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Short communication

Synthesis of nanocrystalline TaC powders via single-step high temperature spray pyrolysis from solution precursors

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ABSTRACT

Nanocrystalline powders for high temperature ceramics (HTC) and ultra-high temperature ceramics (UHTC) are important materials for aerospace and other important industrial applications. In this study, a low cost, *single-step* synthesis method for nanocrystalline HTC and UHTC powders is reported, which is based on high temperature spray pyrolysis (HTSP) process. The synthesis starts with solution of oxide and carbon precursors dissolved in common organic solvents, which are broken into fine droplets (e.g., via a nebulizer). The droplets then go through processes of solvent removal, thermolysis, and rapid *in situ* carbothermal reduction (CTR), all in one single pass in a tube furnace operated at high temperature. The synthesis method was demonstrated successfully using the example of tantalum carbide (TaC) from precursors of tantalum chloride ($TaCl_5$) and phenolic resin in a *single-step* HTSP process with maximum temperature of 1650 °C in one pass that finished within minutes, yielding agglomerated nanocrystalline TaC UHTC powders.

1. Introduction

High temperature ceramics (HTC) and ultra-high temperature ceramics (UHTC) are ceramic materials that typically have melting points above ~2500–3000 °C. HTC and UHTC, in the form of powders, monolithic ceramics, or composites, find many important applications from grinding and cutting materials (e.g., WC, TiC, c-BN) in machinery and mining industries to thermal insulation tiles, missile nozzles, and hypersonic vehicle leading edges (e.g., SiC, TaC, ZrB_2) in the aerospace industry [1,2]. Reducing the size for HTC and UHTC powders from microns to submicron and even nanometer range (i.e., < ~100 nm) offers additional benefits such as simplified post-synthesis powder processing by reducing the need for extensive grinding, lowering the sintering temperature and associated energy consumption for materials processing and densification, and helping produce manufactured parts with sub-micron or even nano-sized grains, which often leads to further improved mechanical properties such as strength, hardness, and toughness for the ceramic materials [3,4] . In addition, nanopowders will offer flexibility in subsequent processing to make either bulk ceramics via powder consolidation or coatings via techniques such as plasma spray.

Although synthesis of nano-sized HTC and UHTC powders have been studied for some time, most methods reported in the literature suffer from some drawbacks either in terms of cost, product quality, or process safety. For example, nano TaC has been synthesized using the RF plasma method in a quick one step process, but the method uses costly organometallic precursors and hydrogen gas, and several steps in the operation have to be carried out in a glove-box [5]. Similarly, combustion synthesis or self-propagating high-temperature synthesis (SHS) method offers a very fast fabrication process, but it suffers from limitations related to the nature of batch process and the difficulty in process control due to too short reaction time. In addition, mechanical milling is often involved for SHS produced powders, which also raises concerns with contamination. Even for synthesis based on solution processing that involves carbothermal reduction reaction (CTR) as the final step, despite the relative inexpensive starting materials used and the success with obtaining various nano carbide powders, the methods reported typically consists of *separate steps* of solution or sol processing, drying, inert atmosphere thermolysis, and finally high temperature CTR heat treatment, with each step lasting for hours or even days. As a result, the synthesis is still a batch process with long-reaction time, which severely limits productivity [6,7].

On the other hand, spray pyrolysis, also called aerosol decomposition, is a technique in which a precursor solution (e.g., salt or mixed salts solution) or a fine colloidal suspension is broken, via an atomizer or a nebulizer, into tiny droplets or aerosols, which then go through thermal treatment, often in a preheated furnace, and experience subsequent physical/chemical processes including solvent evaporation,

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precipitation and drying of the (mixed) solutes, thermolysis or decomposition into inorganic phases (e.g., oxides) to produce fine powders in one single-step. Due to the simple principle and easy setup, it has been widely used for producing fine, well-dispersed powders including nanopowders for ceramics, especially oxide materials (see related reviews [8–10]).

Nevertheless, despite the apparent advantages of spray pyrolysis, there have been very few studies on using this technique for the synthesis of *non-oxide* ceramic powders, especially HTC and UHTC ceramics. To the best of the authors' knowledge, nitride ceramics of Si_3N_4 and hexagonal BN (*h*BN) have been prepared using spray pyrolysis, but the approaches adopted do not seem scalable for manufacturing due to i) strict requirement of "oxygen-free precursors" (e.g., polysilazane for Si_3N_4 [11] and poly(borazinylamine) [12] or borazine [13] for *h*BN) and "oxygen-free solvents" (e.g., benzene [11] and liquid anhydrous ammonia [12,14]) and ii) the requirement of a separate high temperature annealing for the conversion of the amorphous products to the corresponding crystalline nitride powders. Cerovic *et al.* appears to be the only group reporting the use of spray pyrolysis for producing carbide of β-SiC [15]. However, in that study, spray pyrolysis is still only an *intermediate step* to produce a SiO_2-C mixture, which then had to go through a *separate* CTR heat treatment at 1500 °C for 1.5 h, yielding micron-grained SiC powders. For borides, only the low-melting point MgB_2 has been prepared with the use of hydrogen as the reducing agent, which raises safety concern for the operation [16].

Here, the authors report the successful synthesis of nano TaC UHTC powders using a single-step, high temperature spray pyrolysis (HTSP) method that incorporates the various processes including drying/solvent evaporation, thermolysis, and rapid, *in situ* CTR *all in one single pass* that finishes within a few minutes or shorter. The synthesis process is inherently a continuous process and could be scaled up for industrial production easily. The results on characterizing the nanocrystalline TaC products from the HTSP is discussed briefly, and the directions for future research are pointed out.

2. Experimental

Fig. 1 gives the schematic for the HTSP set up. It starts with low cost, common soluble precursors that are fed and broken into fine, micron-sized droplets via an atomizer or a nebulizer. The fine droplets are then carried into the hot zone of a tube furnace by an inert carrier gas. Different from the conventional spray pyrolysis that typically operates at temperatures only up to ~1000 °C [8,11,12], for the HTSP process, the "pyrolysis" step will include not only drying and thermolysis, which is the removal of low molecular weight species to form oxides and carbon, it is also extended to incorporate *rapid* (i.e., within a few minutes or even seconds) *in situ* CTR reaction at sufficiently high temperature (e.g., > ~1600 °C) to achieve the synthesis of nanopowders of HTC and UHTC (e.g., carbides) in a fast, simple process all in *one single step*.

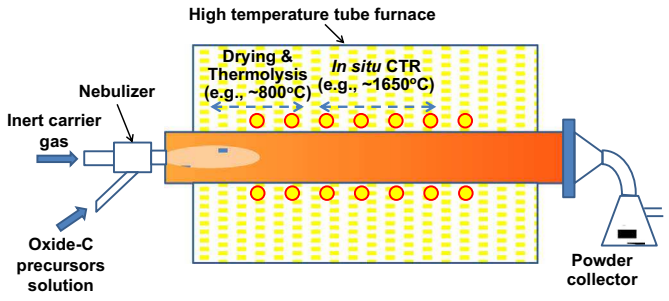

Fig. 1. Schematic illustrating the high temperature spray pyrolysis (HTSP) setup that incorporates solvent drying, thermolysis (removal of low molecular species), and *rapid in situ* carbothermal reduction reaction (CTR) between oxide and carbon to form HTC or UHTC nano powders all in one single pass. Note that the hot zone of the furnace is maintained at high temperature (e.g., ~1650 °C or higher).

Table 1
Summary of recipes for different mixed solutions used for the synthesis of nanocrystalline TaC powders.

Recipe	Tantalum chloride (g)	Phenolic resin (g)	Ethanol (g)	1-Pentanol (g)	2 M ammonia solution (g)	C: Ta_2O_5 molar ratio[a]
R1	0.330	0.138	11.835	2.840	–	10: 1
R2	0.796	0.300	11.828	–	0.856	9: 1

[a] Assuming phenolic resin gives a carbon yield of 40 wt% after thermolysis [18].

In particular, for the synthesis of nanocrystalline TaC UHTC powders via the single-step HTSP process, the starting tantalum precursor used is tantalum pentachloride ($TaCl_5$, 99.8%, Alfa Aesar #14164), the carbon precursor used is Novolac phenolic resin (Plenco, 14353, R5420), and the solvents used are absolute ethanol (99.5+%, Acros Organics #61509-0020) or 1-pentanol (99+%, Alfa Aesar # 30898). Two recipes were adopted, as summarized in Table 1: for recipe R1, phenolic resin was first dissolved in ethanol to form an orange-colored solution. $TaCl_5$ was dissolved separately in 1-pentanol, into which the phenolic resin-ethanol solution was then added. For recipe R2, ethanol was used as the solvent for both phenolic resin and $TaCl_5$. The precursor solutions were either used directly for HTSP as carried out for R1, or mixed with a small amount of ammonia solution (2 M solution in ethanol, Sigma-Aldrich #392685) to remove Cl ion as precipitated NH_4Cl crystals from the precursor solution and then used for HTSP as carried out for R2. To break the solution into fine droplets, a commercial medical nebulizer was used, and Argon (UHP grade, Airgas) was used as the carrier gas at a flow rate of ~1 L/min. (Note that UHP Ar gas has to be fed also to the inlet of the medical nebulizer so that the nebulizer does *not* suck air into the system, which causes oxidation of the product in the HTSP.) The fine droplets from the nebulizer was brought into a high temperature tube furnace (MHI industry, model H18-40HT) fitted with an alumina tube with outside diameter of 50 mm and inner diameter of 44 mm and sealed appropriately. During the HTSP operation, the temperature in the constant temperature zone (~30 cm long and also the highest temperature region) of the furnace was 1650 °C, and the temperature decreases at distance extended away from the constant temperature zone. As explained, droplets of the precursor solutions would go through complex processes of solvent evaporation, thermolysis, and finally CTR as below

$$Ta_2O_5 + 7\quad C = 2TaC + 5CO\uparrow \tag{1}$$

to produce TaC. The powder product from HTSP was collected into a plastic bottle and analyzed by XRD and SEM for characterization of phase and microstructure.

3. Results and discussions

Fig. 2 shows the XRD patterns of the synthesized TaC powders from the HTSP method. For both recipe R1 and R2, clear peaks corresponding to TaC (JCPDS card #00-035-0801) were identified apart from peaks corresponding to NaCl (JCPDS card #00-005-0628), which is a contaminant in the processing. The identification of TaC demonstrates the concept that TaC UHTC powder could be synthesized via single-step HTSP from typical oxygen-containing precursors/solvents since both phenolic resin as the carbon source and ethanol as the solvent contain oxygen. The origin for Na (as in NaCl) is not exactly clear, but is most likely due to impurity either in the phenolic resin or $TaCl_5$ source material. By comparing the XRD pattern for the products from recipe R1 with R2, it is seen that insufficient carbon was used for recipe R2, as

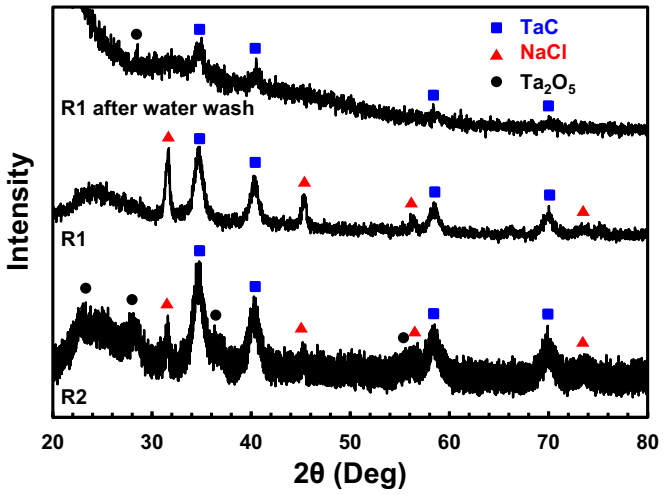

Fig. 2. XRD patterns for the synthesized nanocrystalline TaC powders via single-step high temperature spray pyrolysis (HTSP) using recipe R2, R1, and R1 after washing in DI water, respectively.

evidenced by the diffraction peaks corresponding to crystalline Ta_2O_5 (JCPDS card #00-019-1299). It is noticed that despite the treatment with ammonia solution (as described for recipe R2) to try to remove Cl compounds via precipitation of NH_4Cl in the ethanol solution, a small amount of NaCl is still identified in the product. Because of this, washing of the products in DI water was carried out. Upon drying, XRD for the products was obtained, and the result for TaC powder from R1 after waster washing is also shown in Fig. 2, confirming the removal of NaCl. For both powders from R1 and R2, the wide width of the diffraction peaks for the synthesized TaC suggests the grain size is < ~100 nm. It is noted that grain size analysis using Scherrer equation seems to underestimate the grain size to be only ~10 nm, which might be due to line broadening associated with possible deviation from the 1:1 stoichiometry for the Ta-C system [17]. In addition, because of the current setup only adopts a commercial medical nebulizer to generate the fine droplets, the amount of TaC powder produced in the experiments was small - on the order of hundreds of milligram per hour of operation, with some falling into the downstream tube section while others falling into the collection bottle. This combined with the loss in the water washing process limited the amount of sample available for the subsequent XRD analysis for the R1 sample after water washing and contributed to the relatively low signal to noise ratio in the XRD pattern for that sample.

Fig. 3 shows SEM images for the obtained TaC powders via the HTSP method. Two types of morphologies can be observed: one corresponds to fine porous powders with grain size in the range of ~20–50 nm that are agglomerated together, as in Fig. 3(b, c, e); while the other corresponds to micron-sized spherical powders as expected from the conventional spray pyrolysis process, as in Fig. 3(a, b, d, e, f). Elemental analysis via EDS suggests the agglomerated nano particles contain Ta and C and almost no O, which indicates the nanocrystalline particles are TaC. On the other hand, the micron-sized spherical particles are fairly dense, as seen from one cross-section prepared by focus ion beam (FIB) milling, as in Fig. 3(f). Such relatively dense, micron-sized particles are attributed to unreacted Ta_2O_5 – rich regions, which is rational due to the relatively low melting point of Ta_2O_5 (T_m=1872 °C) compared with TaC (T_m=3880 °C). It is also consistent with the recipes used. As shown in Table 1, the C: Ta_2O_5 molar ratio is 10:1 for R1 and 9:1 for R2, while the low-mag SEM images (see Fig. 3(d, e)) clearly show much more micron-sized, dense spherical particles for the powder from recipe R2 that is relatively carbon poor, and this correlates well with the clear presence of diffraction peaks of Ta_2O_5 in the XRD pattern for the product from R2.

Finally, consider the flow rate of argon was 1 L/min and the alumina tube inner diameter was 44 mm, the linear velocity of the droplets was ~1 cm/s. Given the center uniform temperature zone of the furnace is 30 cm long, the total CTR reaction time is estimated to be ~30 s and the total process time for one pass from solution to the final TaC powder is ~2 min – this compares very favorably with existing methods of synthesizing nanocrystalline UHTC powders using soluble precursors, which in most cases take much long time of hours [6] or even days [7].

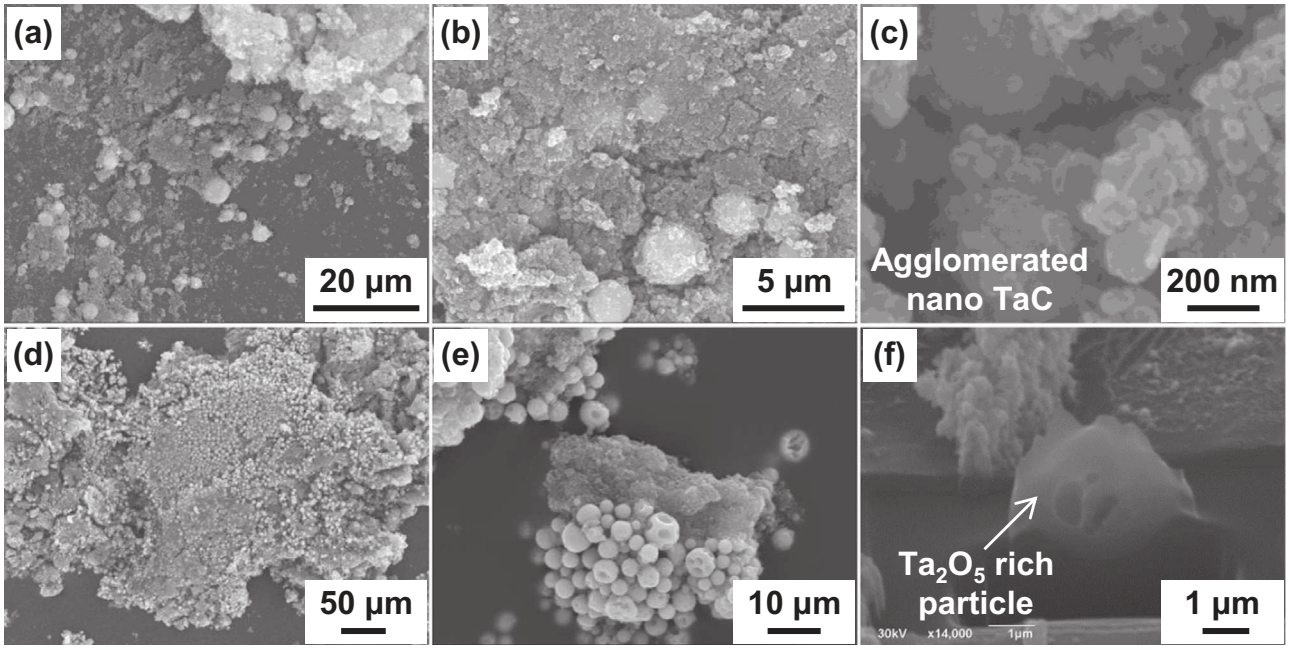

Fig. 3. SEM images at different scale for the synthesized nanoscrystalline TaC powders from high temperature spray pyrolysis (HTSP) in a single pass: (a, b, c) are for recipe R1 (designed C: Ta_2O_5 molar ratio of 10: 1); (d, e, f) are for recipe R2 (designed C: Ta_2O_5 molar ratio of 9: 1) that leaves significant amount of unreacted Ta_2O_5 in the product. Note that (c) shows the nanocrystalline TaC powder in R1 is highly agglomerated while (f) is for a large micron-sized spherical particle after focus ion beam (FIB) milling to reveal the cross-section, and it is attributed to unreacted low-melting point Ta_2O_5–rich region in the product.

4. Conclusions

Nanocrystalline powders of tantalum carbide have been synthesized using a single-step, high temperature spray pyrolysis (HTSP) method. The precursors used are low cost $TaCl_5$ and phenolic resin while common oxygen-containing organics such as ethanol and/or 1-pentanol are used as the solvent. The entire synthesis process lasts less than a couple of minutes from solution to crystalline TaC powders with grain size of ~20–50 nm. Such results prove that HTSP, which incorporates rapid *in situ* CTR, is a promising method for low cost, continuous lab-scale synthesis as well as industrial production of nano-crystalline high temperature and ultrahigh temperature ceramic powders. Further experiments aimed at understanding the detailed processing-structure relationships for this method and exploring it for the synthesis of other HTC/UHTC (e.g., SiC, HfC, and HfB_2) nano powders will be carried out in future. In addition, optimization of the system such as replacing the medical nebulizer with an atomizer that can generate much higher quantities of fine droplets and searching for better operating conditions will also be carried out to improve the productivity and reducing the extent of powder agglomeration for this process.

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