

Green Synthesis of Ceramic Powders for Tribological Applications Using High-energy Ball Milling

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This paper actually presents the mechanochemical high-energy ball co-milling of TiO₂ and SiC. Three systems are presented, a 6:1 SiC:TiO₂ weight ratio, a 3:1 ratio, and as-received SiC, all milled in steel vessels with steel balls at 1100 rpm for 2 and 5 h. The resulting materials were characterized by powder X-ray diffraction and SEM-EDS. It can be observed that sheets of TiO₂ rapidly plate SiC particles, and that a small amount of TiO₂ improves the shape and crystallinity of the resulting microparticles. However, the presence of a large amount of TiO₂ appears to be detrimental to the crystallinity of the particles.

1. Introduction

High-energy ball milling uses mechanical action to introduce deformations into a material's crystalline lattice, which can be used to form a different kind of new materials. This method has already been used in the making of advanced electroceramic materials (Dulian et al., 2013; Licheri et al., 2007) as well as various other intermetallic compounds, catalysts (Rakoczy et al., 2013), ceramics and composites (Wieczorek-Ciurowa, 2010). As mechanochemical treatments are conducted at room temperature and are solid-state, they are simple and potentially represent a large energy savings over other methods. While there has been extensive study directed towards finding the ideal combination of polymer fillers for tribological applications, as well as extensive study of milled materials, to our knowledge relatively little research has been conducted using ball milling to create fillers for composite materials.

Polymers and polymer composites are attractive materials for use in engineering applications because they are lighter than metals or ceramics. This is particularly important from a fuel-efficiency and emissions standpoint in the automotive field (Garcés et al., 2000). Unfortunately, pure polymer is not sufficiently strong or wear-resistant to be used in tribological applications (Briscoe and Sinha, 2008), and must be reinforced by a variety of fillers (Cosoli et al., 2007). Such fillers include glass, carbon, and basalt fibers (Hufenbach et al., 2012; Liu et al., 2006; Wetzel et al., 2006; Zhang et al., 2008; Friedrich et al., 2005), carbon nanotubes (Ruckdäschel et al., 2008), nanodiamonds (Neitzel et al., 2012), solid lubricants such as graphite, heteropolymers such as PTFE (Briscoe and Sinha, 2008) and nanoparticles such as TiO₂ (Chang et al., 2005). These fillers improve wear resistance as well as tailor the coefficient of friction (μ).

The exact mechanisms by which polymers are reinforced is the subject of continuing debate. In general, filler particles limit crack propagation (Zhao et al., 2008) and assist in the formation of a thin and smooth transfer film on the abrasive countersurface (Zhang et al., 2002). There is also evidence that certain spherical nanoparticles such as TiO₂ "roll" in contact with the countersurface, and serve as a third body in a three-body abrasion mechanism. Both of these mechanisms serve to further reduce friction and wear (Chang and Zhang, 2006).

The high hardness of SiC makes it potentially attractive for the abrasion of countersurface asperities and therefore useful in reducing polymer wear. Adding TiO₂ may improve the toughness of the SiC particles. As fracture toughness can be shown to be an important component of improving wear resistance (Zum Gahr,

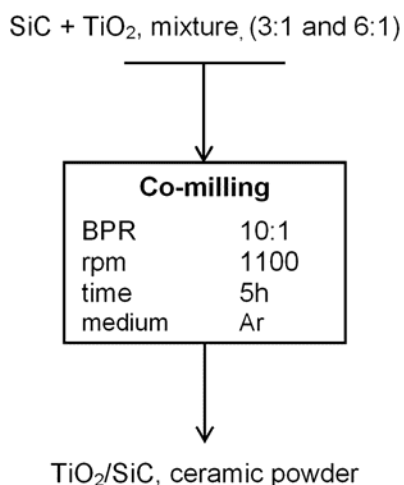
1998), a TiO₂-enhanced SiC microparticle should demonstrate improved tribological properties. SiC and TiO₂ have already been investigated separately as polymer additives for tribological applications, with TiO₂ (6-6.5 Mohs hardness) known to reduce wear and SiC (9.2-9.5 Mohs hardness) actually increasing it (Bahadur and Sunkara, 2005). SiC nano and microparticles have been shown to improve polymer mechanical properties such as tensile strength and tensile modulus (Chisholm et al., 2005). However, to our knowledge the combination of SiC and TiO₂ in order to investigate possible synergistic effects has not yet been attempted. As making Si-Ti bonds requires excessive temperatures (Murray, 1987), it is worth exploring a ceramic powder combining these compounds as an alternative. We propose a mechanochemical method for making a SiC-TiO₂ ceramic powder that may be tougher and therefore more useful tribologically than SiC by itself. Herein we present the co-milling of SiC and TiO₂ and the characterization of the resulting material with a pseudo-core-shell structure for use as filler in a polymeric tribosystem. Our future work will consist of a series of tests to determine if this filler is useful for reducing wear and tailoring the coefficient of friction in polymers.

2. Experimental

TiO₂ was purchased from POCH S.A. (Polish Chemicals and Reagents S.A., Gliwice, Poland) and F 1200 SiC was purchased from KOS Korund P.P.U.H. (Kolo, Poland). Reagents were used as received without any further modification.

A Novosibirsk Corp. Activator 2S mill (Novosibirsk, Russia) was used for all high-velocity ball milling experiments. Milling was conducted at 1100 rpm in a steel reaction vessel using steel balls 10 mm in diameter in dry conditions under argon atmosphere, with a ball to powder weight ratio (BPR) of 10:1. Milling time was 5 h, with samples taken for analysis at 2 and 5 h. 10 g of sample was added to each reaction vessel. In series A, this was composed of a 6:1 weight ratio of SiC:TiO₂, and in series B the ratio was 3:1 respectively (Scheme 1). Series C consisted of as-received SiC milled under identical conditions as a comparison.

The products of these co-millings were analyzed using powder X-ray diffraction (XRD) on a Philips X'Pert instrument with CuK α source between 10-90 ° 2 θ with a step size of 0.05 °. SEM-EDS measurements were conducted on a Hitachi S 4700 instrument at 20 kV and at a magnification of 10,000X. A Noron VANTAGE microanalysis system was used for EDS.



Scheme 1: Experimental setup of high energy ball milling process

3. Results and Discussion

As none of the post-milling XRD patterns (Figures 1b and 2) show the presence of TiO₂ after as few as 2 h of milling, this compound either entirely plates SiC or is amorphous or is in too small amount to be detected by XRD. SEM-EDS results suggest that the former explanation is more likely correct as the particles present generally have the same elemental composition, a mixture between SiC and TiO₂. Furthermore, the SEM micrograph shows that the particles present are all very bright, suggesting that a heavy element is present on the surface. Thus it is reasonable to conclude that the SiC particles are plated with TiO₂ that has been flattened into a series of sheets. Also interesting to note is the behavior of series B, the 3:1 ratio between SiC:TiO₂. After 5 h of milling the powder diffraction pattern suggests that the vast majority of material present

is amorphous, as the intensity of all of the patterns is quite weak. In contrast, series A, shown in Figure 1a, actually has very intense XRD patterns after 2 h of milling, and therefore it is reasonable to conclude that this sample is highly crystalline. Indeed, the signal intensity of the 6:1 SiC:TiO₂ mixture is in fact higher than that of the pure SiC system after both 2 and 5 h of milling. This suggests that a small amount of TiO₂ plated onto the surface of the SiC particle plays an important role in maintaining the crystallinity and integrity of the microparticles. However, considering the loss of crystallinity after 5 h in the 3:1 system, it appears that an excessive amount of TiO₂ may make the microparticles more brittle and prone to fragmentation.

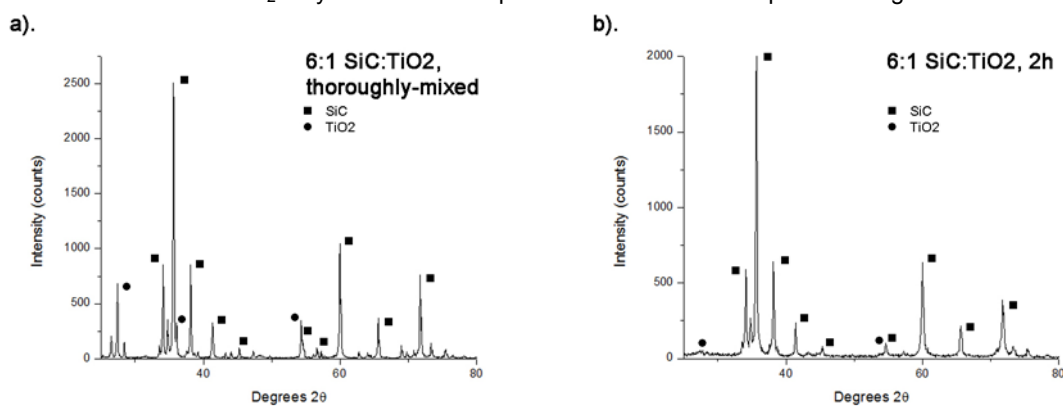


Figure 1: XRD pattern of a). 6:1 thoroughly-mixed SiC:TiO₂; b). 6:1 SiC:TiO₂ (Series A), after 2 h milling

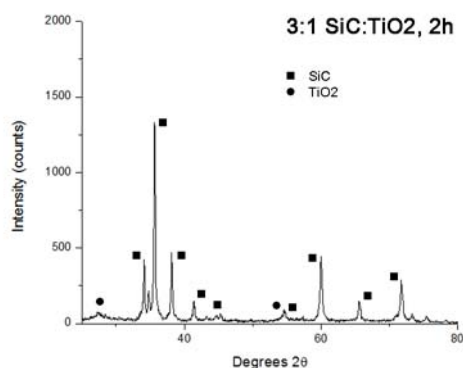


Figure 2: XRD pattern for 3:1 SiC:TiO₂ (Series B), after 2 h milling

SEM-EDS micrographs and elemental analysis results are collected in Figures 3-5 and Table 1 and 2. Milling of brittle and hard SiC causes fragmentation of grains (Figure 3b). After thorough mixing (Figure 3a) of SiC-TiO₂ system, there are clearly two separate types of particle, one composed of SiC that is large and angular and the other composed of TiO₂ that is small and circular. The significant difference in the hardness of the components causes TiO₂ and SiC to overlap during milling (ductile-brittle coupling mechanism). By comparing the micrographs of mixed components with those that have been milled (Figures 4 and 5), it is clear that the TiO₂ particles have coated the SiC grains by plating. EDS analysis shows that over time particles have roughly similar compositions, with the SiC:TiO₂ mass ratio consistent with the theoretical mass ratio of milling substrates (Table 1). Furthermore, the ratio between SiC and TiO₂ observed in the milled system is relatively independent of milling time (Table 2). This suggests that the disappearance of TiO₂ from the XRD powder patterns is due to the attachment of that compound to the SiC particles rather than the amorphization of independent TiO₂ particles – titanium dioxide plates the SiC surface. The EDS results indicate the effect of milling time on the homogeneity of TiO₂ layers on SiC grains; in thoroughly-mixed SiC:TiO₂, the weight percent of titanium dioxide varies considerably from point to point (Table 2, spectra 1 and 2). Milling caused uniform TiO₂ plating on SiC, observed at every measuring point (Table 2, spectra 5 and 6), after both 2 and 5 h of milling.

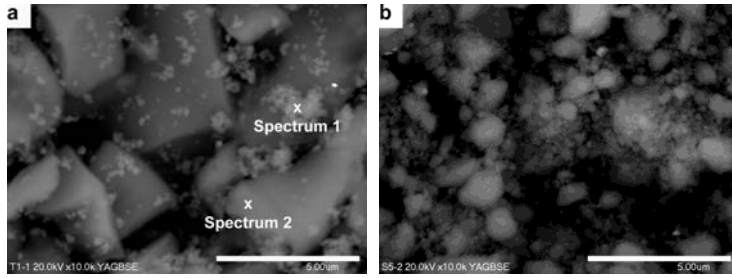


Figure 3: (a) SEM micrograph of a thoroughly-mixed SiC:TiO₂; (b) SEM of as-received SiC after 5 h of milling

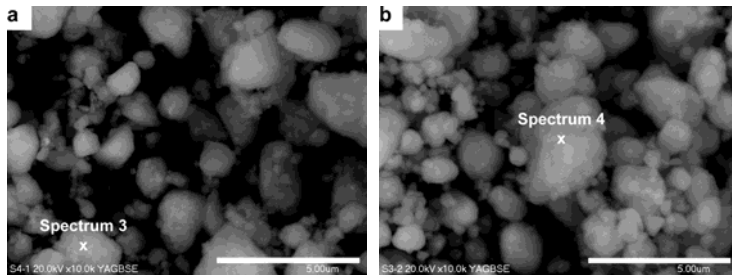


Figure 4: SEM micrographs of 6:1 SiC:TiO₂ (series A) system, (a) after 2 h; (b) after 5 h of milling

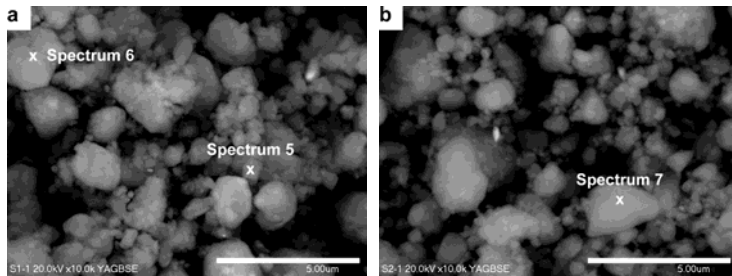


Figure 5: SEM micrographs of 3:1 SiC:TiO₂ (series B) system, (a) after 2 h, (b) after 5 h of milling

Table 1: Theoretical SiC:TiO₂ ratio (before milling)

SiC:TiO ₂ ratio	3:1	6:1
Weight % Si	77.81	86.88
Weight % Ti	22.19	13.12

Table 2: EDS results

Spectrum	Weight % Si	Weight % Si error	Weight % Ti	Weight % Ti error
1	72.57	+/- 0.10	27.43	+/- 0.09
2	91.89	+/- 0.11	8.11	+/- 0.06
3	86.17	+/- 0.47	13.83	+/- 0.39
4	90.22	+/- 0.57	9.78	+/- 0.42
5	78.03	+/- 0.49	21.97	+/- 0.53
6	81.24	+/- 0.54	18.76	+/- 0.52
7	78.96	+/- 0.52	21.04	+/- 0.52

These SEM images suggest that the ratio between SiC and TiO₂ is a more important determinant of microparticle morphology than milling time, as larger differences can be observed when changing

compositions than when changing the amount of time an individual series is milled. In general, within each system it is extremely difficult to notice any particular differences between the samples milled for 2 h and those milled for 5. However, the differences between the 6:1, 3:1 and entirely SiC samples are stark. Samples containing a 6:1 ratio of SiC:TiO₂ are generally smaller, rounder, smoother, more regularly shaped and appear in a narrower size range than in the 3:1 system (Figure 4b and 5b). In addition, the 3:1 system contains a great deal of debris scattered about each image, as well as particles that are more irregularly shaped and appear to be disintegrating. Furthermore, none of these small particles appear smaller than about 0.5 μm, suggesting that the loss of XRD signal intensity after 5 h of milling is due to loss of crystallinity rather than fragmentation of the particles to a size where they no longer diffract. The pure SiC system (Figure 4b) is similar to the 3:1 system in that it also features a great deal of debris and smaller, irregularly-sized particles. Indeed, the pure SiC system has no observed particles larger than 1.5 μm whereas the other two series each have particles greater than 2 μm observed. This suggests that TiO₂ may bind particles together when it is present in smaller amounts, but that in larger amounts TiO₂ disrupts the integrity of the primarily SiC particles.

4. Conclusions and future work

We were successfully able to make ceramic SiC microparticles coated by TiO₂ plates via a simple high-energy ball-milling process, and characterize these particles using powder X-ray diffraction and SEM-EDS. TiO₂ was observed to cover SiC after as few as 2 h of milling. Additional milling does not appear to significantly affect morphology. A 6:1 ratio between SiC and TiO₂ gives smooth and round microparticles with good crystallinity, whereas a 3:1 ratio gives poorly-shaped and largely amorphous particles. Based on these results we believe that TiO₂ is flattened into a series of scales that plate underlying SiC microparticles, and that a small amount of TiO₂ improves microparticle cohesion. Plating of TiO₂ on SiC and formation of titanium oxide coating may improve tribological properties of ceramic-polymer composites. However, a large amount of TiO₂ is detrimental to the structure of the SiC particles.

As morphological differences between the 3:1 and 6:1 systems are clearly visible, this may present an excellent occasion to elucidate the effects of morphology on tribological performance. As a rounder particle may “roll” and reduce both wear and friction, the importance of this mechanism is easily checked by comparing systems with rounder and more jagged microparticles.

Finally, it is still unclear as to whether 5 h of milling are required to give a useful product. These results seem to suggest little difference between products obtained after 2 and 5 h of milling. Ultimately, how much time this system needs to be milled will be decided by its tribological performance. Our future work will focus on the making of further co-milled systems, discovery of how well they interact with a variety of polymers, and thorough testing of such systems' performance as fillers for tribological applications in polymers.

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