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Journal of the European Ceramic Society 29 (2009) 2355–2361

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Facile synthesis of bimetallic carbonitrides, $V_{1-x}Ti_x(C,N)$, by microwave carbothermal reduction–ammonolysis/carburisation (MW-CRAC) methods

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Received 29 August 2008; received in revised form 5 January 2009; accepted 13 January 2009
Available online 13 February 2009

Abstract

New quaternary carbide nitrides in the $V_{1-x}Ti_x(C,N)$ ($0 \le x \le 0.4$) system have been synthesised rapidly (0.5–1.5 h) by carbothermal reduction, carburisation and ammonolysis *via* microwave heating using a custom-modified, multimode cavity microwave reactor. The products were structurally characterised by powder X-ray diffraction (PXD), while scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used to examine morphology and composition. The resulting carbonitrides crystallise with the rock salt structure and the cubic lattice parameters vary linearly with increasing titanium concentration (x), hence following Vegard's law. Particle sizes typically range from 250 nm to 2 μm.

Keywords: Microwave processing; Powders-solid state reaction; Carbides; Nitrides; Transition metals

1. Introduction

Metal carbides and nitrides find utility in a wide range of applications. Many display high melting points, hardness, strength and tribological properties that make them attractive for use in cermets and as coatings.[1,2] Magnetic and electronic properties have also been investigated,[3] with relevance for use in high temperature electronic devices.[4] Early transition metal (TM) nitrides and carbides also form an exciting and developing class of catalysts that exhibit high activity, selectivity and stability, particularly for industrially important hydrotreating processes, where they have been found to display surface electronic behaviour similar to that of the precious metal catalysts traditionally used, such as platinum and palladium.[5]

Many binary carbides and nitrides with the sodium chloride structure show complete mutual solubility, forming a continuous series of solid solutions[6] and are stable over a wide range of sub-stoichiometries.[7] There is scope for enhancing the properties of these materials and other comparable TM carbides and nitrides by compositional variation over a potentially huge range of ternary and quaternary compositions. The variation in properties with composition for a limited number of bimetallic carbides and nitrides has been reported and, for example, $Ti_{0.6}Hf_{0.4}C$ is among the hardest of known materials (43.1 GPa).[7] Likewise, monometallic carbonitrides such as $Ti(C_xN_{1-x})$ can show superior properties compared with the corresponding binary carbides and nitrides.[8] There remain a huge variety of ternary and quaternary compositions that require further investigation, particularly with regard to enhancing mechanical, electronic and catalytic properties, for example.

The use of microwave synthesis in solid-state chemistry and materials science has received significant recent attention.[9,10] These methods offer some notable alternatives and some considerable advantages when compared to conventional heating and particularly: drastically reduced reaction times, selectivity in the energy transfer to reactants, reduced energy consumption, rapid heating without temperature gradients in reagents/mixtures[11] and increased densification of products.[12] Reducing temperature gradients may be especially advantageous in the synthesis of interstitial TM carbides and nitrides in overcoming diffusion

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doi:10.1016/j.jeurceramsoc.2009.01.018

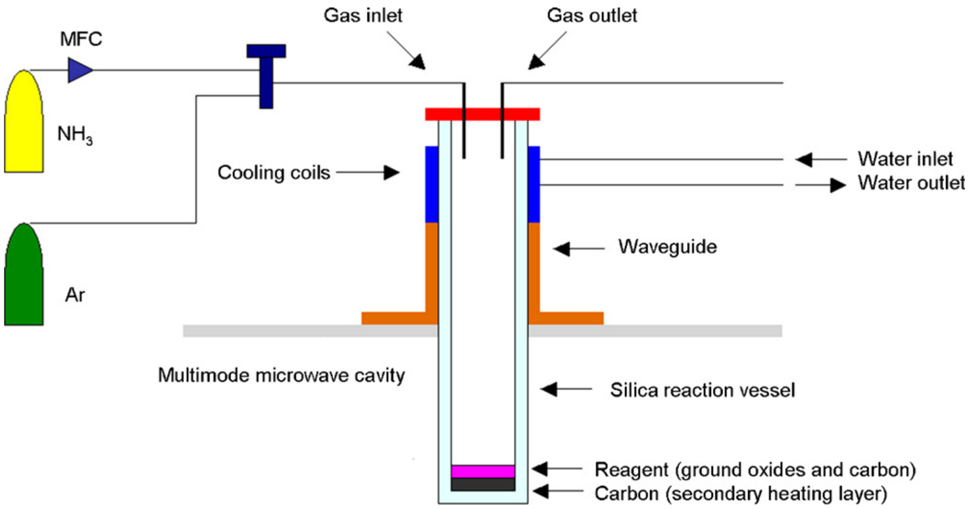

Fig. 1. Schematic of the modified DMO MW-CRAC reactor.

barriers caused by formation of surface layers.[13,14] Heating by microwaves requires that at least one of the reactants couple effectively with the microwave field, i.e. be good susceptors of microwaves at room temperature. The ability of a material to be heated by microwave absorption is proportional to its loss tangent ($\tan\delta$). The loss tangent is a function of two dielectric properties of the material, both of which are temperature and microwave frequency dependant[11] (Eq. (1)).

$$\tan\,\delta = \frac{\varepsilon''}{\varepsilon'} \tag{1}$$

where ε' is the relative permittivity and ε'' is the dielectric loss of the material.

The total power absorbed per unit volume (P) of a material by the absorption of microwave energy is given by (Eq. (2))[15]:

$$P = 2\pi f \varepsilon_0 \varepsilon_r' \tan\,\delta |E|^2 \tag{2}$$

where f is the microwave frequency, ε_0 is the permeability of free space, $\varepsilon_r{}'$ is the relative dielectric constant and E is the magnitude of the internal electric field.

Amorphous carbon is particularly effective at coupling with microwaves[10] and hence carbon can act not only as a reactant in the formation of carbides but also as a susceptor and secondary heat source sustaining the high temperatures required for processes such as reduction and carburisation.[16,17] Microwave methods have been demonstrated to be effective in the synthesis of binary nitrides *via* ammonolysis.[10] In this paper, we describe how by using a bespoke microwave reactor system, it is possible to develop the processes of microwave carbothermal reduction–carburisation and microwave ammonolysis to synthesise quaternary transition metal carbonitrides. We report how this technique has been successful in preparing the new bimetallic carbonitrides $V_{1-x}Ti_x$(C,N) on timescales that are dramatically reduced over the conventional high temperature, energy intensive methods for synthesis of TM carbides and nitrides.

2. Experimental

Compositions of $V_{1-x}Ti_x$(C,N) ($0 \leq x \leq 0.4$) were prepared by MW-CRAC methods using a reactor designed taking a modified domestic microwave oven (DMO) as a basis (Fig. 1). The reactor design enables reactions under anaerobic conditions and control over feed gases and flow rates facilitating both solid-state and solid–gas phase reaction chemistry in a microwave field. The gas-tight silica reaction vessel is inserted into a modified DMO (Panasonic NN-T535 operating at 2.45 GHz; maximum power output 1 kW) through a Cu waveguide and cooling coils constructed around the reaction vessel external aperture and outside the DMO cavity itself. The reaction vessel is inserted into a position where the sample is located at a point of high field intensity within the cavity, i.e. a mode. The reactor vessel itself can be removed to allow handling in an inert atmosphere glove box (either N_2 or Ar). The DMO used is capable of scaleable power inputs of 440, 600, 900 or 1000 W as opposed to varying pulse durations at full power.

For the synthesis of the quaternary carbonitrides, stoichiometric amounts of the respective oxide powders V_2O_5 (Sigma–Aldrich 99.6%) and TiO_2 (Sigma–Aldrich 99.95+ %) were ground in a 2:1 weight ratio with amorphous carbon (BDH > 99.5%; i.e. C excess), where the latter is intended to act as reductant, carbon source and MW susceptor. The powdered reagents (typically *ca.* 160 mg) were placed atop an additional, identical quantity of amorphous carbon that acted as a secondary hearing layer. This ensemble was contained in a gas-tight silica reaction tube which was inserted into the modified DMO apparatus and subsequent reactant gas flow was set using a mass flow controller. In all cases, the reactor was flushed with NH_3 (BOC 99.99%) for 10 min prior to heating. A flow of 120 ml min^{-1} of NH_3 was maintained during heating and cooling. The reactor was subsequently flushed with argon (BOC 99.995%) for an additional 5 min before the product was retrieved. The reaction time, applied power and number of cycles required for the synthesis of various compositions are shown in Table 1. Samples were reground after each cycle as required.