}$$

for median cracks,[49] and

$$K_{Ic}(Palmqvist) = \varkappa \left(\frac{E}{H}\right)^{2/5} \left(\frac{H\delta}{c_x^{1/2}}\right) \qquad \textbf{(49)}$$

for cracks of the Palmqvist type.[50] The numeric factors, ϰ and ς, have been determined empirically by averaging fitted values for a wide range of ceramics. The means and standard deviations were found to be 0.016 ± 0.004 for median cracks[49] and 0.018 ± 0.004 for Palmqvist cracks.[50]

When discrepancies arise among fracture toughness values determined by indentation tests, use of an inappropriate expression should be high on the list of suspected causes. A useful preliminary guide to the appropriate expression is provided by the ratio of the crack size and the indentation diagonal. It has been observed[50] for a variety of materials that the expression for Palmqvist cracks is often appropriate when $2c_0/\delta < 3$. Using the wrong expression for a given type of crack can result in an estimate of the fracture toughness that is incorrect by as much as a factor of 2.[44]

6.3.2.6 System Dependent Data

{***Example:*** Friction and wear}

In most considerations of materials properties, the measured characteristics are regarded as pertaining exclusively to the material. However, when different material bodies are allowed to interact, it is possible to define characteristics or properties that are meaningful only with respect to the assembly of interacting materials. The coefficient of friction of one material sliding against another is a classic example of such a property.[51, 52] The coefficient of friction is meaningful only when there is a complete specification of the interacting materials, the contact environment, the topological characteristics of the interacting surfaces, and the contact conditions, such as temperature, sliding speed, and contact stress. Properties of this nature are said to be system dependent.

All tribological properties are system dependent. Consequently, much effort has been made in the field of tribology to provide useful representations of the wear and friction behaviors of materials, and we may gain from that effort an indication of the considerations important to the evaluation of system dependent properties.

A primary objective in the study of system dependent properties is to identify what influence the intrinsic material properties have on the system dependent interactions. In this context, the focus of the analysis is often on the development of normalized measures of the material responses. The dimensionless wear coefficient, K_{W}, is a case in point.[53, 54]

$$K_W = \frac{V_W H}{F_n D_s} \tag{50}$$

where V_{W} is the wear volume, H is the hardness, F_{n} is the normal force acting between the surfaces, and D_{s} is the total sliding distance. This quantity is prone to having a very large measurement uncertainty because the total wear volume may be influenced by the topological changes at the wear contact as the test proceeds, including the shape of the contact, the stress distribution, the temperature gradient, and the presence of accumulated wear debris. Additional uncertainty arises from the value of the hardness, a procedural variable, whose value may depend on the stress level at the contact and the extent and nature of microcracking around the contact (see section 6.3.2.4 Procedural Properties).

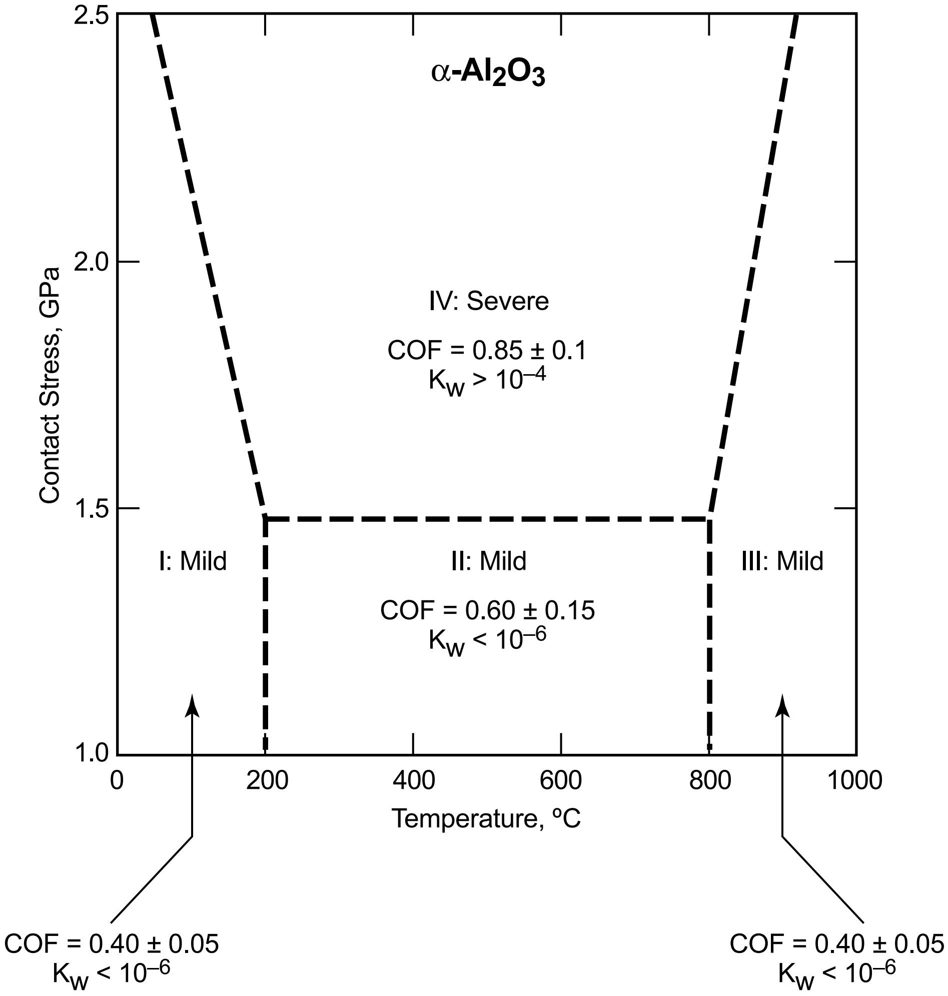


Figure 6.15. *A wear transition diagram illustrating the variation of the dominant wear mechanism depending on the tribological contact conditions.*[57]

In spite of this large numeric uncertainty, the order of magnitude of the wear coefficient has proven to be useful in classifying the wear behavior of materials into wear regimes distinguishing between conditions of mild and severe wear. When this measure of wear is coupled to the measurement of the coefficient of friction, it becomes possible to construct useful wear mechanism maps[55,56] or wear transition diagrams,[57] Figure 6.15, as a function of the operating conditions denoted by the contact temperature and stress. Such diagrams then can serve as a guide to the specification of acceptable operating conditions in tribological contacts and can help to avoid conditions of potentially excessive wear that may shorten the useful lifetime of the material components. In that respect, a potentially useful correlation between the coefficient of friction and the ratio of sliding speed to contact stress has been noted in the case of TiB_2,[58] Figure 6.16. A power law trend is clearly perceptible along each isotherm, while the data as a whole appear to separate into two temperature dependent clusters. The latter observation suggests the onset of a distinguishable tribological mechanism at elevated temperature, perhaps through the formation of B_2O_3 in the wear track.

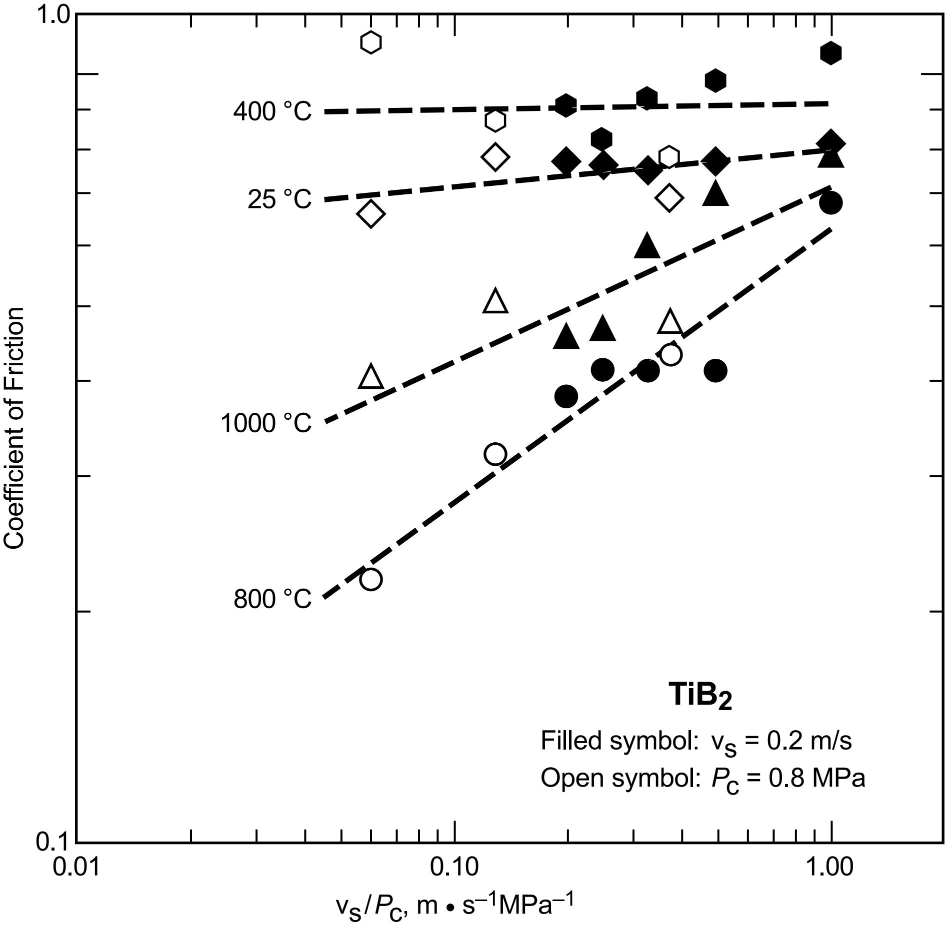


Figure 6.16. *Correlation of the coefficient of friction and the ratio of sliding speed to contact stress in the case of* TiB_2.[58]

6.4 Stage IV: Modeling (Issue: Predictability)

A set of property data for a given material may be said to form a representation of the behavior of that material. Numeric representation, however, does not constitute conceptual understanding, and it is the attainment of such understanding that forms the fundamental essence of materials science. An expression of a conceptual understanding of an observed material behavior is generally called a model. Models that may be expressed mathematically are especially pertinent to data evaluation because they form the basis for establishing or confirming the consistency of independently measured property values, the adherence to common trends, and the identification of exceptional behavior.

6.4.1 Derived Correlations

{***Example:*** Toughness *vs.* strength}

Most theories of material behavior focus on one particular aspect of an observed phenomenon and arrive at a relationship between that observation and one or more other characteristics describing or pertaining to the phenomenon. Such relations subsequently may form the basis of correlations among more readily measurable quantities or may assist in the interpretation of empirically observed correlations.

Linear fracture mechanics, for example, has a primary focus on the development and propagation of cracks in a brittle material.[59–63] An ideally brittle material is one that fractures as a result of the sudden, catastrophic propagation of a crack. Clearly, the factors controlling the propagation of the crack must include the stress at the tip of the crack and the strengths of the bonds that must be broken to extend the crack. The theory of linear fracture mechanics yields a general relationship among three factors: the critical stress intensity factor (commonly known as the fracture toughness), K_{Ic}, the fracture strength of the material, σ_{f}, and the size of the crack (or, more generally, the critical flaw), c_{o}, such that

$$K_{Ic} = Y \sigma_f c_o^{1/2} \qquad \textbf{(51)}$$

where Y is a dimensionless numeric factor that depends on the location and shape of the flaw. This relation plays a central role in understanding the fracture behavior of brittle materials. However, there is a subtlety that should be considered when this relation is applied.

Empirically, it has been observed that a plot of fracture strength against toughness often can be fit by a straight line, from which it is concluded that the flaw size is constant. This conclusion generally is not correct.[64] Properties such as fracture toughness and strength are not among the fundamental, independent variables of the material system. Rather, they are consequences of the interactions of the constituent particles of the material system, and, as such, they are themselves functions of other variables such as composition, bond strength, and microstructure.

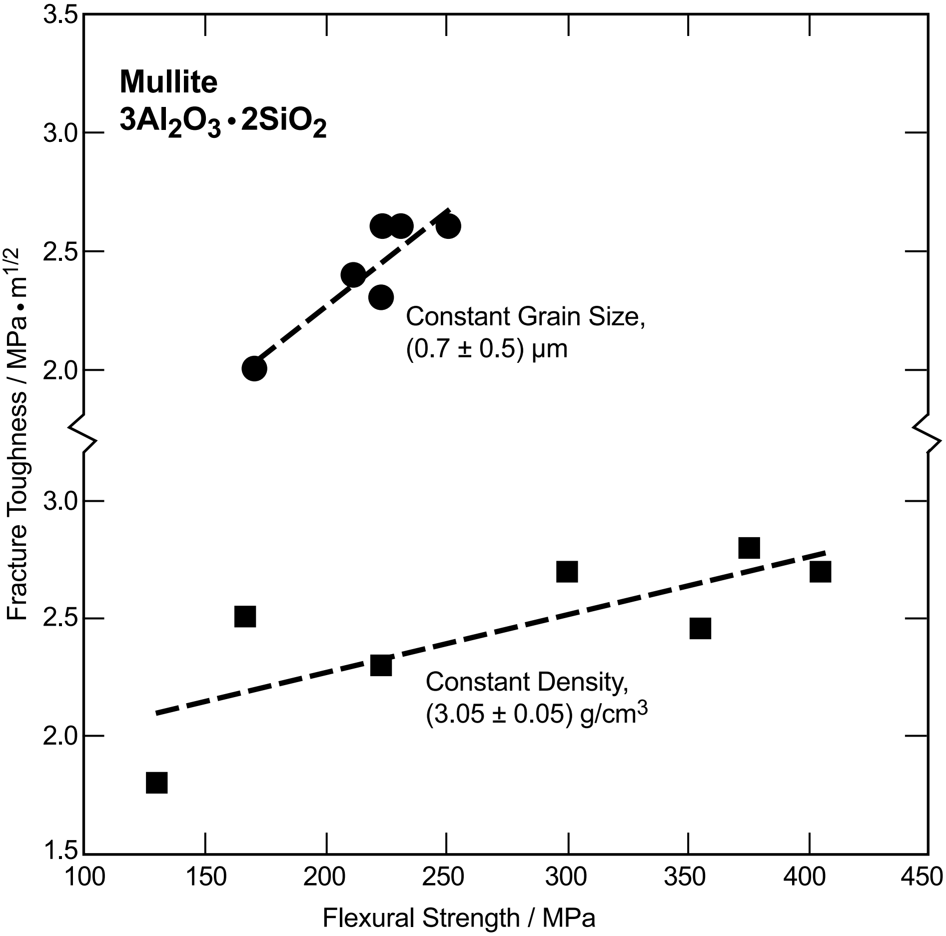


Figure 6.17. *The correlation of fracture toughness and fracture strength may differ under the conditions of constant grain size and constant density.*[64] *[Data: See* Additional Source References, *Figure 6.17.]*

Formally, we may assume the existence of a complete set of independent variables, $\{x_i\}$, which does not include K_{Ic}, σ_f, or c_o. If we then consider the variation of K_{Ic}, σ_f, and c_o with respect to the set of independent variables, it can be shown that for each x_k in the set $\{x_i\}$,

$$\left(\frac{\partial K_{Ic}}{\partial \sigma_f}\right)_{[x \neq x_k]} = Y c_o^{1/2} \left[1 + \frac{\sigma_f}{2 c_o} \left(\frac{\partial c_o}{\partial \sigma_f}\right)_{[x \neq x_k]} \right] \qquad \textbf{(52)}$$

in which the subscript, $[x \neq x_k]$, indicates that all independent variables except x_k are held constant. The significance of this derived relation is twofold. First, the variation of toughness with strength depends explicitly on the variation of the flaw size. Second, the variation of toughness with strength depends on which independent variable produces the variation in the properties. Thus, for example, the variations under the conditions of constant grain size and constant density are not necessarily the same, as seen in Figure 6.17. Further, if we impose the empirical observation that the plot of K_{Ic} varies linearly with σ_f, then we find explicitly that the flaw size is not constant, but rather varies as

$$c_o = \left(\Lambda_1 + \frac{\Lambda_2}{\sigma_f} \right)^2 \qquad \textbf{(53)}$$

where Λ_1 and Λ_2 are constants. Consequently, when evaluating data relating fracture toughness and strength, it is essential to distinguish the conditions under which the data were obtained and to be wary of conclusions dependent on constant flaw sizes.

6.4.2 Harmonic Theories

{***Example:*** Debye theory of specific heat}

Harmonic theories are well developed in the literature and are treated thoroughly in many text books that are widely available.[65, 66, 67] As such, the reader is likely to be well versed in this subject or will have ready access to thorough discussions of it. However, there are a few points that have a special relevance to the evaluation of materials property data, and an effort is made here to emphasize those points, but only with as much discussion as is needed to preserve the logical continuity of the topic.

In solid materials, the constituent atoms interact sufficiently strongly that their positions are relatively well localized within the volume of the material. Within crystals or the crystallite grains of polycrystalline materials, the atoms are localized to well-defined positions in periodic arrays. When an external static stress is applied to the bulk material, the resulting strain is manifest by the displacements of the atoms by a small amount from their unstressed equilibrium positions. Upon the release of the external stress, the atoms return to their normal positions. In a similar manner, the addition of thermal energy to the body is manifest by the displacement of the atoms in vibrations of relatively small amplitude about their equilibrium positions. When energy, whether thermal or mechanical, is transported through the body, the propagation of the energy is accomplished by the collective modes of these vibrations called phonons. The simplified picture of the solid material that evolves from these microscopic descriptions of the static and dynamic behaviors of the material is that of a collection of mass points interconnected by springs obeying an effective Hooke's law, *i.e.*, a collection of classical harmonic oscillators. It should not be surprising, then, that numerous theories of material properties have been based on various aspects of this schematic picture, more generally called the harmonic approximation.

For the evaluation of material property data, the most important application of the harmonic approximation is probably the Debye theory of specific heat. Einstein had established the utility of the harmonic approximation[68] by considering a collection of independent oscillators, all having the same frequency of oscillation. The Einstein model rather successfully accounted for the temperature dependence of the specific heat of relatively simple material compositions, such as copper and diamond, except at relatively low temperature. The difficulty with the Einstein model was that it considered only one mode of vibration and, therefore, did not distinguish between the case at high temperature, in which very high frequencies of vibration might occur, and the case at low temperature, in which only very low frequencies of vibration would be likely to occur.

Debye resolved this difficulty[69] by allowing all frequencies from zero up to an accessible maximum cutoff value to occur. To treat this frequency range, Debye assumed that the allowed vibrational modes were acoustic with a constant phase velocity; *i.e.*, the dispersion relation was analogous to that of light waves, [speed of sound] = [wavelength] × [frequency]. The cutoff frequency then was determined by requiring that the total number of allowed vibration modes was 3N, the number of independent vibrational modes of N point particles (*i.e*., particles lacking internal degrees of freedom) in a space of three dimensions. As fully derived in many introductory texts on statistical mechanics and solid materials, the resulting expression for the molar heat capacity in the Debye model, at constant volume, was found to be

$$C_V^{(M)} = 3\, N_A\, k_B\, f_D(\Theta/T) \qquad \textbf{(54)}$$

$$f_D(x) = \frac{3}{x^3} \int_0^x \frac{e^y}{(e^y - 1)^2}\, y^4\, dy \qquad \textbf{(55)}$$

where Θ is a parameter known as the Debye temperature defined in terms of the Debye cutoff frequency, ω_D, such that $k_B\Theta = \hbar\omega_D$, and $\hbar$ is Planck's constant divided by 2π. The theoretical estimate of the Debye temperature for a specimen of density ρ and molar mass M_W was found to be

$$\Theta = \frac{\hbar\, v_m}{k_B} \left(\frac{6\, \pi^2 N_A\, \rho}{M_W} \right)^{1/3} \qquad \textbf{(56)}$$

where v_m is the sound velocity. The dispersion relation of the original Debye model implies that the material is elastically isotropic. In practice, the velocities of the longitudinal and shear modes differ. To allow for this difference, v_m is taken as the mean sound velocity calculated as

$$\frac{3}{v_m^3} = \frac{1}{v_L^3} + \frac{1}{v_{S1}^3} + \frac{1}{v_{S2}^3} \qquad \textbf{(57)}$$

where the terms on the right side of the equation represent the one longitudinal mode and the two shear (a.k.a., transverse) modes.

At high temperature, Θ/T tends towards zero, and the Debye function easily is found to have the limit $f_D(0) = 1$. Consequently, the Debye molar heat capacity at high temperature is the classical Dulong and Petit limit, $3N_A k_B = 3R$ for a monatomic species. (For polyatomic species, see the discussion in the sidebar.)

Of particular interest to the evaluation of material property data is the limit at low temperature.

Specific Heats of Composites and Compounds

A composite material consists of multiple, but separable, phases. The total mass of the composite, M_c, is the sum of the masses of the constituent phases,

$$M_c = \sum_{i=1}^{N_{phases}} m_i$$

To raise the equilibrium temperature of the composite by 1K, the temperature of each constituent phase must be increased by 1K. Consequently, conservation of energy requires

$$C_{P,c} M_c \delta T = \sum_{i=1}^{N_{Phases}} C_{P,i} m_i \delta T$$

from which follows simply

$$C_{P,c} = \sum_{i=1}^{N_{Phases}} \mu_i C_{P,i}$$

where $\mu_i = m_i/M_c$ is the mass fraction of phase number i in the composite. It should be noted that a principal condition of this derivation is that the phases are separable. Interactions between the separable phases are assumed to contribute negligibly to the internal energy of the composite and, hence, may be ignored in the energy conservation relation. The same situation is approximately true for compounds, although the approximation is somewhat less reliable for compounds than for composites.

A compound is a single phase material consisting of multiple atomic species. The interactions between species are not negligible and may not be ignored. Consider, for example, the special case of a binary compound in which the structure of the material is *conceptually* separable into two interpenetrating sublattices of one pure species each. The internal energy of the compound, U_c, would consist of three terms,

$$U_c = U_1 + U_2 + U_{1,2}$$

corresponding to the internal energies associated with the two sublattice components, considered separately, and the energy from the interactions

Specific Heats of Composites and Compounds *(continued)*

between the two sublattices. If the interaction is favorable to the formation of a compound, then it would be expected that $U_{1,2}$ would reduce the total internal energy. Consequently, simple additivity of the atomic specific heats would be expected to yield an overestimate of the specific heat of the compound. For example, SiC at room temperature has a molar heat capacity of approximately 26.9 J/mol • K, while the additive contribution of the constituents would yield 28.5 J/mol • K. In this case, the additive approximation is approximately 6% higher than the measured value. In a survey of 75 compounds, the ratio of the composed value to the measured value ranged from 0.9 to 1.6 with the average value being 1.15 with a standard deviation of 0.14.

In a similar manner, it is often assumed that the vibrations of the atoms of a compound at sufficiently high temperature may be treated as independent and uncorrelated oscillations, such that the extended law of Dulong and Petit (sometimes known as the Kopp–Neumann rule for compounds) would be expected to be obeyed approximately by compounds. Thus, a compound of the form A_pB_q consisting of p moles of A and q moles of B would be expected to have a high temperature limit of approximately $p \cdot 3R + q \cdot 3R = (p+q) \cdot 3R$. For Al_2O_3 at 1500 °C, $C_p(Al_2O_3) = 1330\ J\ kg^{-1}\ K^{-1}$ yielding $C_p^{(M)}(Al_2O_3)/(2+3) \approx 3.3R$, in fair agreement with this expectation.

$$C_V^{(M)} = \frac{12\,\pi^4}{5} N_A\, k_B \left(\frac{T}{\Theta}\right)^3, \ for\ T \ll \Theta \qquad \textbf{(58)}$$

The proportionality to T^3 in the low temperature limit often is used as a means of evaluating the Debye temperature and may be compared for consistency with the theoretical estimate given by Equation (56). For pure elements such as Al or Cu, the estimates based on the elastic measurements, Equation (56), and the heat capacity measurements, Equation (58), tend to be in good agreement.

For more complex materials, the more detailed analysis of lattice dynamics[70] indicates that the Debye approximation does not adequately represent the frequency dependent dispersion relation and, hence, that the elastic and calorimetric estimates of the Debye temperature may differ appreciably.

A further consequence of the approximate nature of the Debye model is the observed temperature dependence of Θ. In the Debye model, Θ(T) = constant. In practice, however, Θ usually has a minimum at low temperature and rises approximately asymptotically to a constant value at elevated temperature.

6.4.3 Heuristic Theories

{***Example:*** Weibull distribution}

Materials are sufficiently complex bodies that the derivation of an appropriate theory from fundamental principles often is untenable for realistic material compositions. Conversely, simplifying assumptions applied to make a model mathematically tractable often result in material constraints that are unrealistic. A pragmatic alternative to these two extremes may be possible when experimental observations can be transcribed directly into a descriptive model of the material's behavior. Such descriptive modeling fulfills an intermediate role between fundamental theories and empirical correlations. The Weibull distribution of the fracture strength of a brittle material is, perhaps, one of the most successful and enduring examples of this heuristic approach to modeling.[71,72]

An intrinsic characteristic of all polycrystalline materials is the presence of microstructural inhomogeneities, commonly called flaws, that are distributed throughout the material.[73–75] The fracture of a brittle material inevitably originates at one of those flaws within the stressed volume of the material, usually at the flaw that is most susceptible to stress intensification. Weibull transformed this experimental observation into a weakest link statistical model of fracture.

In this model, if any one flaw fails, the whole specimen fails. Suppose the flaws in the specimen are numbered from 1 to N_f, and let $\mathcal{P}_k(\sigma)$ be the probability that flaw number k fails at stress σ. Taking $\mathcal{P}(\sigma)$ to be the probability that the whole specimen fails, then the probability that the whole specimen survives, $1 - \mathcal{P}(\sigma)$, is

$$1-\mathcal{P} = [1-\mathcal{P}_1][1-\mathcal{P}_2]\ldots[1-\mathcal{P}_{N_f}] \qquad \textbf{(59)}$$

which may be written more conveniently as

$$\ln[1-\mathcal{P}] = \sum\nolimits_k \ln[1-\mathcal{P}_k] \qquad \textbf{(60)}$$

With these relations, it is possible to define a mean population fracture strength, $\bar{\sigma}$, by noting[76] that the number of specimens that fail at stress σ is the difference between the number of specimens surviving at stress $\sigma - \delta\sigma/2$ and the number of specimens still surviving at stress $\sigma + \delta\sigma/2$. Thus,

$$\bar{\sigma} = \frac{1}{N_f} \sum_{\sigma} \Big([1 - \mathcal{P}(\sigma - \delta\sigma/2)] N_f - [1 - \mathcal{P}(\sigma + \delta\sigma/2)] N_f \Big) \cdot \sigma \qquad \textbf{(61)}$$

Expanding this expression to first order in $\delta\sigma$, the summation can be converted to an integral yielding,

$$\bar{\sigma} = \int_0^{\infty} \mathcal{P}'(\sigma) \cdot \sigma \, d\sigma \qquad \textbf{(62)}$$

where $\mathcal{P}'(\sigma) = d\mathcal{P}/d\sigma$ is the first derivative of $\mathcal{P}(\sigma)$ with respect to σ.

While this model can be developed further in considerable complexity, we can obtain a useful result for the purposes of data evaluation by considering a rather simple case. In particular, consider the case of uniformly distributed, unimodal flaws in a specimen bearing a uniform stress. Because the distribution is unimodal, we may assume that a single function of the local stress governs the survival probability at each site, which we may write as $\ln(1 - \mathcal{P}_k) = \Phi(\sigma_k)$. Further, because the stress is uniform, $\Phi(\sigma_k) = \Phi(\sigma)$ for all k. Consequently,

$$\ln[1 - \mathcal{P}(\sigma)] = \sum_k \Phi(\sigma_k) = \Phi(\sigma) \sum_k 1 = N_f \Phi(\sigma) \qquad \textbf{(63)}$$

If we now assert the two-parameter Weibull model, for which $\Phi(\sigma) = -(\sigma/\sigma_0)^m$, where m is called the Weibull modulus and σ_0 is the Weibull characteristic strength, we can evaluate the integral for the mean fracture stress.

$$\bar{\sigma} = \frac{Q(m)}{N_f^{1/m}} \sigma_o \qquad \textbf{(64)}$$

$$Q(m) = 2\int_0^\infty y^{1+(2/m)}\, e^{-y^2} dy \tag{65}$$

where $Q(m)$ is a slowly varying function of the Weibull modulus; $Q(m=2) = \pi^{1/2}/2 \approx 0.89$, and $Q \rightarrow 1$ as $m \rightarrow \infty$.

This result shows quite reasonably, and in complete accord with experimental observation, that the mean strength decreases as the number of flaws increases. Suppose further that we want to compare the mean fracture strengths from two sets of measurements that are identical except for the size of the stressed volume. Because the number of flaws in each specimen is proportional to the volume of the specimen, $N_f(V) \sim V$, it follows that

$$\frac{\bar{\sigma}(V_1)}{\bar{\sigma}(V_2)} = \left(\frac{V_2}{V_1}\right)^{1/m} \tag{66}$$

The practical significance of this result for data evaluation is that fracture strength is a procedural property. When apparent discrepancies occur among reported strength values, an assessment of the differences requires a comparison of the measurement details. Two determinations of the fracture strength of a given material on a given apparatus may be quantitatively different, for example, if the sizes of the specimens are different. Similarly, two determinations may yield different results if two different techniques are used. For example, even when identical specimens are used, the measured fracture strength will be larger when determined by three-point bend tests, Figure 6.18(a), than when determined by four-point bend tests, Figure 6.18(b), because the four-point test stresses a larger volume.

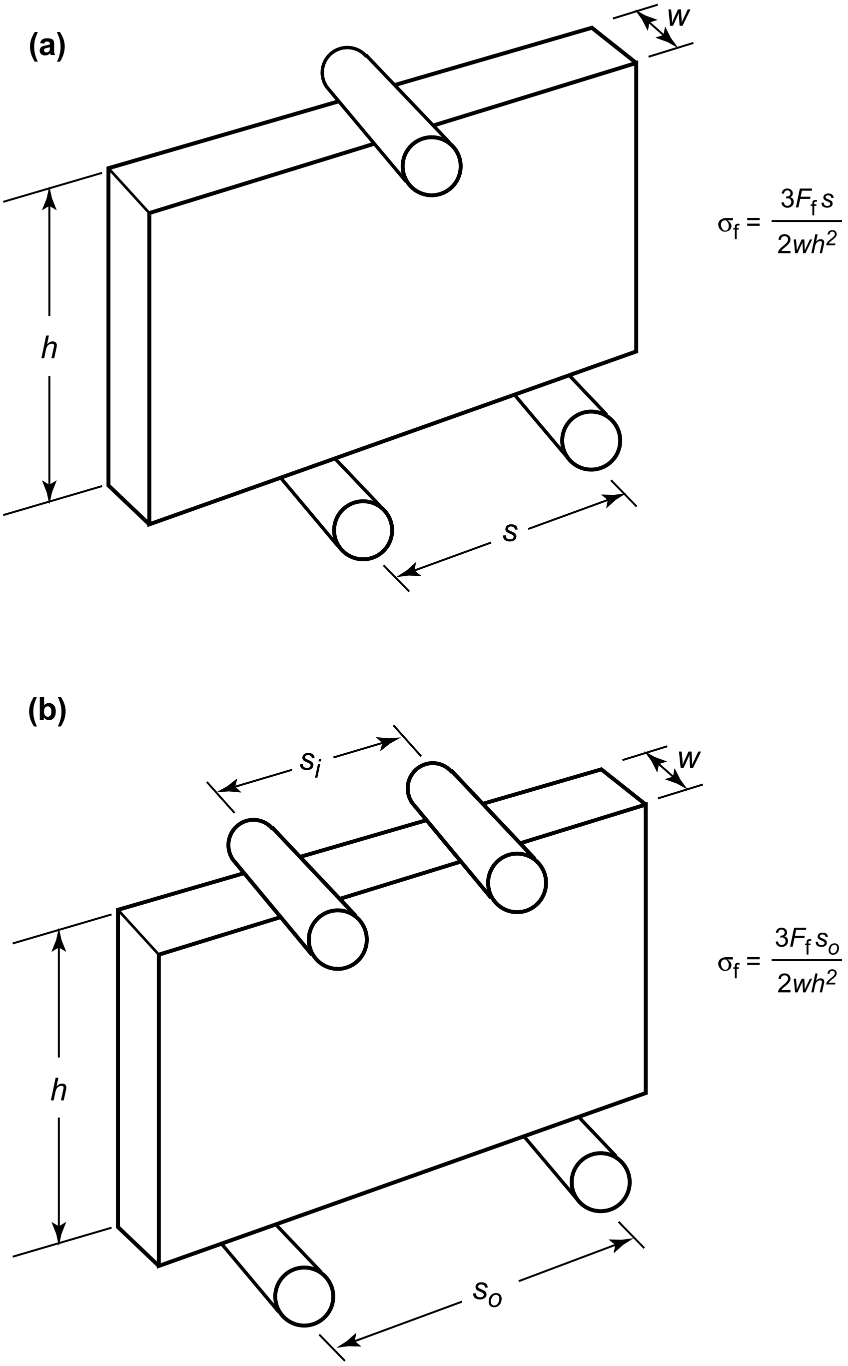


***Figure 6.18.** Schematics of two flexural tests: (a) three-point bend; (b) four-point bend.*

6.4.4 Dominant Mechanisms

{***Example:*** Porosity dependence of bulk moduli}

Within the complexity of material behavior, it may happen that there is a dominant mechanism that accounts for the major features of an observed trend. When this situation occurs, it may be possible to focus very crudely on one single aspect of the material composition to obtain an analytical description of the principal trend. While myriad subtleties may be lost in such descriptions, a more insightful understanding of the physical behavior may be gained. Additionally, the resulting analytical expressions may be directly useful for interpolation and extrapolation purposes and may provide a basis for understanding other empirical correlations. An example possessing these virtues is the effective medium theory of the porosity dependence of bulk moduli.[77]

Porosity refers to the presence of holes or gaps in a material body. In polycrystalline materials, porosity can result from the stacking of misaligned grains or from vacancies and inclusions within grains. The local disruption of material contiguity associated with these porous features may diminish the capacity of the material to transmit forces or to diffuse energy through its microstructural components. Consequently, the elastic moduli tend to decrease with increasing porosity. Given the nonuniformity of the distribution of pores and the irregularity of pore shapes, it is readily understandable that detailed mathematical models of the effects of pores in a material might be highly intractable. However, we can gain some useful insight into the porosity dependence by means of an effective medium theory.

There are three principal aspects to an effective medium theory. First, there is a reference system, usually of an idealized nature, in which all the relevant mathematics can be performed. Second, there is a renormalization of a metric (a length scale in the present case) which reflects the transformation of the ideal system into the nonideal system. Third, there is a consistency condition that ensures that the effective medium conforms to a known characteristic of the nonideal system.

The classical model of an ionic solid provides the essential reference system for the present purpose. The ionic model consists of a simple crystal lattice in which each lattice point is occupied by an ion. The ions have pairwise interactions described by a potential energy function with both attractive and repulsive terms,

$$\Phi_{ij} = -\frac{\psi_1}{r_{ij}^{p}} + \frac{\psi_2}{r_{ij}^{q}} \qquad \textbf{(67)}$$

where r_{ij} is the distance between ion number i and ion number j.
For the ideal lattice, the sum over all interacting pairs can be performed, and the result can be expressed in terms of a characteristic volume.

$$\Phi = -\frac{\lambda_1}{V^{p/3}} + \frac{\lambda_2}{V^{q/3}} \qquad \textbf{(68)}$$

From the equilibrium condition ($\partial\Phi/\partial V = 0$ at $V=V_{eq}$) and the definition of the bulk modulus ($B = -V(\partial^2\Phi/\partial V^2)$, an expression for the bulk modulus can be obtained in closed form.

$$B = \frac{p(q-p)\lambda_1}{9\,V_{eq}^{(p/3)+1}} \qquad \textbf{(69)}$$

To introduce porosity into this ideal system, we note that porosity causes the mean molar volume to increase and, hence, that mean interparticle distances must be increased. To permit this effective scaling, we renormalize the distance scale by a factor χ. The renormalized bulk modulus then can be written as

$$B = \chi^{-p} B_o \,(V_o / V_{eq})^{(p/3)+1} \qquad \textbf{(70)}$$

where B_o and V_o are the values of the bulk modulus and the volume, respectively, at zero porosity. For the porous system, if we now impose the consistency condition that $V_{eq} = V_o + V_p$ where V_p is the additional volume due to pores, we obtain

$$\chi = (1 + V_p / V_o)^{1/3} \qquad \textbf{(71)}$$

and

$$B = B_o\,(1-\phi)^{(2p/3)+1} \qquad \textbf{(72)}$$

where $\phi = V_p/(V_o + V_p)$ is the volume fraction of porosity. The efficacy of this result, illustrated in Figure 6.19, enables data evaluation to assess the consistency of bulk moduli determined for specimens of differing porosities or densities and to resolve apparent discrepancies among reported values.

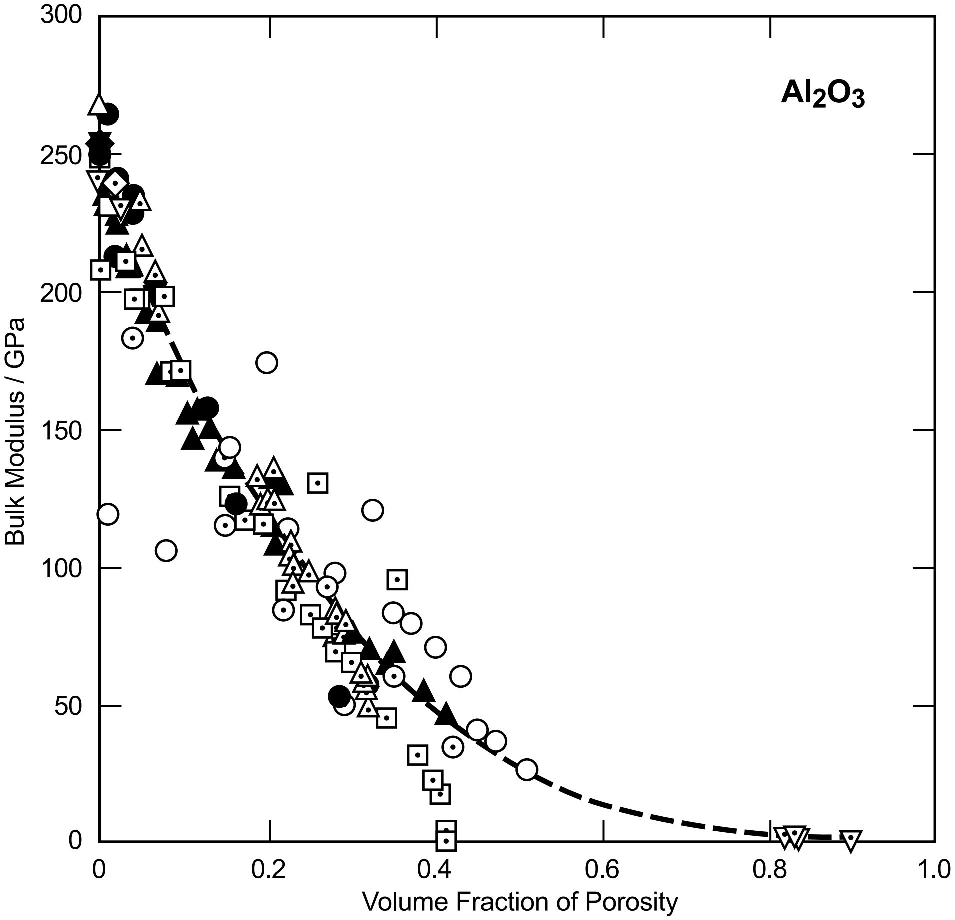


Figure 6.19. *An illustration of the porosity dependence of the bulk modulus of polycrystalline alumina. The dashed curve is the fit of Equation (72).[77] [Data: See* Additional Source References, *Figure 6.19.]*

6.4.5 Bounded Values

{***Example:*** Voigt and Reuss bounds for the elastic moduli of composites}

Composite materials often present a special challenge to data evaluation. Being composed of multiple phases, comparable studies of similar materials often are difficult to find and possibly do not exist. It is often the case, however, that the relevant property values are known independently for the individual constituent phases. In this case, it clearly would be desirable to have a reasonable estimate of the composite property based on the corresponding values for the individual constituents. The challenge is to determine what constitutes a reasonable estimate.

6.4.5.1 Voigt and Reuss Bounds

We have seen one example of this situation already, the estimate of the specific heat of a composite material (sidebar to section 6.4.2). For the specific heat, a weighted average of the specific heats of the individual components, weighted according to the mass fractions of the components in the composite, was found to be an appropriate estimate based on the principle of the conservation of energy. For other properties, however, there may be some ambiguity in deciding what criteria are appropriate. For example, there is more than one reasonable estimate that can be made for the elastic modulus of a composite material.

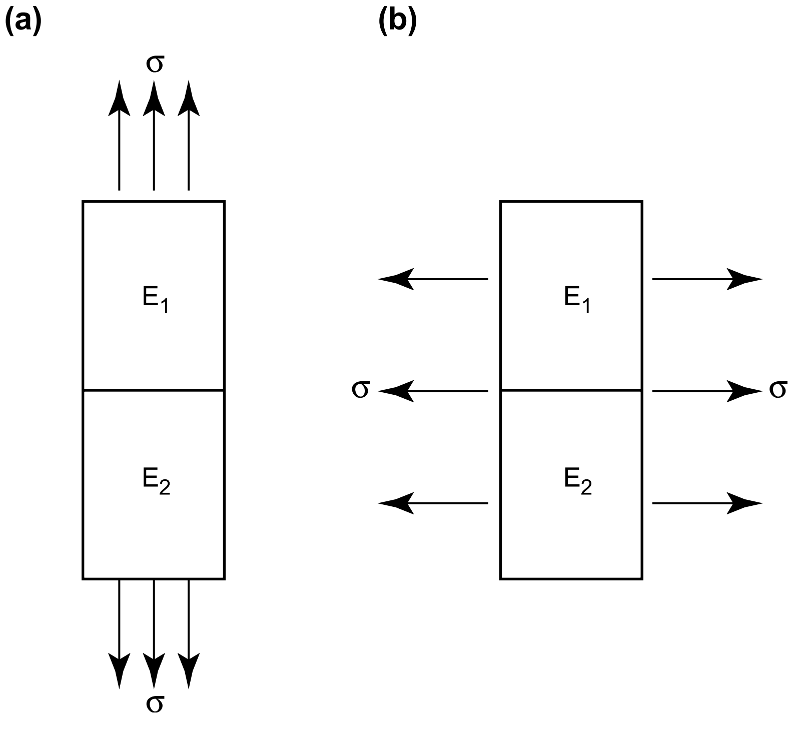


Figure 6.20. Schematics for estimating the effective elastic modulus of a simple composite material consisting of two elastic components: (a) Reuss approximation; (b) Voigt approximation.

We can see how two such estimates arise by considering two fairly simple, but distinct, examples. In Figure 6.20(a), a composite material, consisting of two components connected in series, is subjected to a stress. The strain resulting from the uniform stress of the composite is easily found to be

$$\epsilon \equiv \frac{L - L_o}{L_o} = \left(\frac{L_{1,o}}{L_{1,o} + L_{2,o}}\right)\epsilon_1 + \left(\frac{L_{2,o}}{L_{1,o} + L_{2,o}}\right)\epsilon_2 \qquad \textbf{(73)}$$

where ϵ_1 and ϵ_2 are the strains of the individual components. Recalling that $\epsilon = \sigma/E$, it follows readily that the effective modulus, E_R is given by

$$\frac{1}{E_R} = \sum_i \mho_i \cdot \frac{1}{E_i} \qquad \textbf{(74)}$$

where $\mho_i$ is the volume fraction of component number i. This estimate using uniform stress is known as the Reuss approximation.[78]

In Figure 6.20(b), the same composite is subjected to a stress applied parallel to the interface of the two components and resulting in a condition of uniform strain: $\epsilon_1 = \epsilon_2 = \epsilon$. Mechanical equilibrium requires $\sigma_1 A_1 + \sigma_2 A_2 = \sigma A$, where A_i is the surface area of component i and A is the total area. Using $\sigma = \epsilon E$ and converting to volume fractions, the effective modulus is

$$E_V = \sum_i \mho_i \cdot E_i \qquad \textbf{(75)}$$

This estimate using uniform strain is known as the Voigt approximation.[79]

In a polycrystalline material with randomly oriented grains, it would be expected that the effective modulus would have a value intermediate to these two bounds, such that $E_R \leq E \leq E_V$. These bounds on the elastic modulus have proven to be sufficiently useful that the arithmetic average of the two values, known then as the Voigt–Reuss–Hill average,[80] often is taken as a reasonable estimate of the elastic modulus of a composite material.

6.4.5.2 Characteristic Ranges

The full domain of solid materials is commonly subdivided into classes such as ceramics, glasses, metals, polymers, and composites. The rationale for this classification is that there exists recognizable similarities among materials of the same class and clear distinctions among the principal characteristics of different classes. It may be expected that the similarities and differences should be manifested quantitatively in the ranges of values observed for the respective material properties. Given that the observed properties are fundamentally consequences of interatomic interactions, many of the properties for a given material should exhibit correlations. It follows that it may be possible to form dimensionless products and ratios of properties that characterize those correlations for

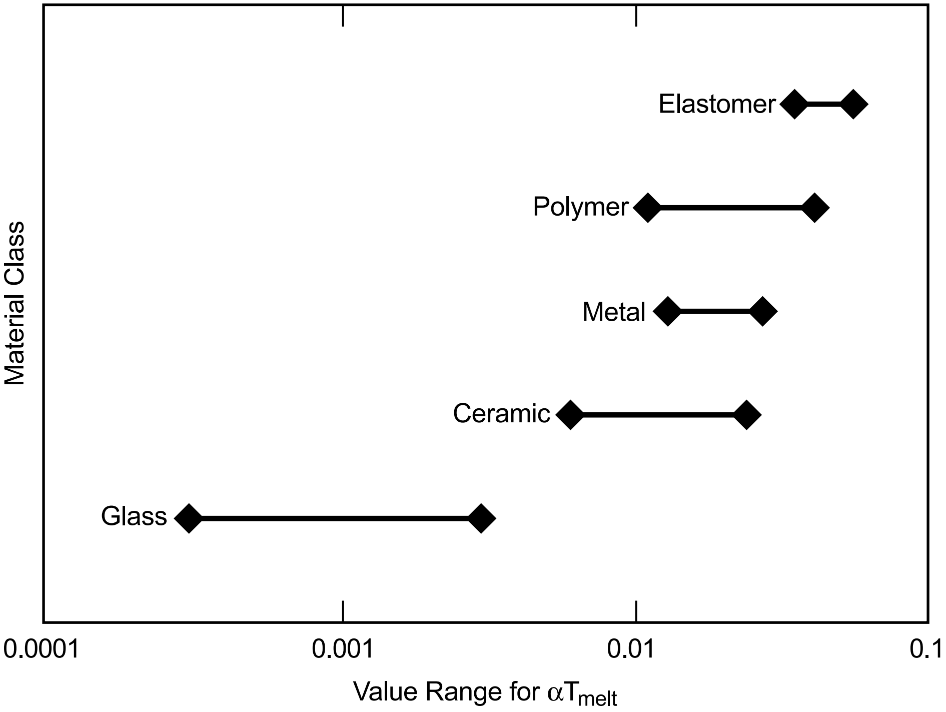


Figure 6.21. *An illustration of characteristic ranges, using values of the dimensionless product of thermal expansion and melting temperature, viewed as a function of material class.*[81]

each entire class of material. The distinctions between classes would then occur as quantitatively different bounds on the values of the normalized correlations. An example[81] of such bounds and their distinctions between material classes is shown in Figure 6.21 for the case in which a dimensionless quantity is formed by the product of the coefficient of linear expansion and the melting point temperature. In practice, numerous correlations may be developed,[81] and the bounds on their values may be established empirically through a statistical analysis[82] of the data compiled for each material class. These bounds may then be used to provide a useful validation of the order of magnitude of new results reported subsequently.

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Figure 6.4, Critical Temperature

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Figure 6.5, Lattice Parameters

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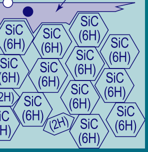
7. Conclusion

Undoubtedly, there is a great deal of work yet to be performed towards understanding property relations and their intrinsic role in data evaluation. Some of the relations that have been employed in this work have already stood a brief test of time. More will be joined to that list in the future, while others will be refined, replaced, or otherwise disabused in short order. The principles set forth in this work are amenable to such changes and, indeed, clearly anticipate them. It is a certainty that every such advance in our conceptual understanding of properties, procured by empirical observations and captured in theoretical or heuristic models, will enhance our ability to use data more wisely. Application of this evolving knowledge in the course of data evaluation will contribute significantly to our ability to ensure the credibility of materials property data. In this effort, striving to attain reliability, consistency, and accountability shall remain the primary goal, the focal responsibility, and the fundamental testament of data evaluation.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