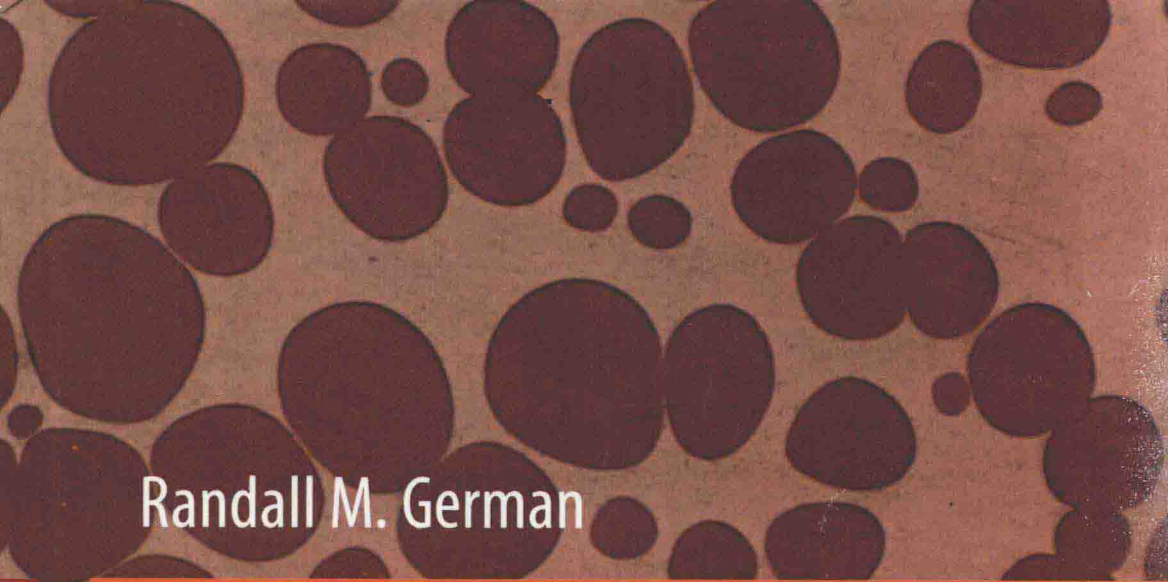

Randall M. German

Particulate Composites

Fundamentals and Applications

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Preface

Engineering materials continue to encounter challenges for new property combinations, and these challenges are leading to many hybrid materials known as composites. Particulate composites are formed using powders to create property combinations not available in traditional engineering compositions. This book provides engineers with information relevant to meeting the challenges on synthesis, selection, fabrication, and design associated with applying composites to demanding applications. Growth in the field is accelerating as we learn more about how to deliver novel property combinations. Further, the shaping flexibility associated with particles provides compelling economic benefit.

Growth in the particulate composites is evident in patents, journal publications, and press releases. For example, a new composite of gold and titanium nitride is employed in the newest smart watches. The 18-karat watch has exceptional wear resistance beyond that of traditional jewelry. The 75 wt% Au (46 vol.%) gives elegance, while the hard, gold-colored TiN provides 400 HV hardness, tenfold higher than pure gold. This is just one of many ideas. Millions of formulations are possible, with tremendous flexibility in composition, microstructure, properties, and performance. Although the field is challenging to master, at the same time the performance gains are most attractive. Only now are we appreciating the full spectrum of opportunities.

Although particulate composites are everywhere, the field is poorly organized. Predictive calculations are ignored or missing. Consequently, product development efforts rely on the empirical approach to see what works. In this book, the underlying principles are emphasized with attention to the critical factors. Important aspects are detailed with regard to the relations between phases, composition, powder characteristics, microstructure, fabrication, and properties. The resulting composites are isotropic, unlike long fiber graphite and fiberglass composites. Accordingly, a wide array of products are treated as part of this book. The intent is to introduce particulate composites in a manner relevant to training the next generation of innovators.

San Diego, CA, USA　　　　Randall M. German

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Author Biography

Professor German's research and teaching deal with the net-shape fabrication of engineering materials for applications ranging from wire drawing dies to jet engine bearings. He is Professor of Mechanical Engineering at San Diego State University, having previously served as Associate Dean, Chaired Professor, and Center Director at Rensselaer Polytechnic Institute, Pennsylvania State University, and Mississippi State University. In addition he was Director of Research for two companies and staff member at Sandia National Laboratories.

Rand obtained his PhD from the University of California at Davis, MS from The Ohio State University, and an honors BS degree from San Jose State University. He completed management development programs at Hartford Graduate Center and Harvard.

He has an honorary doctorate from the Universidad Carlos III de Madrid and is a Fellow of three professional organizations. His awards include the Tesla Medal, Nanyang Professorship, Japan Institute for Materials Research Lectureship, Penn State Engineering Society Premiere Research Award, University of California at Davis Distinguished Engineering Alumni Award, The Ohio State University Distinguished Engineering Alumnus Award, San Jose State University Award of Distinction, and Honorary Member of Alpha Sigma Mu. He served on three National Academy review boards and helped form a dozen start-up companies.

Rand supervised more than 100 theses and 200 postdoctoral fellows. These efforts resulted in 1025 published articles, 25 patents, and 18 books, including *Sintering Theory and Practice*. He edited 19 books and co-chaired 30 conferences. His publications have been cited more than 22,000 times.

Contents

Chapter 1
Introduction

Particulate composites deliver property and cost combinations not available from traditional single-phase materials. These composites involve many combinations where at least one phase starts as a powder. Basic concepts are introduced in this chapter and first details are given on nomenclature, property models, and some compositions in use. The benefits from starting with coated particles are introduced.

Context

Composites use two or more phases to attain property combinations not possible from either phase alone. Chocolate is an everyday example of a composite consisting of sugar, milk solids, cocoa, and cocoa butter. Different ratios of the ingredients lead to semi-sweet, milk chocolate, or dark chocolate.

Particulate composites are around us everywhere. Concrete with steel reinforcement bars is a widely used construction material. Rebar strengthened concrete consists of rock and sand mixed with hydrated calcium silicate. If we performed random spot chemical analysis, at some points the composition is low carbon steel (Fe-0.4C), other places it is silica (SiO_2), and other places it is hydrated calcium silicate (a mixture of calcia (CaO), silica (SiO_2), and water). Engineers ignore this "granularity" and treat concrete as a homogeneous material.

Some composites involve fibers, while others rely on particles, including elongated particles (whiskers) and flat particles (flakes) [1–10]. Especially important are particulate composites with metal or ceramic phases enmeshed in a metal, ceramic, or polymer. The added phase is selected to improve performance of the continuous matrix phase.

The number of possible phase combinations is enormous. This book treats the subject using a wide range of compositions. Some attention is given to polymer matrix composites; however, interfacial bonding to the matrix requires an active interface that is often absent from polymer composites. Thus, more attention is

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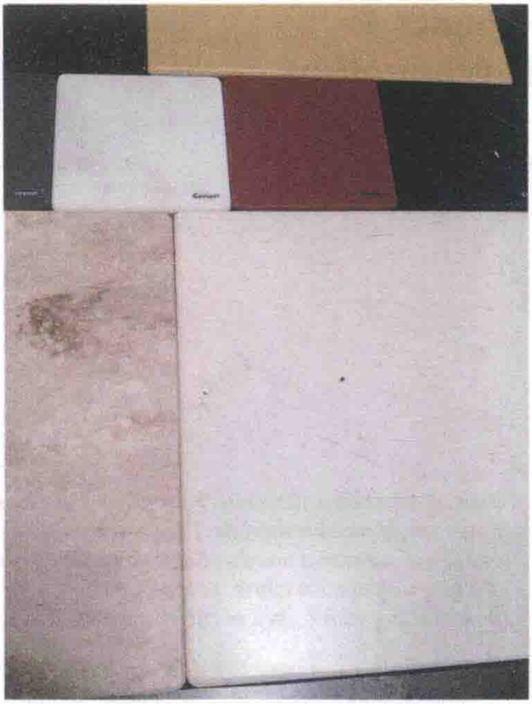

Fig. 1.1 Samples of various kitchen counter tops with different colors and swirl patterns. The composites are a mixture of alumina trihydrate and acrylic polymer

directed toward systems where either a chemical or thermal treatment induces a strong bond between phases. The resulting applications are diverse, and include electrical switches, metal cutting tools, electric bicycles, golf clubs, computer servers, automobile engines, practice bullets, concrete cutting tools, and kitchen counter tops. Often these very common applications are forgotten, yet they are frequently used every day. For example, Fig. 1.1 is a photograph of different styles and colors of manmade composites used in kitchens. Durability is quite important to the commercial success of this composite.

Composites

A composite is a mixture of two or more phases. Each phase remains distinct in the structure as evident using microscopy. Properly formulated composites deliver attractive property combinations. As an example, iron particles coated with a polymer are consolidated to form magnets used in electric bicycles. Iron provides magnetic behavior while the polymer matrix makes the composite nonconductive. This composite avoids eddy current energy losses in high frequency electric motors. Eddy currents arise when a moving magnetic field induces electrical current flow in the structure. Thus, the composite has desirable magnetic response without the inefficiency from eddy currents. Likewise, composites used for cutting concrete, marble, or granite rely on hard diamond particles dispersed in a tough metallic phase such as cobalt. The combination delivers exceptional cutting performance for

Table 1.1 Examples of particulate composites

System	Application	Ingredients
Paint	Spreadable surface coating	Mixture of solvent, opaque particles, and polymer such as an acrylic emulsion
Ink	Printing on paper	Small graphite particles in a mixture of solvent and polymer
Porcelain	Dishes, dental crowns, electrical insulators	Mixture of oxide ceramic crystals and glass phases
Electrical contacts	Make-break circuit switches	Arc resistant refractory phase (W, WC, Mo) and high electrical conductivity phase (Ag, Cu)
Heat sinks	Redistribution of heat in computers, rocket engines, high intensity lighting	High conductivity phase (Cu, Ag) with low thermal expansion phase (W, Mo, WC)
Brake pads	Transformation of kinetic energy into heat to stop mechanical systems	Mixtures of graphite, polymers, metals, and ceramics
Electromagnetic shields	Absorption of radio wave interference in devices such as computers	Polypropylene or other polymers with electrically conductive dispersed conductors of nickel and graphite
Permanent magnets	Flexible magnets for use in headphones, stereo speakers, electric motors	Polymer mixed with high capacity magnetic compound
Correction fluid	Opaque cover up for typographical errors or drawing mistakes on paper	White titania (TiO_2) particles dispersed in a solvent-softened polymer
Cemented carbide	Provide hard surfaces for drawing, machining, drilling, shearing, extrusion of metals	Interlocked network of hard carbide (WC) particles in a tough metal matrix (Co)
Wear resistant aluminum	Air conditioner rotors, endurance horseshoes, sporting equipment	Mixture of hard silicon carbide (SiC) particles in aluminum alloy matrix
Inertial weights	Selective mass to balance gyroscopes, aircraft wings, helicopter rotors, vibrators, fishing, and golf club weights	Composite consisting of mostly tungsten (W) mixed with transition metals, such as Cu, Fe, Ni, Mn, Co
Low toughness projectiles	Lead-free frangible ammunition where the bullet has sufficient strength for firing but disintegrates on target impact	Variants include tungsten (W) bonded with nylon or copper (Cu) bonded with tin (Sn)
Foamed ceramic	Insulation for high temperature heating pipes with low thermal conductivity up to 1000 °C	High porosity foamed hydrous calcium silicate with a density near 0.2 g/cm^3

hard structures. Neither the diamond or cobalt alone would survive the harsh conditions, but the composite proves exceptionally durable. Particulate composites arise in many fields as illustrated in Table 1.1 for various compositions and applications.

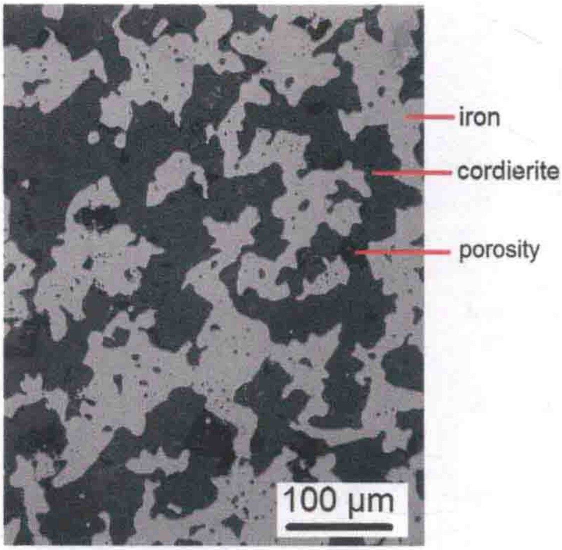

Fig. 1.2 A cross-section microscope image of a two phase composite formed from iron (Fe) and a complex oxide compound known as cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$), where both phases form interlaced networks [courtesy L. Shaw]

Within a composite, each phase is distinct with regard to composition and atomic structure. The microscopic difference between phases is readily evident. Figure 1.2 is an image of an iron-cordierite composite. In this case there is some residual porosity. This cross-section image contrasts the phases based on a difference in reflectivity. The phases form interlaced networks. In terms of properties, the iron is soft, conductive, magnetic, and ductile while the cordierite consists is an oxide compound ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$) that is hard, nonconductive, nonmagnetic, brittle, and stiff, with a lower thermal expansion coefficient. The two phases are insoluble in one another, so the composite is magnetic, but low in thermal expansion. This combination of properties is desirable for use in the automated assembly of electronic diodes.

Some composites form naturally, such as bones, seashells, bamboo, and wood. These biological composites have a broad array of properties, ranging from soft skin to hard dental enamel [11, 12]. Biological composites provide evidence of the importance to the phase arrangement, what is known as the morphology. For example, abalone shell consists of calcium carbonate and rubbery biopolymer. Neither phase is noteworthy, but the composite provides significant toughness. Intentional control of phase morphology is part of composite design.

Microstructure refers to the image in a light or electron microscope. Each phase has easily identifiable attributes. Microstructure can dominate properties. For dilute compositions, one phase is dispersed in the other phase. At higher concentrations, both phases are connected, resulting in an interlaced three-dimensional structure. The level of phase connectivity is critical to properties. A composite microstructure is captured in Fig. 1.3 using a polished cross-section. The cross-section shows low thermal expansion Invar (Fe-36Ni) as the darker phase and high thermal conductivity silver (Ag) as the lighter phase. This composite is known as *Silvar*. The two phases are distinct, forming three-dimensional, intertwined networks. At 40 wt%

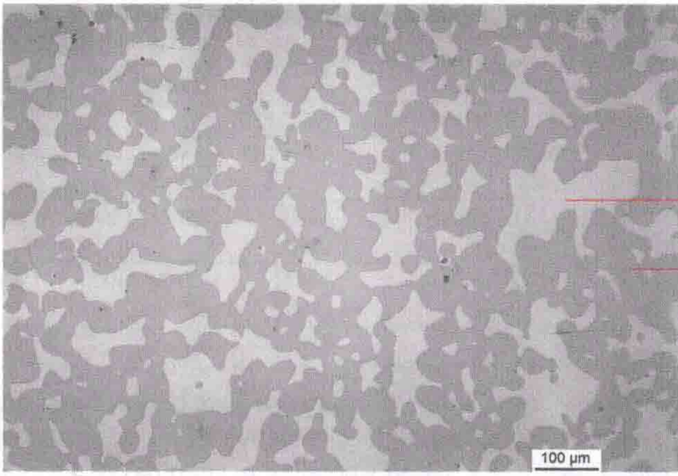

Fig. 1.3 Microstructure of a two phase particulate composite consisting of low thermal expansion Invar (Fe-36Ni) as the dark phase and high thermal conductivity silver (Ag) as the light phase. Both phases are interconnected in three dimensions [courtesy B. Lograsso]

Table 1.2 Thermal properties of silver, Invar, and *Silvar* composite (*Silvar* = Invar-40Ag)

Property	Silver (Ag)	Invar Fe-36Ni)	Silvar (Invar-40Ag)
Density, g/cm^3	10.5	8.2	8.9
Tensile strength, MPa	180	500	200
Thermal conductivity, W/(m °C)	420	14	160
Thermal expansion, 10^{-6} 1/K	20	1	8

silver (34 vol% silver) a desirable combination of properties arises, as summarized in Table 1.2. These properties are useful in heat dissipation devices that cool microelectronic chips. The high thermal conductivity reduces heating while the low thermal expansion coefficient minimizes thermal fatigue. The on-off cycles in a computer expand and contract the semiconductors, leading to fatigue failure after repeated cycles. To avoid thermal fatigue failure, the heat spreader must match the semiconductor expansion and contraction strains.

Interest in particulate composites derives from novel property and cost combinations. In general there are four options:

1. properties are dominated by one phase,
2. properties are intermediate between the two phases,
3. properties are synergistically advanced over that attainable with either phase,
4. properties are degraded below that of either phase.

Most often composites are formulated to deliver improved properties. Using hardness, Table 1.3 compiles examples for each of the four situations listed above. In the first case of WC-8Co, the composite is nearly the same as harder phase; tungsten carbide dominates the composite hardness. In the second case of