Milling Efficiency of Ceramic Composite Slurries

Introduction

Ceramic matrix composites (CMCs) based on reinforcements of carbon fibers and matrices of silicon carbide (called C/SiC or C/C-SiC composites) represent a relatively new class of structural materials. Silicon carbide is a non-oxide ceramic and is not only the lightest but also the hardest ceramic material and is very resistant to acids and bases.

Specialty carbon materials based on silicon carbide, such as CMCs, are used because of their stable physico-chemical properties, low cost, excellent chemical stability, wide operating temperature range, and long cycle life. CMCs exhibit a combination of useful physical and mechanical properties such as high mechanical strength and high corrosion resistance even at high temperatures as well as improving thermal shock resistance. Moreover, they provide enhanced performance capabilities in reinforced composites and offer significant benefits in their ability to be engineered for specific stress, temperature, and environmental conditions. As such CMCs have found use in a variety of important applications. For example, in the aerospace industry CMCs are used to fabricate combustion chambers and turbine blades for gas turbines engines.

CMCs are created as dispersions, and an important consideration when working with any ceramic material is milling. Milling is an important tool available to both the R&D formulator and process engineer. However, attention must be paid to any process of attrition or comminution as it impacts the overall dispersion process, and not just the particle size of the ceramic material. It is not a case of one-size method fits all. The state of dispersion of any solid material directly affects the properties of any suspension. The fundamentals of the dispersion process are discussed in Mageleka White Paper 3 (at www.mageleka.com).

Achieving stable, effective, and elegant formulations containing particulates is a matter of *proper and correct* milling (see Mageleka White Paper 5). For example, if excessive mechanical energy is used it can easily result in a submicron-sized fraction of “fines”, especially for crystalline material where fracture can occur at defect crystal planes. Such fines cannot be detected using either image analysis or particle size analysis (using Fraunhofer diffraction). Indeed, monitoring the presence of nanoparticles in suspensions that have a broad particle size distribution is a general problem for current particle sizing instrumentation.

With ceramics, the presence or absence of fines in the milling process influences the mechanical properties of the finished part as well as the degree of shrinkage and green body strength. Additionally, additives (such as surfactants) are used to impart good flow properties to the ceramic slurry, and the quantity of surfactant needed is related to the total available surface area of the dispersed particles.

However, studying these systems *in situ* is not straightforward, as the formulations are opaque and are often highly concentrated dispersions in a variety of aqueous and non-aqueous liquids. There are few tools available with which to *directly* measure the suspension characteristics.

> *“The Mageleka RelaxoMeter XRS™ can be a fast, simple tool for studying the efficiency of different milling processes.”*

MAGELEKA, Inc.
3122 Heather Glen Court
Naples, FL 34114 USA

Worldwide: +1 617 331 1130
Europe: +44 (0)1744 325005

www.mageleka.com

Nuclear magnetic resonance (NMR) relaxation is a technique that is easy to employ, produces rapid results, and requires limited input data. Importantly, and as we will explore in this Application Note, it is an ideal technique for measuring suspensions at high solids loadings because it does not make any assumptions about the size, shape, or concentration of particles, or the liquid in which they are suspended.

About NMR Relaxation

NMR spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. Traditional devices employing NMR technology require high magnetic fields and, hence, large magnets and related instrumentation. However, the advent of small powerful magnets has allowed instruments such as the Mageleka XRS™ *R*elaxo*M*eter to be designed that have small footprints and are suited to normal, routine laboratory analysis.

The basic technique used in the *R*elaxo*M*eter is NMR relaxation. The relaxation time is a fundamental intrinsic property of solids and liquids (under the influence of a magnetic stimulus), and its measurement provides direct information about the extent and nature of any particle-liquid interface (i.e., suspensions; see Mageleka Technical Note 1).

The actual relaxation value obtained by NMR for the bulk liquid is an average that is dependent upon the exact composition of the suspension. This is somewhat analogous to the zeta potential of a material where the value depends critically upon the exact composition of the dispersion fluid.

What the *R*elaxo*M*eter measures is the extent of molecular motion as protons interact when perturbed by local magnetic fields. The liquid in contact with a particle surface relaxes much more rapidly than does the rest of the liquid, which is free (i.e., "bulk" liquid). This surface relaxation is typically of the order of microseconds, compared with the NMR relaxation time for the bulk liquid (i.e., in the absence of particles), which can be of the order of seconds. For many dispersions of interest, we can assume that there is a fast, dynamic exchange between the liquid associated with the particle surface and the bulk liquid. We measure a dynamic average which reflects the properties of the interface.

What does the *R*elaxo*M*eter do?

The *R*elaxo*M*eter provides complementary information to traditional particle characterization devices. But it also provides additional interfacial insight not possible with those devices.

The *R*elaxo*M*eter's measurement technique is noninvasive and nondestructive, and it can work with suspensions at any industrially relevant concentration. This latter feature is especially important for ceramic slurries that can be highly concentrated.

Of practical utility, the *R*elaxo*M*eter eliminates the dilution issues inherent in making measurements using, for example, traditional light scattering techniques. Since dilution is never an innocuous process, wherever possible slurries or suspensions should be analyzed as they are prepared (see Mageleka Technical Note 5). Moreover, the simple measurement technique using the *M*agno*M*eter takes only minutes (see Mageleka Technical Note 2).

Using the *R*elaxo*M*eter to determine the efficiency of milling techniques

In this case study, the T_2 NMR relaxation time was measured (using the CPMG pulse sequence method of analysis) for a ceramic composite slurry to determine the efficiency of three different milling processes: a standard roller mill, a rotor-stator mill, and a two-step system comprising a combination of roller/rotor-stator milling.

The ceramic slurry is a complex mixture of solids and solvents (Table 1), and it is based on the MSDS sheet supplied with the sample and comprises at least seven identifiable materials.

Table 1. Composition of Ceramic Slurry

Ingredient Name
Silicon carbide
Carbon black
Isopropyl alcohol
n-Butyl acetate
Furfuryl alcohol
Formaldehyde/phenol/oligomeric reaction products

The design and choice of milling equipment must be chosen with care for both the initial wetting of a powder (and sometimes de-aeration) – often called the premix stage – and for final dispersion. In all cases the minimum mechanical agitation must suffice to avoid unwanted problems. The choice of equipment also depends on factors such as the nature of the mill-base and the quality and volume required. Two well-known mixing devices are the three-roller mill and the rotor-stator mill. Each provides a different degree of processing shear (see Mageleka White Paper 5 at www.mageleka.com).

In the example below, three ceramic slurries of the same composition were prepared using a roller mill, a rotor-stator, and a roller mill followed by a rotator-stator. The *R*elaxo*M*eter measurement results are summarized in Table 2 and shown graphically in Figure 1.

Table 2: Summary of T_2 relaxation time measurements. SD = standard deviation; CV = coefficient of variation.

Slurry batch ID	Milling device	Average T_2 Relaxation time (ms)
19-3	Roller	96.8 SD=1.6; CV=1.7
19-1	Rotor-stator	41.9 SD=0.7; CV=1.6
19-1 & 19-3	Roller + Rotor-stator	80.3 SD=1.2; CV=1.5

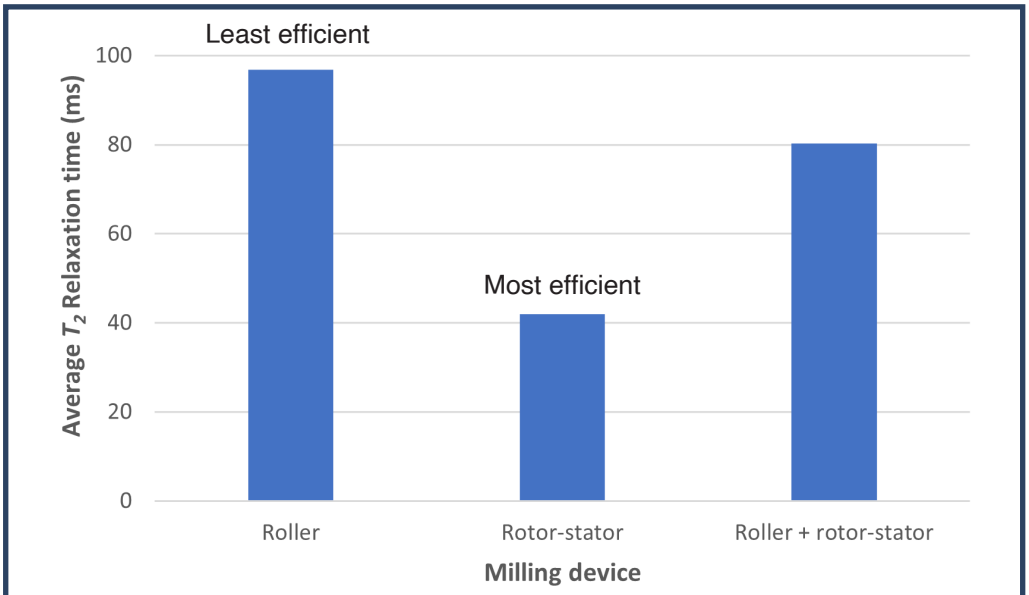

Figure 1. Comparison of efficiency of different milling techniques using nuclear magnetic resonance (NMR) relaxation time measurements.

The repeatability of measurements for the samples was quite good (CV <2%) and so we can conclude that the results are statistically robust. For a given (fixed) solids concentration), a *larger* relaxation time is typically indicative of a *smaller* available wetted surface area (larger particles). Thus, in this study, the data suggests that the most efficient comminution arises from using the rotor-stator mill and the least efficient is using a basic roller mill. Using the combination does not provide any advantage.

Note that the total solids concentration (silicon carbide plus carbon black) for these samples was sufficiently high (50%-70%) that, together with the fact that the slurry sample was also opaque (black), it would be impossible to obtain a precise characteristic analysis from microscopy or light scattering instrumentation. Additionally, for the latter devices, the product must be diluted extensively. Since the ceramic slurry is multi-component, to accomplish this correctly without consequence requires some degree of skill and knowledge.

In contrast, measurement of the NMR relaxation time using the Mageleka *R*elaxo*M*eter, is relatively straightforward, and a sample can be analyzed at virtually any concentration. Moreover, because the NMR methodology is quantifiable, fast, and non-invasive – *without the need to dilute slurries* – it offers practical advantages. For example, it measures fundamental characteristics and is neither a function of the instrument nor of the operator.

It is also important to note that only a *single* relaxation time (T) is determined for any system; it is essentially the *average* sum result of all the relaxation times of all the composite components. This is somewhat analogous to the zeta potential of a material where that value depends critically upon the exact composition of the dispersion fluid. Thus, for a ceramic slurry of known composition, prepared by a fixed process, the average relaxation time should – within experimental error – be the same.

This is illustrated in Table 3 which shows the relaxation time measured on four batches of a ceramic slurry of the same composition that was manufactured on different dates. It is assumed that the processing conditions were identical.

MAGELEKA, Inc.
3122 Heather Glen Court
Naples, FL 34114 USA

Worldwide: +1 617 331 1130
Europe: +44 (0)1744 325005

www.mageleka.com

Table 3. Relaxation time for different batches of a ceramic slurry. SD = standard deviation; CV = coefficient of variation.

Slurry batch ID	Average T_2 Relaxation time (ms)
1	121.5 SD=1.3; CV=1.1
2	122.4 SD=1.5; CV=1.2
3	123.2 SD=1.4; CV=1.1
4	121.5 SD=1.6; CV=1.3

The repeatability of measurements for the samples was quite good (CV <2%) and so we can conclude that the results are statistically robust. Batches 1 and 2 were two lots formulated on the same day. So, we can conclude that the batch-to-batch and lot-to-lot variations are within the experimental error of the measurement. If sufficient data were available, it would be possible to define upper and lower control limits for quality control purposes (QC).

In Conclusion

The NMR relaxation data presented above demonstrates how the *R*elaxo*M*eter can be a fast, simple tool for studying the efficiency of different milling processes, as well as the quality control of batch-to-batch and lot-to-lot variations, when processing ceramic slurries. The ability to monitor milling and comminution processes – in almost-real-time, on opaque samples, and without dilution – gives NMR relaxation a major practical advantage over other particle characterization techniques (especially particle sizing by light scattering methods). As such, the *R*elaxo*M*eter can be used in process management.

A major advantage of the *R*elaxo*M*eter is that it has no moving parts and requires no alignment or calibration. An in-line stop-flow version of the instrument – the *R*elaxo*F*low – allows for laboratory studies to monitor mixing/milling processes in real-time and under industrially relevant conditions. It is ideal for applications involving heterogeneous suspensions where batch sampling is problematic.

Finally, in quality assurance, NMR measurements from the *R*elaxo*M*eter can enable release of complex systems which can currently only be characterized by the incoming raw materials alone. In other words, the *R*elaxo*M*eter can characterize the manufactured product itself, reducing or eliminating the need to measure the component materials.

For more information, to send samples, to arrange a demonstration of the MagnoMeter at your facility, or to talk to one of Mageleka's technical applications specialists, please email roger@mageleka.com

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