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Research article

Waste conversion into high-value ceramics: Carbothermal nitridation synthesis of titanium nitride nanoparticles using automotive shredder waste

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ABSTRACT

Environmental concern about automotive shredder residue (ASR) has increased in recent years due to its harmful content of heavy metals. Although several approaches of ASR management have been suggested, these approaches remain commercially unproven. This study presents an alternative approach for ASR management where advanced materials can be generated as a by-product. In this approach, titanium nitride (TiN) has been thermally synthesized by nitriding pressed mixture of automotive shredder residue (ASR) and titanium oxide (TiO_2). Interactions between TiO_2 and ASR at non-isothermal conditions were primarily investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry. Results indicated that TiO_2 influences and catalyses degradation reactions of ASR, and the temperature, at which reduction starts, was determined around 980 °C. The interaction between TiO_2 and ASR at isothermal conditions in the temperature range between 1200 and 1550 °C was also studied. The pressed mixture of both materials resulted in titanium nitride (TiN) ceramic at all given temperatures. Formation kinetics were extracted using several models for product layer diffusion-controlled solid-solid and solid-fluid reactions. The effect of reactants ratio and temperature on the degree of conversion and morphology was investigated. The effect of reactants ratio was found to have considerable effect on the morphology of the resulting material, while temperature had a lesser impact. Several unique structures of TiN (porous nanostructured, polycrystalline, micro-spherical and nano-sized structures) were obtained by simply tuning the ratio of TiO_2 to ASR, and a product with appreciable TiN content of around 85% was achieved after only one hour nitridation at 1550 °C.

1. Introduction

ASR is an industrial waste generated in the shredding facility of End-of-life vehicles (ELVs). In the shredding process, ELVs are torn into small shreds of ferrous, non-ferrous and polymeric materials. Ferrous and non-ferrous materials are classified and separated by specific arrangements of magnetic drums and eddy current separation techniques. The polymeric material remaining after these operations is the ASR, sometimes referred to as auto fluff. Ferrous and non-ferrous fractions are recycled through pyrometallurgical routes, while ASR ends up in landfills. ASR accounts for almost 20–30 wt% of the total mass of an ELV and consists primarily of plastics (e.g., polypropylene, polyethylene, polycarbonate, polyurethane, acrylonitrile butadiene styrene and polystyrene) and oxide minerals (e.g., titania, alumina and silicates). The ASR content of plastics can accumulate in the environment and cause some environmental implications. The ASR also might comprise heavy metals and undesirable content (Sakai et al., 2014; Singh and Lee, 2015; Mayyas et al., 2016a; 2016b). The large and increasing production volumes of ASR have raised concern in some countries and directives regarding ELVs were introduced (Sakai et al., 2007; Ilgin and Gupta, 2010; Council of the European Union, 1999; European Parliament 2, 2000). These directives, in summary, urge more ELVs materials to be processed and at the same time impose more restrictions on ASR waste disposal. Several solutions were proposed

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such as co-incineration with other waste streams, pyrolysis (at low and moderate temperatures) and use as a cement feedstock (Dutta et al., 1997; Redin et al., 2001; Gendebien et al., 2003; Rossetti et al., 2006; Van Caneghem et al., 2010). However, these processes suffer from several drawbacks and remain economically unproven (Gendebien et al., 2003; Generowicz et al., 2011; Vermeulen et al., 2011; Ni et al., 2013).

While the volume of waste materials continues to increase, the production of materials from new sustainable sources has become of great importance (Iglesias Martín et al., 2013; El-Amir et al., 2016). Advanced ceramic materials such as nitrides, carbides and borides are widely used in a variety of applications. Among these ceramics, a great deal of attention has been recently paid to TiN owing to its unique characteristics. TiN has outstanding chemical, physical and mechanical properties and it is extensively used as hard and wear-resistant coatings for cutting-tool materials (Groza et al., 2000; Samokhin et al., 2014). They also can be used in microelectronic devices, supercapacitors and other industrial and military applications (Joshi et al., 2005; Avasarala et al., 2009; Dong et al., 2011). However, the suitability of TiN for each application depends greatly on its particle size and morphology (Dong et al., 2011; Palmero, 2015). Most of bulk ceramics, with a particle size ~1 μm, are conventionally fabricated at high temperatures from a mixture of naturally-occurring mineral oxide (i.e., TiO_2) and petroleum coke via carbothermic reduction and nitridation reactions (Dewan et al., 2010a; 2010b A; Rezan et al., 2012; Wan et al., 2013). The resulting product is typically a mixture of 10–30% bulk ceramics (~1 μm particle size), 15–30% free C, 40–60% unreacted mineral oxide and 1–5% ash. Ceramics can be then separated from this mixture and purified by mature technologies (Guichelaar, 1997). Such process involves several problems; the product comprises high C content, particle size is large and its morphology is difficult to control. Large particle size ceramics (i.e., monoliths) usually have insufficient mechanical strength and are difficult to process (Groza et al., 2000; Palmero, 2015). For this reason, nanoceramics and their fabrication techniques have recently received great attention. Several techniques have been developed to fabricate nano-crystalline TiN including reactive ball mill method (RBM) (Sherif El-Eskandarany et al., 1998), direct nitridation (Aghababazadeh et al., 2007), sol-gel (Kim and Kumta, 2003a; 2003b A; Kim and Kumta, 2003a; 2003b B) and plasma chemical synthesis (Samokhin et al., 2014). In the RBM method, pure Ti nanopowder is milled using a high energy ball mill at room temperature under N_2 flow for prolonged periods of time. The resulting nanoparticles have a very small particle size around 5 nm. Such small particles are difficult to be further processed by the conventional sintering techniques since small nanoparticles are highly reactive and have high tendency to oxidize. In the direct nitridation method, TiO_2 nano-powder is simply purged with ammonia at temperatures between 700 and 1000 °C. This method, however, results in a product with unfavorable morphology and particle size. In contrast, sol-gel and plasma chemical synthetic techniques are tedious and require many different chemicals; some of these chemicals can pose threat to human and environment. In this present study, a new sustainable approach for ASR processing and TiN production has been suggested; TiO_2 was incorporated into ASR as a catalyst, which was primarily believed to reduce some deleterious emissions. When a hot-pressed mixture of both materials is heated to a sufficient temperature in N_2 atmosphere, TiN ceramic was formed with different unique morphologies. This paper will only discuss some preliminary observations on the catalytic effect of TiO_2 by comparatively studying the non-isothermal degradation kinetics of ASR and TiO_2:ASR mixture. The possibility of producing TiN by nitriding an intimate mixture of ASR and TiO_2 at several reaction conditions was investigated, and a special emphasis was paid on the formation kinetics and morphology of the resulting TiN.

2. Materials and methodology

ASR sample was obtained from OneSteel Recycling Company, Australia. The plastic content of ASR was primarily identified and estimated by sorting particles of different density through heavy-media separation method; further classification was achieved visually by sorting particles that have distinguishing colour and texture. Sorted particles were identified by PerkinElmer-Fourier transform infrared (FTIR) spectrometer and their percentages in ASR were estimated. To prepare an intimate mixture of ASR and TiO_2, as-received ASR was ground by a cryogenic mill (Fig. S1-a and b, supplementary materials). A Titanium IV oxide powder (TiO_2, anatase, 99.8% trace metals basis, supplied by Sigma-Aldrich) was dried at 105 °C overnight and then ball-milled for one hour to reduce particle agglomeration. After that, ASR powder was fed to the ball-mill and left to mix with TiO_2 for an additional one hour. The powder mixture was removed from the ball-mill and hot-pressed into pellets using a uniaxial hydraulic press by applying 3 bar of pressure at 180 °C for 10 min. The interaction between ASR and TiO_2 at non-isothermal conditions was studied using Perkin-Elmer Pyris 1 TGA by heating pressed pellets of 1:4 ratio of TiO_2:ASR from room temperature to 1300 °C at 20 °C min^{-1} under N_2 purge (20 ml min^{-1}).

To investigate the TiO_2 nitridation by ASR, a pressed pellet was cut into two halves to fit inside an alumina crucible (Figs. S1–c, supplementary materials). Several pellets with different TiO_2:ASR mass ratios were prepared. Nitridation experiments were subsequently conducted by placing TiO_2:ASR pellets (3 g each) in a hot tubular furnace (100 cm length × 5 cm diameter) under N_2 purge (1 L min^{-1}) for a given period of time. Following nitridation, N_2 was immediately replaced with Ar, and the product was kept under Ar flow for 30 min to remove any physisorbed N. The resulting materials were denoted as shown in Table 1. Gas evolution during nitridation at different temperatures was conducted in a tubular furnace coupled with an infrared (IR) analyser; the same procedure of nitridation was followed but with 500 mg pellets of 1:5 ratio of TiO_2:ASR. The composition and morphology of the resulting product was characterized by X'pert PRO multi-purpose XRD (MPD system, operating at 40 kV and 40 mA), X-ray photoelectron spectroscopy (XPS) and FEI Nova Nano-SEM 230 (FE-SEM) attached with energy dispersive spectroscopy (EDS). All FE-SEM specimens were sputtered with thin layer platinum for better resolution; the obtained EDS spectra were baseline-corrected and peaks of platinum were accordingly removed. The N content of the resulting material was determined by combustion/oxidation analysis (COA) using LECO TC600; a nitride calibration was performed based on multiple weights of Si_3N_4.

3. Results and discussion

ASR consists of several types of plastics such as polyprolpylene, polyethylene, polycarbonate and polyurethane as shown in Fig. S2 (supplementary materials). Polyprolpylene and polyethylene dominate the composition of ASR, both accounting for more than 50% of ASR. Polycarbonate and polyurethane are also found in significant quantities in ASR, with around 12 and 14%, respectively. Other plastics such as acrylonitrile butadiene styrene and polystyrene are used in automobiles and believed to exist in ASR; however, these plastics were not found in the received sample of ASR and there composition was consequently difficult to estimate. ASR also comprises small quantity of ash ranging between 2 and 3.9%; this value is too low compared to the values reported in previous studies (Kobyashi et al., 2005; Kameda et al., 2009; Lopes