Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 547–553

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of pressure and treatment temperature on the structural evolution of mechanically alloyed Ti(W)(C,N)–Al admixes in boron nitride

Kasonde Maweja[a,*], Kambuyi Katuku[b]

[a]Element Six Production/Diamond Research Laboratory, 1 Debid Road, Nuffield, PO Box 561, Springs 1559, South Africa
[b]Department of Engineering Metallurgy, University of Johannesburg, PO Box 17011, Auckland Park 2028, South Africa

Received 10 April 2012; received in revised form 2 June 2012; accepted 20 June 2012
Available online 29 June 2012

Abstract

The effect of pressure and temperature on the structural changes of admixtures of cBN, Al and $Ti(C_{0.5}N_{0.05})$ or $Ti(C_{0.5}N_{0.5})_{0.6}$ mechanically alloyed powders with 40 mass% W were investigated by means of the X-ray diffraction technique. It emerged that pressure and temperature affected the crystal structures and compositions of the binder phases as well as the behaviour of the contaminating Fe. High pressure–high temperature (HPHT) sintering favoured the formation of Ti(W,Al)(C,N) solid-solutions, whereas vacuum annealing favoured the formation of W(Ti,Al) solid-solutions. Products of Ti(C,N)-based crystal lattices remained stable under high pressure (5 GPa), whereas W based crystal lattices were more stable under vacuum (0.001 Pa). Inert single phase binders were formed in HPHT sintered PcBN compacts. Formation of Ti(W,Al)(C,N) by reactions between mechanical alloyed Ti(W)(C,N) powder particles and liquid Al prevented the formation of AlN, AlB_2, α-AlB_{12}, TiN and TiB_2 particles in PcBN compacts. Sintering of PcBN occurred by dissolution of B and N atoms in Ti(W,Al)(C,N) and re-precipitation on cBN particles.

Keywords: Mechanical alloying; Pressure; Structure; Temperature

1. Introduction

Two major types of interactions are identified between hard ceramics and binder particles sintered by high pressure–high temperature (HPHT) systems, apart from plastic deformation and annealing. The first type of interaction is a catalysis whereby, the binder dissolves the ceramic atoms either in areas where capillary pressures are high (particles are close together) or simply from relatively unstable small particles. The dissolved atoms re-precipitate thereafter on the ceramic particles in areas of lower chemical potential where particles are non-close or simply on relatively big particles. This type of interaction occurs with binders such as Co, Fe, Mn, Ni or a mixture thereof upon polycrystalline diamond (PCD) sintering. The second type of interaction is essentially a solid-state diffusion and a series of sintering reactions through which the binder acts as superglue that holds together the ceramic particles. This type of interaction occurs for example with binders such as TiC, TiN, and Al or a mixture thereof upon polycrystalline cubic boron nitride (PcBN) sintering [1–8].

When sintering PcBN composites without and with Al binder at 8 GPa and 1850 °C, Casanova et al. [9] came to the conclusion that the binder phase would affect both plastic deformation and defect annealing. They indicated that plastic deformation of grains would be the rate-controlling step for sintering at short processing times (< 15 s), whereas defect annealing would be at longer times, when sintering with 5 mass% Al. The binder decreased significantly the stress concentration at the cBN grains, thus reducing the plastic deformation, whereas it builds additional reaction induced-stress and delays significantly stress relief and recrystallisation at longer sintering times.

When sintering PcBN composites with 15 mass% Al and 20 mass% AlN under 5 GPa, Lv et al. [10] found that the

*Corresponding author. Tel.: +27 833650952.
E-mail address: mawejak@yahoo.fr (K. Maweja).

0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.06.062

hardness of PcBN composites sintered with Al was the highest and decreased with the increase of sintering temperature due to the increased formation of AlB_2. However, the hardness of PcBN sintered with AlN increased with the increase of sintering temperature reaching a highest value of 29 GPa due to the formation of Al_2O_3. Zhao and Wang [11] noticed significant contribution by nanodiamond particle addition to the increase of density, strength and heat resistance of Ti-coated cBN sintered with binders containing Si and Al through various reactions products among them TiC, TiB_2, $TiC_{0.3}N_{0.7}$, AlN, $TiAl_2$, Al_4C_3, $TiSi_2$, TiB and TiN. Sintering of PcBN composites respectively with Ta and TaC binders under 7 GPa and at 1750 °C for 3.5 min has been reported by Benko et al. [12]. According to their study, binary compounds such as TaB, TaB_2 and TaN were formed at the cBN/Ta interface. Spark plasma sintering could be a method of efficient sintering of PcBN composites at relatively low pressure and high temperature, without significant cBN to hBN phase transformation and with less reaction products due to a high heating rate and relatively low holding time [13]. In general, in order to get control of fracture toughness affected by crack deflection, particle pull-out, crack bridging and crack branching in sintered ceramics, control of size, aspect ratio and volume fraction of potential precipitates of binary products of reactions between boron nitride and binder constituents are of utmost importance. Such an endeavour would require a study of microstructural features as a function of homogenisation temperature and annealing temperature–time regimes. In this regard, compositions of the mixes and their milling treatment conditions affect most the microstructure [14–15]. Recently a spur of research activities around the processing parameters, characterisation, thermal stability and reactivity of mechanically alloyed (Ti,W,Al)(C,N) powders [15–19] as alternative binders for the sintering of a next generation of stronger, tougher and high thermal stability PcBN compacts, arose. The current study investigated the effects of pressure and temperature on the crystal structural changes in Ti(C,N)–W mechanically alloyed powders admixed with boron nitride powder and aluminium. The occurring transformations in this new type of binders and their interactions with cBN were monitored by XRD analysis of crystal structures at different stages of an industrial process route, which include debinding at atmospheric pressure, out-gassing under vacuum and high pressure–high temperature (HPHT) sintering. Chemical stability of mechanically alloyed (Ti,W,Al)(C,N) solid solutions and formation of single phase binders during HPHT sintering were expected instead of PcBN embrittling binary compounds such as AlB_2, AlN, TiB_2, $TiAl_2$, Al_4C_3 and TiB formed in conventional PcBN compacts. The purpose of forming stable (Ti,W,Al)(C,N) solid solutions via the mechanical alloying route was to minimise chemical reactivity of the binder with cBN during HPHT sintering, thus avoiding the detrimental effects, e.g. thermal expansion mismatch, stress raiser effect, chemical reactivity with workpiece, etc. of the secondary binary products in PcBN cutting inserts. The absence of such embrittling compounds within the binder pools and at PcBN/binder interfaces is expected to enhance the thermal stability and subsequently the tool life.

2. Materials and experiments

Pure powders of $Ti(C_{0.5}N_{0.05})$ or $Ti(C_{0.5}N_{0.5})_{0.6}$ and W respectively supplied by Japan New Metals Co. Ltd and Alfa Aesar were mixed in proportions of 60 mass% Ti(C,N) and 40 mass% W, and were milled for 48 h in an Argon atmosphere in a high energy ball mill machine at a rotation speed of 400 rpm. A Retsch PM400 machine was used for mechanical alloying process. The selection criteria of the particular proportions of starting powders and the transformations induced by the high energy ball milling process have been reported elsewhere [15]. The mechanically milled powders were then mixed with Al powder supplied by Alfa Aesar and cBN powders (Element Six product) of grain size respectively of 5 μm and 2 μm by attrition milling in inert liquid to achieve a mixture containing 60 mass% cBN and 40 mass% of binder materials. The proportion of aluminium in the Ti(C,N)–W–Al binder materials represented 10 mass%. The attrition milled slurries were dried in a rotary evaporator. The effect of applied pressure (0.001 Pa – 5 GPa) on the phase transformations of the mixtures, in the temperature range 1350–1400 °C, was investigated by means of XRD analysis. The vacuum, high pressure and temperature conditions selected corresponded to typical industrial practice for outgassing the pre-composites and HPHT sintering of PcBN [1–3,5–7,19]. A Philips Analytical B.V. X'Pert X-Ray diffractometer, equipped with a hot stage and fitted with a Ni-filtered Co anode was used for the XRD analyses. In this regard, the pressures used were successively 0.001 Pa for the high vacuum annealing, 0.1 MPa for the annealing under an argon atmosphere and 5 GPa for the industrial HPHT sintering for 30 min. The effect of temperature on the phase transformations in the mixtures, under a vacuum of 0.001 Pa, was also investigated by means of XRD analysis. In this regard, temperatures of 25, 650, 750, 850, 950, 1050 and 1200 °C were successively used in the hot stage X-ray diffractometer which allowed running both annealing/sintering and XRD scan in real time. XRD analysis was repeated after cooling from 1200 °C to 25 °C to check the occurrence of any transformations upon cooling.

3. Results and discussion

3.1. Effect of pressure on the structure of the binder phase

The transformations in mixtures of cBN and Al powders with mechanically alloyed $Ti(C_{0.5}N_{0.05})$–W binders treated at ~1400 °C under different pressures are illustrated by the changes in the XRD diffraction patterns represented in Fig. 1. The binder materials of the mixtures heat treated

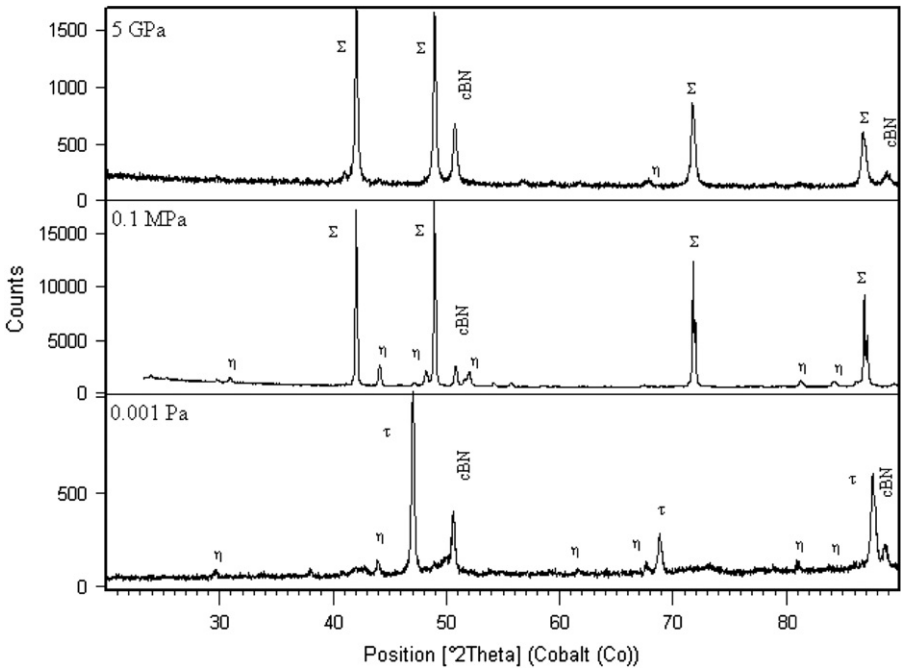

Fig. 1. XRD patterns of cBN and Al powders mixed with mechanically alloyed $Ti(C_{0.5}N_{0.05})$–W powders and treated at ~1400 °C under different pressures, showing the Fe-contaminant product (η), the formation of a BCC phase (τ) under 0.001 Pa and FCC phase (Σ) formed under 0.1 MPa and 5 GPa.

under vacuum contained a W-rich body centred cubic (BCC) product (τ), whose lattice parameters were close to those of the $Al_{0.13}W_{0.57}Ti_{0.30}$ compound in the ICSD Database [20], which suggested the formation of a disordered W(Al,Ti)(C,N) solid solution. The contaminating elements Fe and Cr were alloyed with W to form a hexagonal close packed (HCP) phase (η), whose structure was close to that of Fe_7W_3 according to the same database. However, the major constituent of the binder material of the mixtures annealed under a pressure of 0.1 MPa in an argon atmosphere was a face centred cubic (FCC) phase (Σ), whose structure was close to the $(Ti_{0.8}W_{0.2})C$. These results showed that mobility of Al and Ti atoms were higher under vacuum, which enhanced their dissolution and alloying in W lattices, thus the formation of the disordered W(Al,Ti)(C,N) BCC phase (τ). The fast diffusion of Ti atoms observed under vacuum did not hold at normal and high pressures, where W and Al atoms dissolved in Ti crystal lattices; the ordered FCC Ti(W,Al)(C,N) phase (Σ) was the main constituent of the binder material in products sintered under 5 GPa at 1400 °C as shown in Fig. 1. The contaminant Fe_7W_3 particles (η) formed under normal pressure 0.1 MPa under an argon atmosphere were dissolved in the binder product (Σ) under the high pressure of 5 GPa at 1400 °C; this led to the absence of the main characteristic XRD peaks of (η) from the diffraction pattern of HPHT compacts. Thus, the XRD results indicated that the final product of HPHT sintering of cBN with $Ti(C_{0.5}N_{0.05})$–W mechanically alloyed powder mixed with Al consisted of a FCC Ti(W,Al)(C,N) single phase binder, which acted as inert glue between cBN particles. The XRD patterns of HPHT sintered products contained no characteristic peaks of the binary compounds such as AlN, AlB_2, TiN, TiB_2, etc. encountered in conventional PcBN compacts. The intensities of the XRD peaks of the binder material constituents and those of the contaminating compound (η) formed in PcBN sintered under high pressure (5 GPa) were roughly 10 times smaller than those of the mixtures annealed under normal pressure (0.1 MPa). The short broad XRD peaks indicated the grain size refinement of the FCC binder phase (Σ) formed by HPHT sintering (under 5 GPa) and also the corresponding higher crystallite lattice strains comparatively to those of the same phase (Σ) formed under 0.1 MPa at the same temperature. The second system considered in this study used a different type of titanium carbonitride, the $Ti(C_{0.5}N_{0.5})_{0.6}$, which contained less carbon and nitrogen than the first $Ti(C_{0.5}N_{0.0.5})$. The effect of pressure on the structural changes of the mixtures of boron nitride powder with aluminium and mechanically alloyed $Ti(C_{0.5}N_{0.5})_{0.6}$–W powders treated at ~1400 °C under different pressures is illustrated by the XRD patterns in Fig. 2. A single phase BCC product (τ) was formed during annealing of MA powders under vacuum (0.001 Pa). The $Ti(C_{0.5}N_{0.5})_{0.6}$–W mechanically alloyed materials annealed under a pressure of 0.1 MPa in an argon atmosphere thermally decomposed into two constituents, e.g. a FCC Ti-rich phase (Ω), which coexisted with a BCC W-rich phase (κ). The decomposition product (κ) observed under 0.1 MPa pressure that was not formed under high pressure (5 GPa); a HCP W-rich product (ω) was rather formed under 5 GPa. A high resolution TEM analysis will be required to compare the compositions of the two W-rich products (κ) and (ω) formed in MA $Ti(C_{0.5}N_{0.5})_{0.6}$–W based binders annealed under 0.1 MPa and 5 GPa respectively. The comparison of compositions

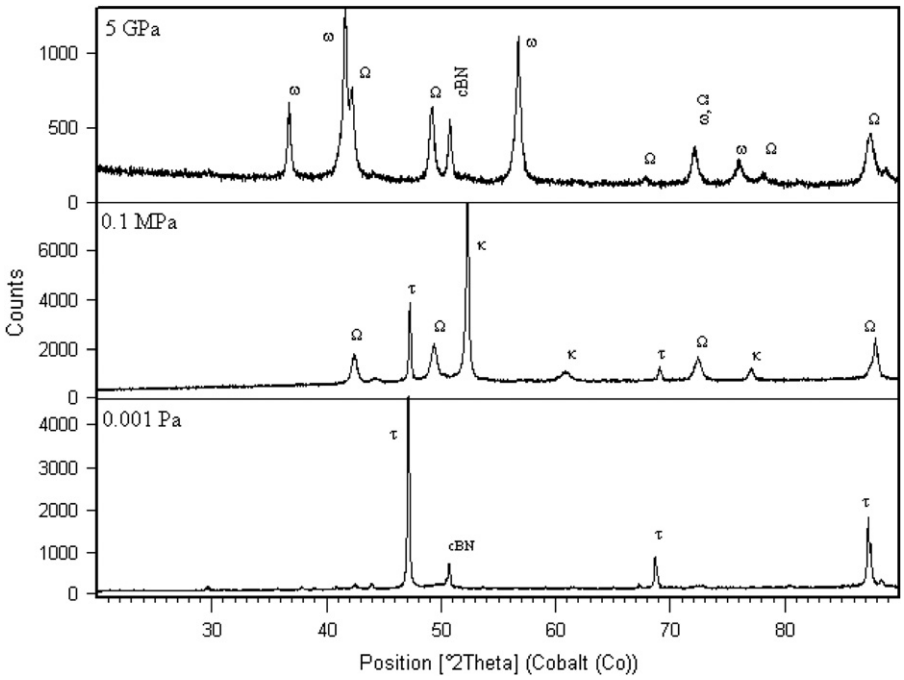

Fig. 2. XRD patterns of cBN and Al powders mixed with mechanically alloyed $Ti(C_{0.5}N_{0.5})_{0.6}$–W powders and treated at ~1400 °C under different pressures, showing the formation of the product (τ) under 0.001 Pa, the phase (κ) under 0.1 MPa and the products (Ω) and (ω) under 5 GPa.

of the two products would enable characterising the transformation mechanism of product (κ) into (ω). The semi-quantitative analysis by the XRD peaks intensities method indicated that the binder of the mixtures annealed under 5 GPa contained about 63 mass% of a FCC Ti-rich product (Ω) and 37 mass% of a HCP W-rich product (ω), whose composition was close to the sub-stoichiometric $WC_{0.9}$ [20]. It inferred from the XRD analysis results that annealing under low pressure enhanced the transformation of $Ti(C_{0.5}N_{0.5})_{0.6}$–40% W mechanically alloyed binders mixed with Al by inversing the behaviour of tungsten from a solute to a solvent of Ti atoms, whereas a decomposition of the binder into two products (Ω) and (ω) was observed under a high pressure of 5 GPa. Thus the high pressure applied before heating in HPHT sintering of PcBN did not prevent the thermally induced decomposition of mechanically alloyed $Ti(C_{0.5}N_{0.5})_{0.6}$–40% W powders as was observed during annealing under an argon atmosphere at normal pressure. The vacuum annealing products of both $Ti(C_{0.5}N_{0.05})$–W and $Ti(C_{0.5}N_{0.5})_{0.6}$–W based systems contained phases formed by dissolution of Ti and Al atoms in W lattices. However, the dissolution or transformation of W-rich products (η, τ and κ) in the Ti(C,N) lattices led to the formation of different high pressure phases in the binder materials depending on the type of Ti(C,N) used. Among the binding phases, TiN and TiC exhibit the highest chemical activity toward BN [21,22]. The calculations of phase equilibria for the BN–TiN and BN–TiC systems were carried out by Benko et al. [3] and Smith and Missen [23] using the Villars–Cruise–Smith (VCS) algorithm for the temperatures 1000, 1400 and 1750 °C in the pressure range 0.0013 Pa–10 MPa based on the thermodynamic data [24]. Their results indicated that TiN can react with BN to form TiB_2, which is the only solid phase present in the equilibrium state at temperature comprised between 1000 and 1400 °C. The decomposition products N_2, B and Ti would coexist with BN in equilibrium at 1750 °C under low pressure ($p < 0.02$ MPa). Klimczyk et al. [7] suggested that the formed amount of TiB_2 did not depend on the annealing temperature, thus one could not neglect the processes occurring during the HPHT sintering. According to the calculations TiC react with BN to form TiB_2 and TiN and their content is dependent on pressure and temperature. Again at low pressure decomposition N_2 and B would coexist in equilibrium with gaseous BN, Ti and C at 1750 °C. Experimental results confirmed the formation of TiB_2 in the cBN/TiN sintered composite, and TiB_2 and $TiC_{0.8}N_{0.2}$ in the cBN/TiC sintered composites [3]. Rong and Fukunaga [2] reported the formation of AlN, AlB_2 and α-AlB_{12} through the reactions between solid cBN and molten Al, and the rapid growth of AlN and AlB_2 particles during HPHT sintering. Rong et al. [5] demonstrated in a subsequent study the suppression of the rapid grain growth of AlN and AlB_2, thus improved the performance of the cutting tools, by addition of a TiN secondary phase in the binder. Unlike in the above mentioned systems, the absence of characteristic peaks of AlN, AlB_2, α-AlB_{12}, TiN and TiB_2 in the XRD patterns of PcBN sintered with mechanically alloyed binders could be ascribed to the limited content or small sizes of the binary product particles formed by reaction between mechanically alloyed Ti(W)(C,N) particles and liquid Al. It is suggested in PcBN sintering with MA binders that atoms diffused from liquid Al and first

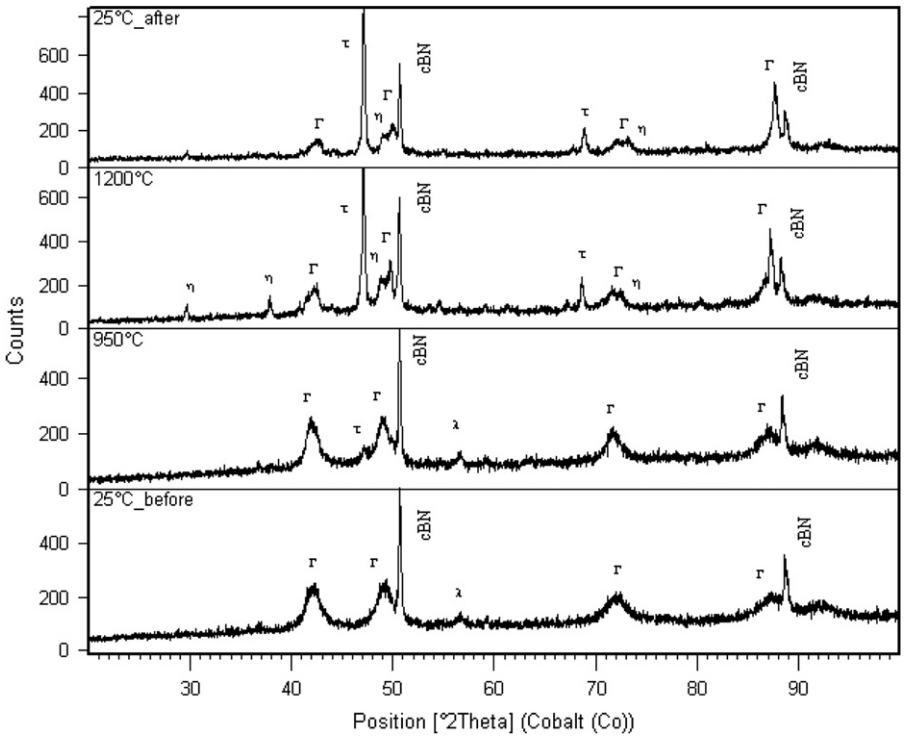

Fig. 3. XRD patterns showing the effect of temperature on the phase transformations in the mixes of cBN, Al and mechanically alloyed $Ti(C_{0.5}N_{0.05})$–W powders under 0.001 Pa vacuum.

reacted with the activated Ti(W)(C,N) particles to form the FCC Ti(W,Al)(C,N) binder phase (Σ). The reactivity between the two materials is ascribed to the fast diffusion of Al atoms under the dislocations in MA Ti(W)(C,N) particles inherited from the high energy ball milling. The strain energy stored in MA powders contributed to the driving force for reaction between MA powders and liquid Al. Thus Al atoms were consumed in this reaction; only undetectable amount to XRD of the binary compounds could be formed by reaction with cBN particles. The fast diffusion of Al atoms under dislocations and reaction with MA binders also occurred prior to the thermal decomposition of $Ti(C_{0.5}N_{0.5})_{0.6}$–W based binders, thus the absence of the binary compounds in the second binder system too. The chemical stability of Ti(W,Al)(C,N) prevented the reactions between the binders and cBN particles. Sintering of PcBN occurred by dissolution of B and N atoms in Ti(W,Al)(C,N) and re-precipitation on cBN particles forming cBN/binder microfaceted interfaces as was shown in previous work [19].

3.2. Effect of temperature on phase formation under vacuum

The structural changes pertaining to the annealing under vacuum of mixtures of cBN and Al powders with MA Ti(W)(C,N) powders at different temperatures are illustrated on XRD patterns in Figs. 3 and 4. The XRD results suggested that the metastable MA $Ti(C_{0.5}N_{0.05})$–W product (Γ) was decomposed into a W-rich product (τ) and a Fe-contamination precipitate (η) at ~950 °C. The peak intensities of the phase (τ) increased as the treatment temperature increased, due the increase in corresponding volume fraction in the annealed material, grain growth and relaxation of the crystal lattices strains inherited from the high energy ball milling process. The Fe-contamination product (η) formed at high temperature remained stable after cooling down to room temperature as shown by the corresponding XRD diffraction peaks in Fig. 3. However, it was observed that the formation temperature of the W-rich phase (τ) in MA $Ti(C_{0.5}N_{0.5})_{0.6}$–W materials was as low as 850 °C (Fig. 4). The contaminating Fe was dissolved in the same phase, contrasting with the precipitation of a Fe-contamination product (η) observed in MA $Ti(C_{0.5}N_{0.05})$–W based mixtures (Fig. 3). The binder material in the mixtures annealed at temperatures below 1050 °C under vacuum still contained the HCP (λ) of crystal structure close to $(W,Al)C_{0.9}$ in the ICSD Database [20] and the FCC Ti(W)(C,N) (δ) phases formed upon mechanical alloying. The HCP $(WAl)C_{0.9}$ product (λ) was dissolved in the FCC phase (δ) at temperatures above 1050 °C, thus leading to the formation of a BCC Ti(W,Al)(C,N) single phase solid solution (τ) as shown in Fig. 4. Once again formation of binary compounds encountered in traditional PcBN compacts due to chemical reactions between binder constituents and boron nitride particles did not occur in mixtures containing mechanically alloyed powders.

4. Conclusion

The effects of pressure and temperature on mixtures of boron nitride and aluminium powders with sub-stoichiometric

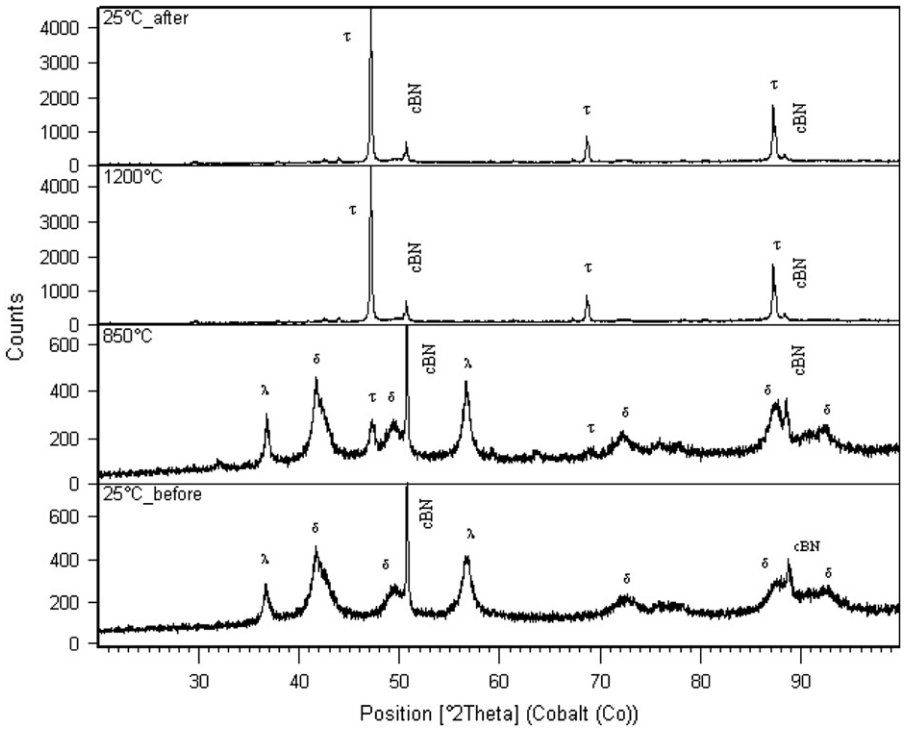

Fig. 4. XRD patterns showing the effect of temperature on the phase transformations in the mixes of cBN, Al and mechanically alloyed $Ti(C_{0.5}N_{0.5})_{0.6}$–W under 0.001 Pa vacuum, stressing the dissolution of $(W,Al)C_{0.9}$ (λ) and (δ) phases formed during high energy ball milling and the formation of a single BCC phase (τ).

Ti(C,N)–40 mass% W mechanically alloyed binders were investigated in this work. $Ti(C_{0.5}N_{0.05})$ and $Ti(C_{0.5}N_{0.5})_{0.6}$ were selected, the first containing more interstitial elements than the second. The applied pressure, heat treatment temperature and composition of Ti(C,N) used, all affected the structural changes, thus the compositions of the phases formed in the binder materials as well as the behaviour of the contaminating Fe. A general observation was that the high pressure–high temperature sintering conditions favoured the formation of Ti(W,Al)(C,N) solid-solutions, whereas W(Ti,Al) solid-solutions were predominantly formed under vacuum. These trends showed that under HPHT conditions Ti(C,N)-based crystals were more stable than W and Al crystals, whereas W crystals were more stable under vacuum, thus the roles of solvent or solute of Ti and W changed. The XRD results suggested no structural transformation of cBN to hBN occurred under the experimental conditions. The stability of W(Ti,Al) crystals under vacuum (0.001 Pa) was attributed to its elevated melting temperature. The mobility of Ti and Al atoms as well as their solubility in W increased under the same conditions. The solvent character of titanium at high pressure was ascribed to the destruction of W and Al crystals under HPHT conditions (5 GPa, 1400 °C) and the subsequent fast diffusion of atoms, which enhanced their solubility in the Ti(C,N) lattices. Formation of Ti(W,Al)(C,N) by reactions between mechanical alloyed Ti(W)(C,N) powder particles and liquid Al prevented the formation of AlN, AlB_2, α-AlB_{12}, TiN and TiB_2 particles in PcBN compacts. Sintering of PcBN occurred by dissolution of B and N atoms in Ti(W,Al)(C,N) and re-precipitation on cBN particles.

Acknowledgement

The authors are grateful for the financial support of the Element Six/Diamond Research Laboratory and for the authorisation to publish this work.

References

[1] F. Ueda, M. Yageta, I. Tajima, Microstructure and mechanical properties of cBN–TiN composites, Journal of Hard Materials 2 (3–4) (1991) 233–243.
[2] X.Z. Rong, O. Fukunaga, Sintering of cubic boron nitride with added aluminum at high pressure and high temperatures, Transactions of the Materials Research Society of Japan 14B (1994) 1455–1458.
[3] E. Benko, J.S. Stanislaw, B. Krolicka, A. Wyczesany, R.L. Barr, cBN–TiN, cBN–TiC composites: chemical equilibria, microstructure and hardness mechanical investigations, Diamond and Related Materials 8 (1999) 1838–1846.
[4] E. Benko, T.L. Barr, S. Hardcastle, E. Hoppe, A. Bernasik, J. Morgiel, XPS study of the cBN–TiC system, Ceramics International 27 (2001) 637–643.
[5] X.Z. Rong, T. Tsurumi, O. Fukunaga, T. Yano, High-pressure sintering of cBN–TiN–Al composite for cutting tool application, Diamond and Related Materials 11 (2002) 280–286.
[6] X.Z. Rong, T. Yano, TEM investigation of high-pressure reaction sintered cBN–Al composites, Journal of Materials Science 39 (14) (2004) 4705–4710.
[7] P. Klimczyk, E. Benko, K. Lawniczak-Jablonska, E. Piskorska, M. Heinonen, A. Ormaniec, W. Gorczynska-Zawislan, V.S. Urbanovich, Cubic boron nitride–Ti/TiN composites: hardness and phase equilibrium as function of temperature, Journal of Alloys and Compounds 382 (1–2) (2004) 195–205.

[8] Y. Zhao, M. Wang, Effect of sintering temperature on the structure and properties of polycrystalline cubic boron nitride prepared by SPS, Journal of Materials Processing Technology 209 (2009) 355–359.
[9] A.C.A.M. Casanova, N.M. Balzaretti, G. Voronin, J.A.H. da Jornada, Experimental study of plastic deformation during sintering of cubic boron nitride compacts, Diamond and Related Materials 8 (1999) 1451–1454.
[10] R. Lv, J. Liu, Y. Li, S. Li, Z. Kou, D. He, High pressure sintering of cubic boron nitride compacts with Al and AlN, Diamond and Related Materials 17 (2008) 2062–2066.
[11] Y. Zhao, M. Wang, Preparation of polycrystalline cBN containing nanodiamond, Journal of Materials Processing Technology 198 (2008) 134–138.
[12] E. Benko, T.L. Barr, A. Bernasik, S. Hardcastle, E. Hoppe, E. Bielańska, P. Klimczyk, Experimental and calculated phase equlibria in the cubic BN–Ta–C system, Ceramics International 30 (2004) 31–40.
[13] M. Hotta, T. Goto, Effect of time on microstructure and hardness of β SiAlON–cubic boron nitride composites during spark plasma sintering, Ceramics International 37 (2011) 521–524.
[14] A. Momozawa, R. Telle, Controlled precipitation of W2B4 platelets and of β-WB nanolaminates for the in situ reinforcement of ternary TiB_2–$W2B_4$–CrB_2 ceramics, Journal of the European Ceramic Society 32 (2012) 85–95.
[15] K. Maweja, L.A. Cornish, N. Can, Transformation and alloying mechanisms in sub-stoichiometric titanium carbonitride–tungsten high energy ball milled powders, International Journal of Refractory Metals and Hard Materials 29 (2011) 312–319.
[16] K. Maweja, L.A. Cornish, N. Can, Annealing behaviour of sub-stoichiometric Ti(C,N)–W mechanical alloy powders, International Journal of Refractory Metals and Hard Materials 29 (2011) 445–451.
[17] K. Maweja, L.A. Cornish, N. Can, Formation mechanism of nanocrystalline tungsten–titanium aluminides by ball milling of Ti(C,N)–W powders at subzero temperature, Powder Technology 211 (2011) 221–225.
[18] K. Maweja, L.A. Cornish, N. Can, Effects of tungsten and aluminium on the oxidation and phase formation in mechanically alloyed Ti(C,N)–W–Al systems, Journal of the European Ceramic Society, http://dx.doi.org/10.1016/j.jeurceramsoc.2012.05.010.
[19] K. Maweja, L.A. Cornish, N. Can, Polycrystalline cubic boron nitride sintered with Ti(C,N)-W-Al mechanically alloyed binders, Journal of the European Ceramic Society http://dx.doi.org/10.1016/j.jeurceramsoc.2012.05.011.
[20] ICSD Database FIZ Karlsruhe 2009-02, version 2.3.
[21] Toshiba, Tungaloy Co., Japanese. Kokai Tokyo Koho, 8 May 1984, Japanese. Pat. 84 78.528.
[22] D.E. Herzog, Cutting tools with compax diamond and BZN compact inserts slash production time and lower part cost, Cutting Tool Engineering (5–6) .
[23] W.P. Smith, R.W. Missen, Chemical Reaction Equilibrium Analysis, Theory and Algorithms, John Wiley & Sons, New York, 1982.
[24] D.R. Stull, M. Prophet, JANAF Thermochemical Tables, 2nd edn., National Bureau of Standards, NSRDS-NBS37, Washington, DC, 1971.