Abstract

Theoretical investigations on the $Zr_xTa_{1-x}O_{1+x}N_{1-x}$ system predict that some of its phases are likely to possess relatively high hardness values.[1] Such materials may be suitable for industrial application as cutting tools. The motive of the project was to investigate the best synthesis route and a method for obtaining well sintered, dense oxynitride phases with a nominal composition TaON (x=0), $Ta_{0.8}Zr_{0.2}O_{1.2}N_{0.8}$ (x=0.2) and $Ta_{0.3}Zr_{0.7}O_{1.7}N_{0.3}$ (x=0.7).

This was achieved through three main steps, i.e. synthesis of the oxynitride powders, high pressure sintering and evaluation of mechanical properties. A sol gel method was used to obtain the precursor oxide powders. $TaCl_5$ and 70wt% zirconium propoxide were used as the starting materials. Oxide gels were formed by dissolving precursor materials in absolute ethanol for 15minutes with continuous stirring, followed by subsequent hydrolysis to form gels which were aged for 24hrs at 80^0C. The gels were dried in air at 100^0C for 12hrs in a drying oven followed by calcinations in a muffle furnace at 600^0C for 6hrs to remove the alkyls and chloride ions. High surface area amorphous powders were obtained (~6.60 ± 0.02 m^2/g in the case of Ta_2O_5) after milling with 4mm steel balls for 4hrs in a planetary mill.

The respective oxynitrides were obtained by thermal nitridation using an ammonia (99.99%) flow method. A temperature of 900^0C maintained for 4hrs in the presence of water vapour at an ammonia flow rate of $50cm^3$/min were found to be the optimum nitridation conditions. The water vapour pressure was realised by bubbling the ammonia through a water bath at room temperature prior to supply to the furnace. The water vapour pressure of such a set up was approximated to be ~$3.1*10^3$Pa. This nitridation process was carried out in a tube furnace using a silica tube of length 1200mm and external diameter of 40mm and an alumina boat as the holding vessel. Approximately 2g of oxide powder were used for each run. The dependency of nitridation on temperature and ammonia flow rate

was investigated for the formation of TaON. Pure TaON formation was found to be more favoured by temperatures of 900^0C with a heating rate of 20^0C/min and by an ammonia flow rate range of 40-50cm^3/min. These conditions were also used for the mixed Ta-Zr oxynitrides. $Ta_{0.3}Zr_{0.7}O_{1.7}N_{0.3}$ formation was found to be dependent on the heating rate with ZrO_2 forming beside the oxynitride solid solution above a heating rate of 10^0C/min. In the present work the phenomenon has been found to be dependent on the kinetics of the crystallisation reactions. At higher heating rates crystallisation of the separate phases is favoured leading to the formation of separate phases. On the other hand with an optimum heating rate the solid solution is maintained to the final nitridation temperature.

The powders were found to be thermally stable in air above 600^0C with TaON being the most stable with a weight change occurring at a temperature of ~690^0C. The powders were stable in pure nitrogen well above 1000^0C. Sintering in a hot press in the temperature range of 900-1400^0C at a heating rate of 50^0C/min and a pressure range of 50-85MPa using previously heat treated h-BN crucibles in argon resulted in porous, partially densified materials. A maximum % theoretical density of 81.6% was obtained for TaON at 1000^0C and 85MPa pressure applied for 1hr. TaON oxidised to Ta_2O_5 above 1000^0C with an oxide phase transition being observed above 1300^0C.

High pressure sintering was carried out in the temperature and pressure regime of 920-1200^0C and 3-5.5GPa respectively in the case of TaON. The mixed Ta-Zr oxynitrides were sintered at 3GPa at a temperature of 1100^0C. No phase transitions were observed in all cases. An average hardness value of ~16.8GPa and fracture toughness of ~3.4MPam$^{1/2}$ were obtained for the TaON phase. $Ta_{0.3}Zr_{0.7}O_{1.7}N_{0.3}$ and $Ta_{0.8}Zr_{0.2}O_{1.2}N_{0.8}$ were found to possess hardness values of 13.4GPa and 13.02GPa respectively under the same sintering conditions. It was observed that the hardness values obtained for TaON are higher than those for ZrO_2 or HfO_2 ceramics, due to the stronger covalent bonding in nitrogen present in TaON. On the other hand the fracture toughness values are as low as those of fully stabilised ZrO_2 materials due to lack of phase transformation toughening.

Dedication

In memory of my mother.

Gladys Matizamhuka

[1958-2000]

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List of Symbols:

B^* : calculated bulk modulus (GPa)

V : denotes a vacancy in a sublattice.

O_i : denotes excess oxygen ions.

O_0^x : oxygen anion at a regular oxygen site.

$V_{\ddot{o}}$: oxygen vacancy in an anionic sublattice.

μ_x : chemical potential of component x.

ΔG_x^0 : standard Gibb's free energy of component x (kJ/mol).

P_x : partial pressure of component x (atm.).

B_0 : theoretical bulk modulus (GPa).

K_p : equilibrium constant.

a_N : activity of component N.

α : extent of dissociation.

D_0 : initial density (g/cm^3).

D_f : final density (g/cm^3).

$\tilde{\varepsilon_c}$: atomic flux.

D_c : lattice diffusion coefficient.

Ω : atomic volume (cm^3).

G : grain size (μm).

k : Boltzmann constant (~1.38065*10^{-23}JK^{-1})

T : absolute temperature (K).

ψ : applied stress (MPa).

E_b : binding energy (kJ).

N_c : coordination number.

b : bond length (Å).

λ : bond polarity.

HV : Vickers' Hardness (GPa)

k_0 : Hall Petch coefficient ($MNm^{-3/2}$).

H_0 : average hardness of pure crystal (GPa).

G_{IC} : crack resistance factor .

E : Young's modulus (MPa).