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Gas tight sintered material for high temperature sublimation setups

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Abstract

Fine powders of WC, TaC and TaC with W and WC additives were cold-isostatically pressed to ceramic discs and pressurelessly sintered at temperatures up to 2100 °C in a second step. Afterwards, the discs were tested as crucible lid under typical AlN growth conditions. The prepared discs should be gas tight and ensure a better alignment of the thermal expansion coefficients of TaC lid and AlN.

Ceramic discs densified by this method reveal a relative density up to 97%. The TaC ceramic discs without additives show a microstructure with grain sizes in the range of 10–200 μm after sintering. The grain enlargement could be reduced by W and WC additives in the range of 1–5 wt.%. The results show that the AlN boules adhere only to WC lids and tungsten containing lids with W contents higher than or equal to 3 wt.%.

Keywords: Sintering; Porosity; Thermal expansion; Carbides; Refractories

1. Introduction

Group-III nitride semiconductor materials possess a number of excellent properties that make them highly desirable for use as substrate material. Wurtzite type GaN, AlN and InN have room temperature direct bandgaps of 3.4, 6.2 and 1.9 eV, respectively. Therefore, group-III nitrides span a continuous range of direct energy bandgap energies throughout much of the visible spectrum well into the ultraviolet wavelengths.[1] This is one of the reasons for the interest in these materials for short wavelength optoelectronic device applications, especially emitters such as the light emitting diodes (LEDs) and monolithic lasers.

Physical vapour transport – the most widely used growth technique for group-III nitride – requires in the case of AlN growth temperatures in the range of 1850–2200 °C and high thermally and chemically resistant crucible materials. For economic reasons, the crucibles must preserve their properties for several growth cycles under these conditions. Crucibles made from refractory materials can meet these requirements. Materials of special interest are TaC and WC without and with small amounts of additives like tungsten, tantalum and niobium.[2–5] The shaping procedures are based on cold pressing followed by a sintering step or on hot pressing.[6–8] These materials are very difficult to densify, due to its highly covalent bonding character and low self-diffusion coefficient.[9] Therefore, additives should improve the sintering process, diminish the grain boundary growth during sintering and align the expansion coefficients of AlN and crucible lid. It is well known that the necessary amount of added substances to ceramics is very different. Thus, an addition of 1–3 wt.% C or of 3–10 wt.% of coarser grain SiC to SiC is sufficient to prevent giant grain growth of SSiCC.[10] On the other hand, smallest amount of foreign phases stimulate partially the sintering and reduce the sintering temperature: e.g. the addition of 0.05 wt.% B to SSiC or alkali to Al_2O_3.[10] Furthermore it is known, that the particle size as well as the particle size distribution are important factors influencing the sinter activity and consequently the densification and the grain growth.[11,12] Hence, the powders used in this work possess average particles sizes in the range of 0.5–0.9 μm and a narrow particle size distribution.

The thermal expansion coefficients of AlN ($\alpha = 4.8 \times 10^{-6}\,K^{-1}$) and TaC ($\alpha = 7.1 \times 10^{-6}\,K^{-1}$) are very different and as a result the grown AlN separates itself from the TaC lid or cracks during cooling down. Thus, crucible lids with expansion coefficients similar to this of AlN are of great interest which can be accomplished by addition of tungsten ($\alpha = 4.4 \times 10^{-6}\,K^{-1}$) or tungsten carbide ($\alpha = 5.76 \times 10^{-6}\,K^{-1}$) to TaC as well as by the use of WC discs. The prepared crucible lids are used under typical AlN growth conditions (TaC crucible, 2050 °C, 600 mbar N_2, small amounts of O_2, gaseous Al species). In addition, the sintered discs have to be gas tight and absolutely flat otherwise back

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side sublimation of AlN takes place which is detrimental for the growth process. In this work, results of the estimation of the relative density, microstructure and phase analysis of the prepared ceramics were presented.

2. Experimental procedures

2.1. Materials

Three types of commercially available ceramic fine powders (Treibacher Industry AG) were used. The average particle sizes (FSSS values – Fisher subsieve Sizer) are given for tungsten (0.5 μm), tantalum carbide (0.9 μm) and tungsten carbide (0.6 μm).

2.2. Preparation of ceramic green bodies and sintering

2.2.1. Mixing

The additions of 1, 3 and 5 wt.% W and 1 wt.% WC to TaC powder were carried out in a three-dimensional shaker mixer (WAB, Turbula T2F).

2.2.2. Pressing

Pressed bodies of 45 mm in diameter and about 60 mm in height were prepared from WC, TaC, TaC with 1, 3 and 5 wt.% W and TaC with 1 wt.% WC via cold isostatic pressing (CIP) in a soft cylindrical PVC (polyvinyl chloride) mold. Pressing was carried out in an isostatic press (EPSI 200-100*250Y) at a pressure of 200 MPa and a dwell time of 10 min.

2.2.3. Sintering

The CIPed samples were pressurelessly pre-sintered in a high temperature graphite furnace (Gero LHT). The compacts were heated in vacuum in a two-stage process: (i) from room temperature to 1200 °C at a heating rate of 3 °C/min and (ii) from 1200 to 1800 °C at a heating rate of 1 °C/min followed by a dwell time of 8 h. The cooling down was carried out in an analog manner. Then, the pre-sintered samples were cut and ground precisely to the right shape of discs with a thickness of 8 mm. Then the discs were finally sintered in a high-temperature furnace at 2100 °C for 8 h in vacuum at 10 mbar N_2. The heating rate was 10 °C/min up to a temperature of 1800 °C and 1 °C/min from 1800 °C to 2100 °C. The cooling down was carried out following the same but reverse procedure.

The denotation of samples is the following:

A_xB_T

where A is the kind of substance (TaC, WC), xB is the amount of additives (W or WC) in wt.% and T is the sintering temperature in °C.

2.3. Characterisation of the sintered materials

The final relative densities of samples (d_{rel}) were determined on the basis of Archimedes' principle (EN 623-2) with distilled water and using the above-mentioned theoretical densities (Table 1).[8,13–17] In order to investigate the microstructure of the surface of sintered specimens, the samples were mounted, grounded by a diamond grinding machine and then single-side polished with 3 μm diamond slurry. After the AlN growth, polished axial sections are prepared from crucible lids with AlN boule. Compositional and microstructural analyses of the products were made by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Nomarski microscopy.

2.4. AlN growth

The growth of polycrystalline AlN took place in a special graphite assembly.[18] The growth temperature measured on the crucible lid was 2050 °C. The temperature gradient between upper source surface and growth interface could be adjusted by changing the coil position with respect to the crucible. The ambient gas during sublimation was high purity nitrogen (99.999%) at a pressure of 600 mbar. The distance between sintered AlN source and crucible lid was 10–20 mm.

3. Results and discussion

3.1. Sintered discs

First attempts of TaC sintering in N_2 at a pressure of 1 bar and temperatures until 2100 °C revealed porosity-related problems. These discs exhibited open porosity up to 10%. Gas tight samples were only obtained after sintering in vacuum at 2100 °C.

3.1.1. Tantalum carbide

TaC discs without any additives have been shrank about 20% during sintering up to 1800 °C and remain nearly unchanged after sintering at 2100 °C. The exact determination of shrinking behaviour was not possible because the discs were not precisely circular. The SEM image (Fig. 1) and density measurements of TaC samples reveal homogeneously sintered materials with a small ratio of closed porosity and a relative density d_{rel} of 0.96 and 0.97 after sintering at 1800 °C and 2100 °C, respectively (Table 2). Furthermore, the TaC_2100 shows a particle size distribution between 10 and 200 μm which is associated with a lower strength in comparison to samples with a narrow particle size distribution. The pores are closed and located along the grain boundaries as well as inside of the grains.

The X-ray diffractograms of the powdery TaC feedstock and the sintered discs show only reflexes of the cubic phase of δ-TaC_{1-x}, there are no evidence of the existence of carbon depleted phases like Ta_2C (Fig. 2a)

Table 1
Theoretical densities of tantalum, tungsten and some of their carbides.

Sample	Theoretical density, d_0 [g/cm^3]	References
Ta_2C	15.10	13
TaC	14.48	13
Ta	16.58	14
WC	15.63	15
W_2C	17.15	16
W	19.30	17

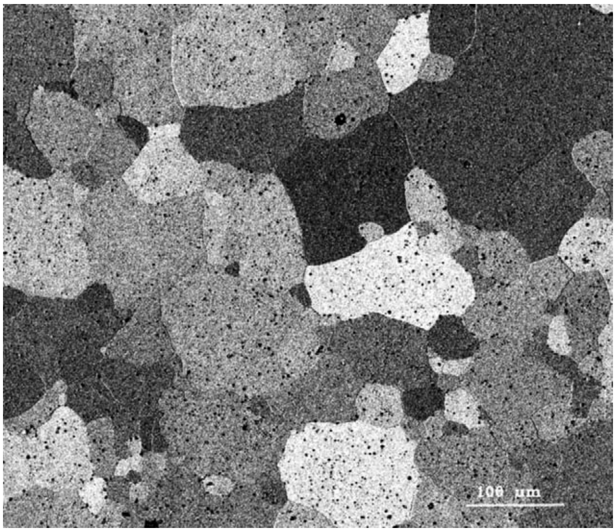

Fig. 1. SEM micrograph of TaC_2100 disc prepared by pressureless sintering at 2100 °C for 8 h in N_2 at 10 mbar.

3.1.2. Tantalum carbide with additives

The addition of W and WC to TaC is used to influence: (a) sintering behaviour, especially the final grain size and (b) thermal expansion coefficient of the sintered discs. The amount of additives was chosen between 1 and 5 wt.% W and 1 wt.% WC, respectively. The TaC samples with 1 wt.% W or WC reveal a minor amount of open porosity of 0.5% and a relative density of 0.96 or 0.95, respectively (Table 2). The open porosity increases with increasing W content from 0.5 to 9% and d_{rel} decreases from 0.96 to 0.87. The shrinkage behaviour developed proportionally while TaC_1W_1800 still shrinks for 20% the TaC_5W_1800 sample shrinks only between 12 and 18% indicating a poor sinter activity. Gas tight samples without open porosity are obtained only after sintering at 2100 °C which is associated with a further shrinkage up to 20% and an increase in relative density to 0.97 or 0.95 (Table 2). The SEM images of the TaC_1W_2100, TaC_1WC_2100 and TaC_3W_2100 samples show equally a small amount of closed porosity and particle sizes between 10 and 50 µm (Fig. 3). Thus, ceramic discs with

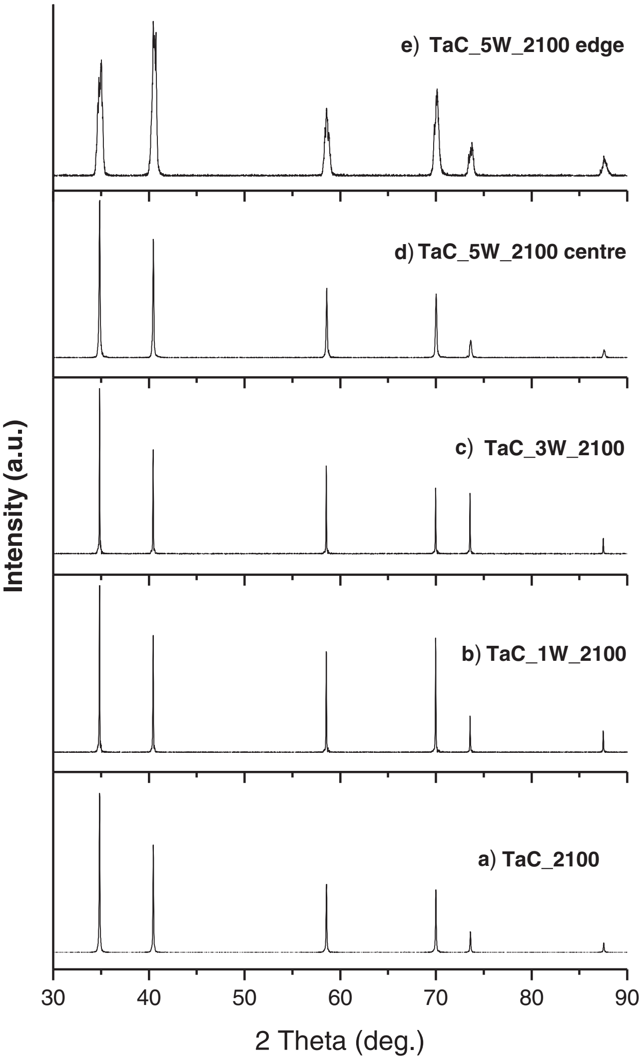

Fig. 2. Comparison of the XRD patterns of TaC without and with W additives sintered at 2100 °C: (a) TaC_2100; (b) TaC_1W_2100; (c) TaC_3W_2100; (d) TaC_5W_2100 centre and (e) TaC_5W_2100 edge.

Table 2
Shrinkage behaviour, open porosity, experimental and relative density d_{exp} and d_{rel} of different ceramic materials sintered at 1800 and 2100 °C.

Sample	Shrinkage [%]		Open porosity	Experimental density, d_{exp}	Relative density, d_{rel}
	Diameter	Height	[%]	[g/cm^3]	d_{exp}/d_0
TaC_1800	20	20	No	13.9	0.96
TaC_2100	20	20	No	14.0	0.97
TaC_1W_1800	20	20	0.5	13.9	0.96
TaC_1W_2100	20	20	No	14.0	0.97
TaC_3W_1800	17	20	1	13.8	0.95
TaC_3W_2100	20	20	No	14.0	0.97
TaC_5W_1800	12	18	9	12.6	0.87
TaC_5W_2100	20	20	No	13.8	0.95
TaC_1WC_1800	17	20	0.5	13.8	0.95
TaC_1WC_2100	20	20	No	13.9	0.97
WC_1800	5	5	30	10.2	0.65
WC_2100	25	25	No	14.7	0.94

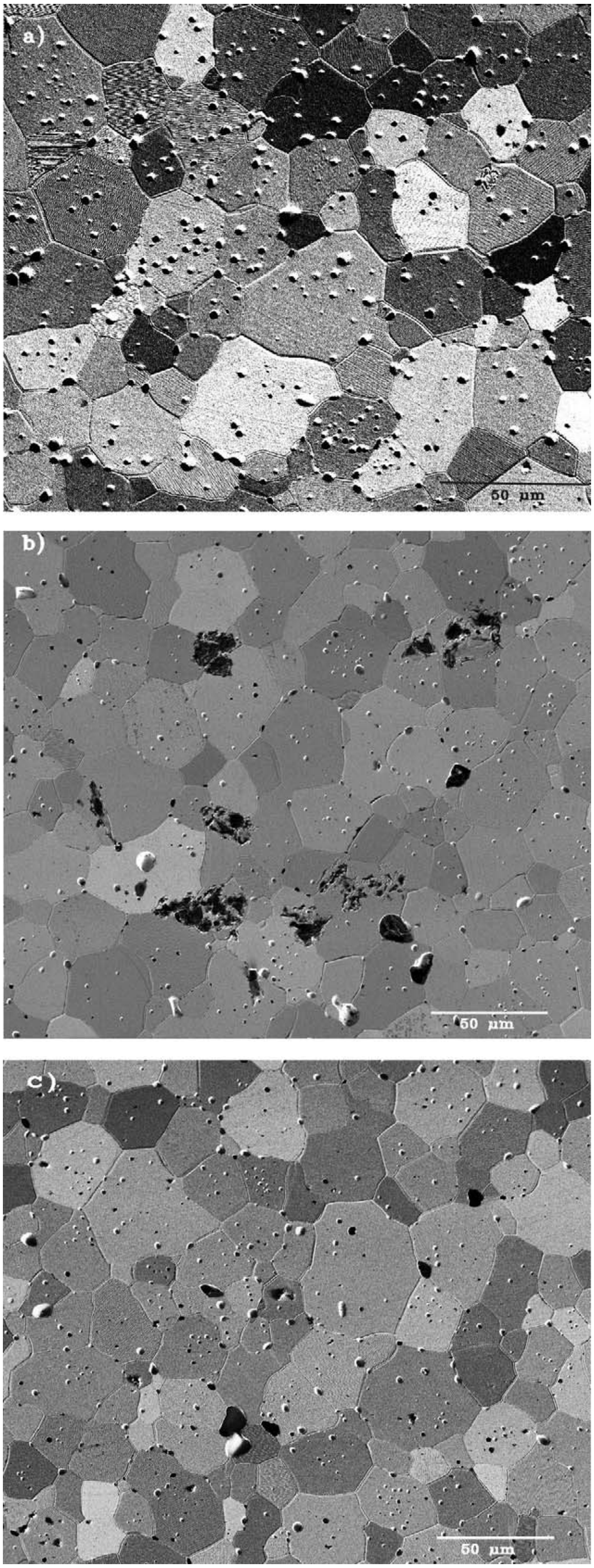

Fig. 3. SEM micrographs of (a) TaC_1WC_2100; (b) TaC_1W_2100 and TaC_3W_2100 discs prepared by pressureless sintering at 2100 °C for 8 h in N_2 at 10 mbar.

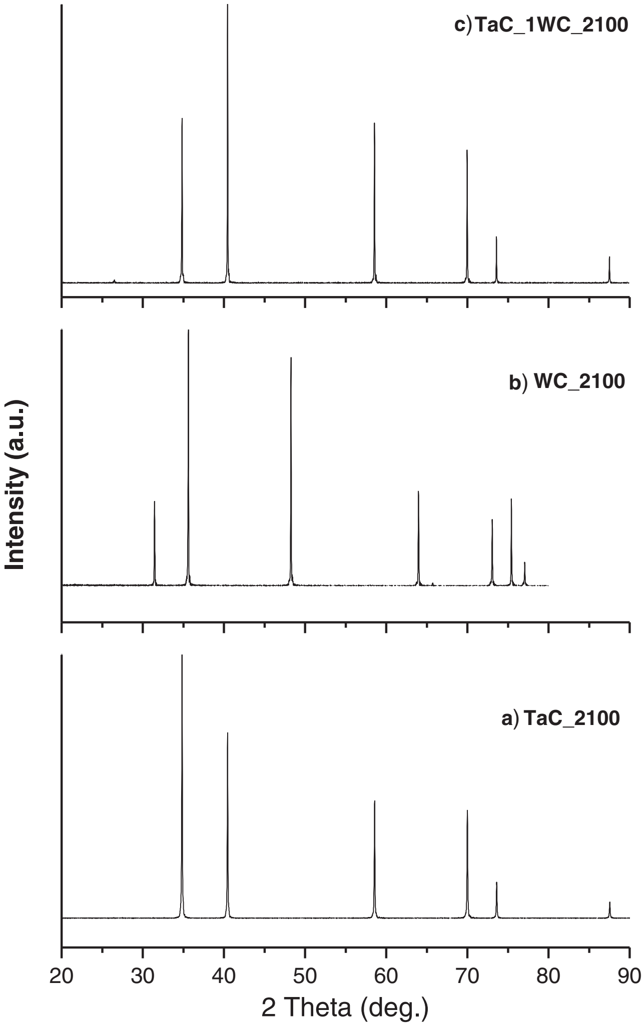

Fig. 4. Comparison of the XRD patterns of TaC without and with WC additive and WC discs.

a smaller mean grain size are obtained after sintering at 2100 °C by the addition of tungsten and tungsten carbide to TaC.

EDX measurements of the W content of these samples could not be correctly quantified because the W and Ta peaks are too close to each other, and the W peak in TaC is relatively low compared to the Ta peak. The TaC_5W_2100 disc could not been analysed as the disc has been bent strongly during the second sintering step. The EDX measurements of the TaC_5W_1800 revealed an uneven distribution of W within the disc. Tungsten was found in the range of 4.5–6 wt.% near the edge and of 1.5–2 wt.% in the centre of the disc, resulting in different expansion values as well as a strong bending of the disc during high temperature sintering.

XRD pattern of all samples containing W (Fig. 2) or WC (Fig. 4) reveal only reflexes of the cubic phase of δ-TaC$_{1-x}$ and the TaC XRD reflexes were not shifted from the standard positions. The measurements of the sample TaC_5W_2100 were carried out at the W depleted centre (Fig. 2d) as well as the W rich edge (Fig. 2e). The reflexes of the latter measurement are very broad probably due to geometric effects because the bent sample could not be aligned properly in the beam path. A possible explanation for the absence of W reflexes at all samples

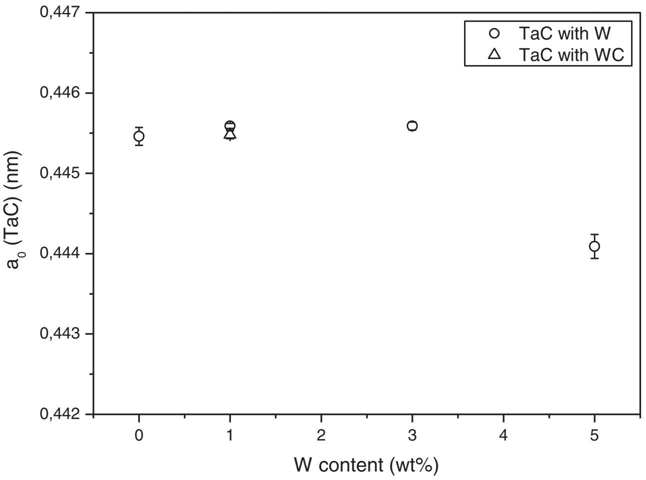

Fig. 5. Lattice parameter a_0 of cubic TaC in dependence of W and WC content.

may be attributed to the formation of small amounts of W_2C and Ta_2C during sintering above 1550 °C.[19] The following reaction equation is received in the case of TaC with 5 wt.% tungsten additive (TaC_5W_2100) (Eq. (1)).

$$0.95\,\mathrm{TaC} + 0.05\,\mathrm{W} \rightarrow 0.9\,\mathrm{TaC} + 0.025\,\mathrm{Ta_2C} + 0.025\,\mathrm{W_2C} \qquad (1)$$

Considering this reaction, it could be suggested that Ta_2C and W_2C can be formed in minor amounts but below the range identifiable by XRD. However, the dissolubility of tungsten in tantalum carbide lattice cannot be excluded despite different lattice parameters of the cubic TaC ($a_0 = 0.44546$ nm) and W ($a_0 = 0.31648$ nm).[20] The calculation of the lattice parameter a_0 of the cubic TaC without and with tungsten and tungsten carbide additives were carried out using the corresponding X-ray diffractograms. The lattice parameter a_0, shown in Fig. 5, remained almost unchanged up to a W content of 3 wt.%. Only at a W content of 5 wt.% the lattice parameter decreased significantly. It is believed that the reported values are due to in homogeneities of the samples. Further samples with different W or WC contents have to prepare and to study by XRD measurements at different points of each sample to reconfirm this presumption.

3.1.3. Tungsten carbide

The WC green body sintered at 1800 °C shrinks only by 5% and is associated with an open porosity of 30% and a relative density of 0.65. Gas tight discs are obtained after sintering at 2100 °C. These discs shrink totally by 25%, exhibit no open porosity and a relative density of 0.94 (see Table 2). The SEM image of WC_2100 shows bright and dark domains of thick needle like crystals with different orientations (Fig. 6). The particle size was in the range of 50–150 μm. The XRD measurement shows only reflexes of a hexagonal WC phase (Fig. 4b).

3.2. AlN crystal growth

Polycrystalline AlN was grown on different gas tight sintered crucible lids. As shown in Fig. 7a–c, the boules are detached

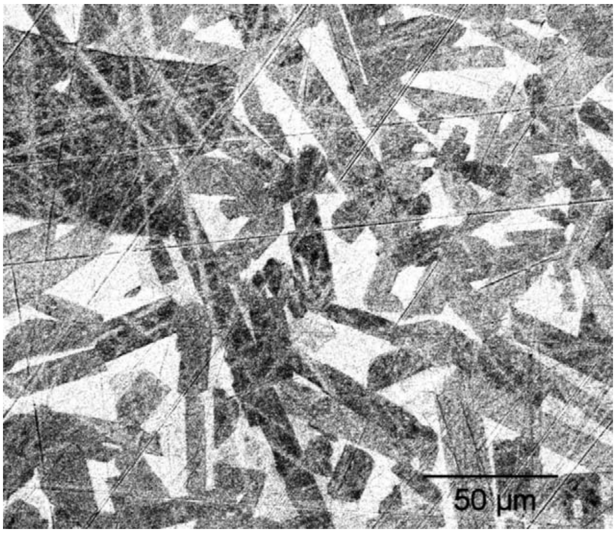

Fig. 6. SEM micrograph of the WC_2100 disc prepared by pressureless sintering at 2100 °C for 8 h in N_2 at 10 mbar.

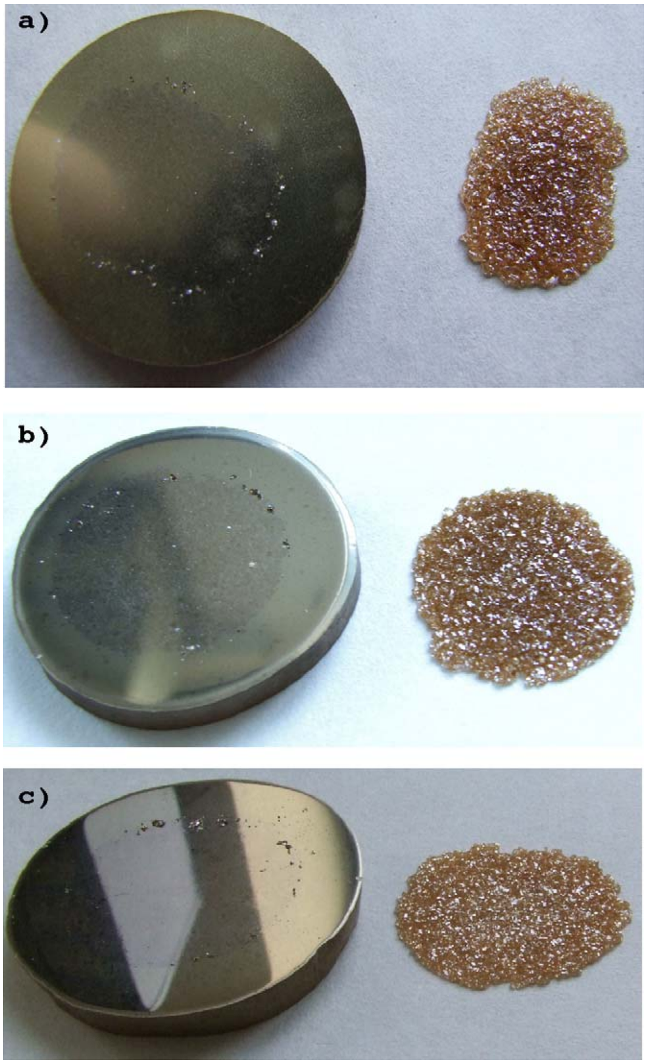

Fig. 7. Polycrystalline AlN boules grown on (a) TaC_2100; (b) TaC_1W_2100 and (c) TaC_1WC_2100 crucible lids; the grown AlN boule is fallen off the lid during cooling step.

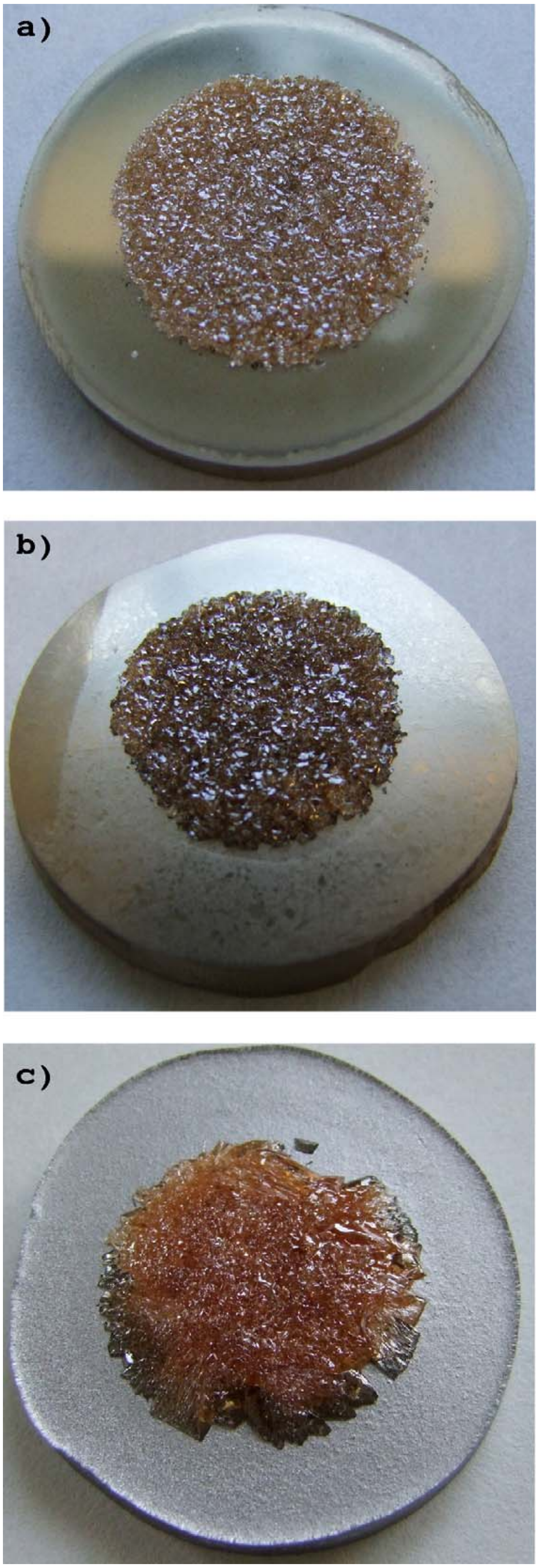

Fig. 8. Polycrystalline AlN boule grown on: (a) TaC_3WC_2100, (b) TaC_5W_2100 and (c) WC_2100 crucible lids.

from the TaC_2100, TaC_1W_2100 and TaC_1WC_2100 lids during the cooling step (Fig. 7). However, AlN grown on TaC_3W_2100, TaC_5W_2100 and WC_2100 adheres well which is probably due to the well adjusted expansion coefficients of lid and AlN (Fig. 8a–c). But the adhesion of AlN boules on these lids is quite different. The microscopic images (Nomarski contrast) of the polished axial sections of the AlN layers on TaC_3W_2100 and WC_2100 show close interfaces as well as interstices between AlN and ceramics. On the other hand, the interface between AlN and TaC_5W_2100 is completely closed without any cavities.

Furthermore, the seeding behaviour of AlN on WC differs significantly from that on TaC ceramics (Fig. 8). In the case of WC, AlN crystallites grow perpendicular to the *c*-direction (0 0 0 1) while it grows mainly in *c*-direction on TaC. Among the possible causes are the preferred direction of the grains and impurities of the materials. Additional investigations are necessary to clarify these results.

4. Conclusions

Using fine TaC, W and WC powders, gas tight ceramic discs with a relative density up to 97% were obtained by pressureless sintering at 2100 °C. The TaC ceramics without additives have a microstructure with a grain size of about 10–200 μm. The addition of tungsten and tungsten carbide to TaC in the range of 1–5 wt.% shows a reduced TaC grain growth. Here the particle sizes were in the range from 10 to 50 μm.

All these ceramic discs were used as crucible lids in the crystal growth of AlN. The grown polycrystalline AlN boules adhere better with increasing tungsten content caused by a changed expansion coefficient of the material. The interface between AlN and crucible lid is completely closed only in case of the TaC_5W_2100 sample. The closed interface crucible lid/crystal can induce to an enhanced crystal quality in the future.

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