Metastable Intermolecular Composites: A New Class of Energetic Materials

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Metastable intermolecular composites (MICs) are a new class of energetic materials (EMs). MICs are materials that have distinct properties that make them applicable in a variety of technologies. Since MICs are EMs, they are materials that store chemical energy (Rossi et al., 2007). They are easy to prepare and have properties which are easy to control (Rossi et al., 2007). MICs can be defined within EMs by means of the division of nanoscale EMs (nEMs) — a type of EMs consisting of nano-size particles — into two classes, organic monomolecular compounds and inorganic composites (Rossi et al., 2007). MICs belong to the class of inorganic composites, those having higher energy densities than organic monomolecular compounds (Dreizin, 2009). MICs are also called superthermites (Dreizin, 2009; Rogachev & Mukasyan, 2010) because they combine metal oxide and metal nanoparticles (Pantoya & Granier, 2005; Rossi et al., 2007) to exhibit thermite behaviour (Miziolek, 2002). The defining characteristics of MICs are their nanoparticle composition and their thermite behaviour.

Particles produced through nanoscience, such as those in MICs, have different properties than their bulk microparticle forms. Nanoscience is generally defined as working with particles that have at least one dimension in the 1-100nm range to produce novel materials and devices that have intrinsically different properties and functions (Klabunde & Richards, 2009; Nagurajan & Hatton, 2008). Nanoparticles have a high proportion of surface atoms to core atoms, which causes nanoparticles to have fundamentally different properties than bulk materials (Klabunde & Richards, 2009; Pantoya & Granier, 2005). The comparison of MICs to bulk thermites demonstrates these trends.

Thermite reactions are highly exothermic (Rossi et al., 2007) and luminescent (Pantoya & Granier, 2005) reduction-oxidation reactions between a metal and a metal oxide to form more stable products (Rossi et al., 2007; Wang, Munir, & Maximov, 1993). They follow the general reaction form: $M + AO \rightarrow MO + A + \Delta H$, where M is a metal, AO is a metal oxide, and ΔH is the heat of the reaction (Rossi et al., 2007; Wang et al.).

The reactions, which are self-sustaining and therefore energy efficient (Rossi et al., 2007; Wang et al., 1993), can be ignited by a combustion wave from a chemical reaction, by an electrical current, or by radiation from a heat source or laser (Wang et al.). A reaction moves in a product forming wave through the reactants (Wang et al.).

MICs are a relatively new area of investigation (Miziolek, 2002; Rossi et al., 2007), with research becoming active within the past decade (Dreizin, 2009; Rogachev & Mukasyan, 2010). They are an important area of research due to their potential for use in combustion-based technologies and for providing a better understanding of the properties of nanoparticles. This article reviews the production and preparation of MICs, the differences between MICs and conventional microparticle thermites, the applications of MICs in technology, and future MIC research activity.

Production and Preparation

Several factors are considered when choosing the components used to produce an MIC. The particle sizes and the metal-to-metal oxide ratio in MICs can be altered to obtain different MIC properties (Dreizin, 2009). Various metals and metal oxides are used as the component reagents in MICs, with different reagents having different reaction properties and energies (Wang et al., 1993). Examples of the metal oxides that can be used are MoO_3, CuO, WO_3, and Bi_2O_3 (Dreizin, 2009). Aluminum is the preferred choice of reducer for MICs (Dreizin, 2009; Rossi et al., 2007), as it is for conventional thermites (Wang et al.). Aluminum is readily available (Rogachev & Mukasyan, 2010; Rossi et al., 2007; Wang et al.), is easily produced (Rogachev & Mukasyan, 2010; Rossi et al., 2007; Wang et al.), is inexpensive (Rossi et al., 2007; Wang et al.), has good reduction potential (Wang et al.), has a high thermal conductivity (Pantoya & Granier, 2005; Rossi et al., 2007), and has a low ignition temperature (Rossi et al., 2007). Nano aluminum is pyrophoric in air, but passivation solves the problem by causing a coating of aluminum oxide to form on the particles' surface during production (Dreizin, 2009; Pantoya & Granier, 2005; Rogachev & Mukasyan, 2010).

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Rogachev and Mukasyan (2010) found that as the size of aluminum particles decreases from 20μm to 30nm, the fraction of active aluminum decreases from 97.5% to 44%. This trend is due to an increase in the proportion of surface atoms relative to the volume of the particle. Only surface atoms are available for passivation, so there is a greater proportional passivation of the aluminum in nanoparticles (Pantoya & Granier, 2005). The disadvantage of passivation is that the energy density of the MIC decreases during the process (Dreizin, 2009), but it can be counteracted by increasing the proportion of aluminum particles in the MIC (Pantoya & Granier, 2005). The advantage of passivation is that the MIC is less sensitive to accidental ignition (Pantoya & Granier, 2005; Rossi et al., 2007). Alternatives to aluminum include nickel, iron, and silicon (Rogachev & Mukasyan, 2010).

MICs are prepared using several different methods, each with a different approach and with both advantages and disadvantages. Factors that influence choice of method include the following: simplicity of the process (Rogachev & Mukasyan, 2010; Rossi et al., 2007); safety of the process (Rossi et al., 2007); process temperature (Rossi et al., 2007); cost of the process (Rossi et al., 2007); ability for the products to be tailored (Dreizin, 2009; Rossi et al., 2007); homogeneity of the product (Dreizin, 2009; Rogachev & Mukasyan, 2010; Rossi et al., 2007); agglomeration ability of the product (Rogachev & Mukasyan, 2010); concentration of product impurities (Rossi et al., 2007); thermal conductivity of the product (Klabunde & Richards, 2009; Rogachev & Mukasyan, 2010); and reaction energy and rate of the product (Rogachev & Mukasyan, 2010; Rossi et al., 2007).

The standard method of production involves mixing separate reactant nanopowders, with each reactant powder obtained separately (Dreizin, 2009; Rossi et al., 2007). Sonication of the resulting powder is used to break up any agglomerates (Pantoya & Granier, 2005; Rossi et al., 2007).

A second method is the sol-gel process, which is used for preparing nanopowders as well as MICs (Rogachev & Mukasyan, 2010). The process produces either an aerogel, a lightweight porous material, or a xerogel, a dense form in which the pores have collapsed (Dreizin, 2009; Miziolek, 2002; Rogachev & Mukasyan, 2010; Rossi et al., 2007). The sol-gel process is similar to crystallization processes, except that it produces a material made of nanoparticles (Rogachev & Mukasyan, 2010). To prepare MICs, a metal oxide aerogel is produced and the metal particles are embedded in the pores of the aerogel (Dreizin, 2009).

Arrested reactive milling is a third method for producing MICs. In this process, mechanical forces act on coarse nanopowders to generate nanoparticles (Dreizin, 2009; Rogachev & Mukasyan, 2010). The process initiates the reaction and then arrests it just before the self-sustaining reaction begins (Dreizin, 2009; Rogachev & Mukasyan, 2010). Its main advantages are that the MIC has a low ignition temperature and a high burning rate (Rogachev & Mukasyan, 2010).

In addition, two newer approaches promise useful results: the formation of layered MICs in which alternating nanofilm layers of reagents are deposited on top of each other by vapour deposition to produce an MIC (Dreizin, 2009; Rogachev & Mukasyan, 2010); and the production of MICs through molecular engineering (Dreizin, 2009; Rossi et al., 2007). The second process uses the properties of molecular self-assembly to create ordered metal or metal oxide nanostructures that can be combined to form MICs (Dreizin, 2009; Rossi et al., 2007).

Unique Properties

MICs have properties that differentiate them from conventional bulk microparticle thermites. Overall, MICs are more reactive than bulk thermites (Rogachev & Mukasyan, 2010), which was shown in a number of experiments. First, MICs have a higher rate of reaction than bulk thermites (Dreizin, 2009; Pantoya & Granier, 2005; Rogachev & Mukasyan, 2010; Rossi et al., 2007). Rossi et al. (2007) found that the burning rate for an Al/MoO_3 thermite increases by a factor of ten when the Al particle size decreases from 20μm to 50nm. This property is due to MICs having a greater homogeneity than bulk thermites and a higher surface-area-to-volume ratio than bulk thermites, which increases availability for reaction sites and decreases the diffusion distances (Pantoya & Granier, 2005). When smaller than a critical particle size, the burning rate becomes independent of the particle size due to the increasingly substantial passivation of the particles (Dreizin, 2009; Rossi et al., 2007). Second, MICs have a lower ignition delay than bulk thermites (Pantoya & Granier, 2005; Rogachev & Mukasyan, 2010; Rossi et al., 2007). Ignition delay for an Al/MoO_3 thermite was found to decrease by two orders of magnitude when the composition particle sizes decreased from micro- to nano-size (Pantoya & Granier, 2005; Rossi et al., 2007). Third, MICs also have a lower reaction initiation temperature than bulk thermites (Rogachev & Mukasyan, 2010).

A significant difference between MICs and conventional bulk microparticle thermites is their reaction mechanism. Micro-sized reagents undergo phase changes before the reaction is completed, as is seen where the reaction mechanism for the bulk Al/MoO_3 thermite is based on a liquid (Al) to gas (MoO_3) diffusion (Pantoya & Granier, 2005; Rogachev & Mukasyan, 2010). Nano-sized reagents undergo complete reaction before any phase changes, as is seen where the reaction mechanism for the Al/MoO_3 MIC is based on a solid-to-solid diffusion (Pantoya & Granier, 2005; Rogachev & Mukasyan, 2010).

Technological Application

The development of MICs allowed for the application of thermites in a broad range of technologies. The original, and still popular, use of the thermite reaction is for the welding of train rails in the field (Wang et al., 1993). Other applications of conventional thermites include their use in industrial metallurgical processes for the production of pure metals and oxides, in pyrotechnics, in the demolition of concrete, in the synthesis of ceramics and composite materials, and in the fuels used for turbine based torpedoes (Wang et al.). MICs are being investigated for their use in weapon explosives and propulsion systems (Miziolek, 2002). The Unites States Department of Defense is working with MICs to develop more powerful and compact bombs (Gartner, 2005). MICs are attractive for explosives researchers because of their fast reactions, high energy densities, and ability to be easily tailored (Gartner, 2005; Miziolek, 2002). The United States Military is working with MICs as fuels for propulsion systems to develop faster striking missiles, rockets, and torpedoes (Gartner, 2005). MICs are attractive fuels because they have a high reaction rate and they are compact and quiet (Wang et al.). MICs have further possible applications in firearm primers (Gartner, 2005; Miziolek, 2002), in infrared flares (Miziolek, 2002), in pyrotechnics (Gartner, 2005), and in microelectromechanical systems (Rossi et al., 2007). The use of MICs in these applications is dependent upon their properties such as their low sensitivity to ignition (Miziolek, 2002), low gas pressure produced by reaction (Dreizin, 2009), and high thermal diffusivity (Rossi et al., 2007).

Further Research

Further research needs to be conducted on MICs since the field is relatively young. Research is restricted by limited computational methods and tools (Rossi et al., 2007), and theoretical models (Dreizin, 2009; Rogachev & Mukasyan, 2010). Quality control in the production and preparation of MICs is an issue (Dreizin, 2009). Critical research needs to be conducted on the reaction mechanism and the reaction front of MICs (Dreizin, 2009; Rogachev & Mukasyan, 2010). Other challenges relate to the properties of MICs such as passivation, homogeneity, and sensitivity to ignition (Rogachev & Mukasyan, 2010). Some interesting approaches to solving these problems include the encapsulation of MICs inside carbon nanotubes (Rossi et al., 2007), and the coating of the nanoparticles with surfactants or inhibitors (Dreizin, 2009; Rogachev & Mukasyan, 2010).

Conclusion

The development of MICs as a new class of EMs has stimulated advances in technology and science. Research conducted on MICs has provided a greater understanding of nanoparticles and their properties. Advances have created new processes for the production and preparation of MICs. The unique properties of MICs make them applicable in a range of technologies. Some of these technologies may be detrimental to humanity, such as the development of stronger bombs or faster striking weapons. The study of MICs offers a field of research where progress is critical to the understanding and advancement of the field, and where progress may lead to other advances in nanoscience.

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