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Development of a processing route for carbon allotrope-based TiC porous nanocomposites

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ABSTRACT

Ti-foils are currently used as a spallation target material to produce radioisotopes for physics research at the ISOLDE facility at CERN. However, radioisotope production rates often decrease over time due to material degradation from high operation temperatures. Due to enhanced release rates, porous nanomaterials are being studied as spallation target materials for isotope production. TiC is a material with a very high melting point making it an interesting material to replace the Ti-foils. However, in its nanometric form it sinters readily at high temperatures. To overcome this, a new processing route was developed where TiC was co-milled with graphite, carbon black or multi-wall carbon nanotubes in order to hinder the sintering of TiC. The obtained nanocomposite particle sizes, density, specific surface area and porosity were characterized and compared using ANOVA. All carbon allotropes mixed with the TiC, were able to successfully stabilize the nanometric TiC, hindering its sintering up to 1500 °C for 10 h.

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1. Introduction

Titanium carbide (TiC) is a well known FCC interstitial carbide and had its properties studied mainly during the 50's and the 60's [1]. Due to its high melting point of 3067 °C high hardness and strength, good thermal and electrical conductivities, thermal shock resistance, and low evaporation rate it is mainly used as a refractory ceramic. It is used in the aerospace industry (rocket and aircraft materials) and in super-hard and wear-resistant tools (as a cermet and as a coating material) [1,2].

For nuclear applications, TiC has been studied as a coating material [3] or as a reinforcement in carbon for plasma facing materials [4] for future fusion plants. TiC has also been subject to numerous irradiation studies as a potential material for nuclear fuel coatings in fission power plants [5]. In the past, at the ISOLDE (Isotope Separator OnLine DEvice) facility at CERN [6], TiC was studied as a potential spallation target material for production of radioactive

ion beams, but the outcome was unsatisfactory due to slow isotope release rates [7,8].

ISOLDE relies on the on-line isotope separation method (Isotope Separator OnLine, ISOL) [6] to produce radioactive ion beams for nuclear, atomic, solid state and bio-physics studies. In this method, a target material kept at high temperatures in vacuum, is irradiated with energetic particles which will induce nuclear reactions in the material, producing isotopes that come at rest in the target. These isotopes have then to diffuse out of the bulk material to the surface where they evaporate and diffuse through the material porosity, defined as effusion. They then effuse through a transfer line into an ion source. The ion source finally transforms the released neutral isotopes into ions and shape a beam for physics experiments [9].

The target materials used for ISOL vary from liquids (low melting point metals or salts), solids in powder, pellet or fiber form (carbides or oxides) or metallic foils [10]. The materials should be as pure as possible, since impurities can produce unwanted isotope contaminants, either through nuclear reactions or vaporization as radiologically stable contaminants. High target material operation temperatures are needed to accelerate the diffusion and effusion processes while being limited by the material melting point, vapor pressure and sintering rates. A highly porous microstructure with the smallest particle size is desired, to reduce the diffusion distances but it has to be stable at the highest operation temperature. Reducing the particle size of the target material either to submicrometric [11,12] or nanometric [10,12–14] has shown in the past

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enhanced isotope release and, consequently, higher beam intensities for short lived species.

Historically, micrometric TiC (1–50 μm) was discarded as a target material due to slow release of isotopes even at 2300 °C [7,8]. Micrometric SiC (1–50 μm) was discarded as well for the same reasons [8], and in recent developments, by reducing SiC particle size to the sub-micron level (0.6 μm) the release of isotopes was shown to be improved [11,12]. We propose to use the same methodology for TiC, reducing its particle size down to the submicron or nanometric level. Additionally, particle size stabilization mechanisms can be employed leading to higher operation temperatures. Such mechanisms can be achieved by doping TiC or by introducing a second highly-refractory inert phase, such as carbon, to reduce the coordination number of TiC particles and hinder sintering.

The sintering driving force is provided by the decrease of the free energy of the system which depends on the total free surface and particle radius and curvature. As such, the sintering kinetics of nanomaterials are enhanced when compared to conventional materials, because of their intrinsic high surface areas. While conventional powders are expected to sinter at about 0.5–0.8 T_m (T_m being the material melting point), in nanomaterials this can happen at 0.2–0.4 T_m [15]. In the literature, TiC powders with 140–170 nm primary particle size, reached 91% density at 1627 °C while 5 μm TiC powders needed 2797 °C to reach the same density [16]. Furthermore, nanopowders are often found in an agglomerated form, having a bimodal pore size distribution: small intra-agglomerate and large inter-agglomerate pores [17]. While the small pores from the intra-agglomerate porosity are easily eliminated during sintering, the large inter-agglomerate pores require significantly higher temperatures. The sintering temperature of nanomaterials often scales up with the agglomerate size, rather than with the primary particle size [15]. Since ISOL targets operate at high temperatures and nanometric materials tend to sinter readily, a solution which allows for high diffusion/effusion and at the same time low sinterability has to be found [14,13].

Dual-phase sintering or constrained sintering is used in ceramics to prevent grain growth by having two homogeneously mixed and interpenetrating phases which have limited or no solid solubility with each other [18,19]. There are examples in the literature where grain growth and densification was successfully hindered in ZnO–SiC [20] systems, Al₂O₃–ZrO₂ [19] and Al₂O₃–Cu [21]. For the TiC–C system a study done by B. Manley et al. [22] shows that additions up to 14 at.% (3.2 wt.%) of C, hinder the sintering of submicrometric TiC by reducing the relative volume changes by more than a factor of 2. Furthermore, in SiC, it has been shown that the addition of very small quantities of carbon (up to 3 wt.%) promote sintering (with 0.5 wt.% B) while further additions, studied up to 16 wt.%, successfully hinder its grain growth [23].

TiC–C (nano)composites can be found in the literature in a wide range of sizes (4 nm to tens of micron), shapes (fibers or particles) and different TiC volumes (5 vol.% to almost 100% TiC) [4,24–35]. A considerable amount of the TiC–C studies are found for fiber shape where normally the carbon is a by-product from the TiO₂ carbothermal reduction with C. Such fibers are used in reinforced polymers with 300 nm fiber diameter [24], semiconductor films with tens of micron diameter fiber [25], filtration membranes, 120 nm mesoporous fibers with 19 nm TiC crystallites [26], solar cells with 200–400 nm fiber diameter with 20 nm TiC crystallite size, 70 wt.% TiC [27] and for supercapacitors with 280 nm diameter fibers, TiC crystallite size 20–50 nm, 40 wt.% TiC [28]. In the rest of the studies found, TiC–C composites include application in electrodes and catalysis (4 nm TiC, 30 wt.% Ti as membranes [29] or 35 nm TiC–C core–shell particles [30]), fuel cells (25–75 wt.% of micrometric TiC in C as coating [31]), as high temperature structural material (tens of micron TiC with 2–40% of C, 15% porous to fully dense [32–34] or with 100 nm TiC crystallite size, 30% porous

with 9/1 – Ti/C molar ratio [35]) and for nuclear applications (5 vol.% \approx 100 nm TiC inclusions in graphite [4]).

Although, TiC–C composites already exist in the literature, as seen above, their processing is either too complex or not suitable for the application described here. Moreover, the structure required is one which should be stable at high temperatures (at least 1500 °C) while keeping nanometric TiC, which was not found in the literature. Additionally, the simplest processing route should be used to reduce and control the possible sources of contamination to the target material. Since the titanium is the element of interest (selected due to the high isotope production cross-sections), one wants the highest concentration as possible while keeping acceptable levels of open porosity. Also, the processing route must be easy to scale up, since TiC targets are expected to have up to 100 g. As a result, in order to stabilize nanometric TiC with size less than 100 nm, a new processing route is developed here where different ratios of carbon allotropes, graphite, carbon black and carbon nanotubes, are added to the TiC. The TiC–C composites obtained were characterized before and after heat treatments in order to assess the degree of stabilization of nanometric TiC.

2. Materials and methods

2.1. Materials

Commercially available nanometric TiC powder was acquired from *Goodfellow*, 99.9% pure, with nominal particle sizes between 80 and 130 nm (Ref. LS396999/1). The carbon allotropes used were: graphite (*Alfa Aesar*, Ref. 40798, 325 mesh – <44 μm), carbon black (*Orion Engineered Carbons*, *Printex A Pulver*, 40 m² g^{−1} – 40 nm primary particle size) and multi-wall carbon nanotubes, MWCNT, (*Nanocyl*, Ref. NC3100, >95% purity, 10 nm diameter, 1.5 μm length). The mixtures were done in isopropanol, IPA, (from *Reactolab SA*, Ref. 99295, 99% pure) using polyvinylpyrrolidone, PVP, (*Fluka*, K-30 mol wt 40k) as a dispersant for the TiC and the allotropic carbon materials [36]. The characteristics of the raw materials can be found in Table 1 and scanning electron microscope microscopy (SEM) microstructures in Fig. 1.

2.2. Methods

2.2.1. Processing

The TiC–C composites were co-milled using an attrition mill (*Union Process*, *01HD*) at 800 rpm in a small volume grinding bowl (70 ml) using 1.5 mm yttrium-stabilized-zirconia (YSZ) milling balls. The milling suspension was added to the grinding bowl with 2.6 vol.% of solids in IPA containing 0.5 wt.% PVP and 130 g of YSZ balls were added to fill the grinding bowl up to 90%. Preliminary studies on the milling of the raw materials were done interrupting the milling process at defined times to take small samples. After these studies and optimizations, 2 h was defined as milling time to produce the TiC–C composites. In the case of the MWCNT, the bulk density (see Table 1) was used to calculate the MWCNT solid volume, because they dominate the mixing behavior. The carbon volumes tested were 25, 50 and 75 vol.%.

In the case of the MWCNT composites an additional composite was produced where the MWCNT were not co-milled with the TiC. This composite, was produced by milling the TiC for 2 h separately and later mixed with MWCNT which were treated by ultrasonication for 15 min beforehand. The TiC milled suspension was added to the MWCNT suspension and sonicated for a further 30 min.

After the milling/mixing process, the suspensions were dried using a rotary evaporator (*Buchi Rotovapor R-114*), at 80 °C in vacuum with constant agitation to avoid segregation of the TiC from the carbon. The obtained powder was deagglomerated manually

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