

Development of an AlN HTCC multilayer system with a tungsten cofiring metallization

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Abstract

The shrinkage behaviour of aluminium nitride HTCC multilayer with a tungsten cofiring metallization was investigated. A new investigation method was used to characterize the shrinkage values of AlN tape and tungsten paste individually. Unlike to common methods small cylinders of dried tungsten paste were manufactured by instrumental pressing, as well as pure AlN laminates were investigated. The tungsten cylinders and the AlN substrates were debindered at 700 °C and sintered pressureless in sintering interruption experiments at several peak temperatures up to 1830 °C under nitrogen atmosphere.

The adaption of the shrinkage mismatch between AlN and tungsten metallization was reached by the use of a variation of the grain sizes of the tungsten metal powders and by the addition of ceramic powders. A bimodal grain size distribution of the tungsten metal powders lead to the shift of shrinkage behaviour above 1400 °C. By the variation of ceramic powders (AlN and Y₂O₃) an increase in shrinkage above 1700 °C was observed. The tungsten carbide formation due to residues of carbon in the tape after debinding is observed.

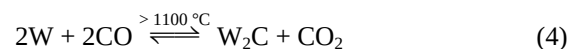
Key words: aluminium nitride, tungsten metallization, shrinkage behaviour, residues of carbon

Introduction

AlN ceramics exhibit a unique combination of properties: high corrosion resistance against refractory metals [1-3], high electric resistivity and an excellent thermal conductivity [4, 5]. There the reasons why the aluminium nitride ceramics are of interest in various microelectronic applications, where power and heat dissipation are important (e.g. power electronics, hermetic packaging).

However AlN is difficult to sinter, rare earth and/or alkaline oxides are often used as sintering aids. The sintering aids (e.g. Y₂O₃) fulfil two requirements: (i) they form a liquid phase that enhance densification and (ii) increase the thermal conductivity by removing oxygen impurities [6-8].

Tape casted AlN/ Y₂O₃ green tapes contain organics which usually leads to residues of carbon after debinding. In sintering of AlN/ W multilayers under a nitrogen atmosphere at 1830 °C, the following reactions occur: the carbothermal nitration (1)-(2) [9] and the tungsten carbide formation (3)-(4) [10-12].



The increase of electrical resistivity and the shrinkage mismatch are consequences of tungsten carbide formation. To improve the electric conductivity of the sintered AlN/ W multilayer and to avoid tungsten carbide it is necessary to reduce the residues of carbon after debinding <0.05 wt.% [10].

Experimental

AlN/ Y₂O₃ green tapes were manufactured by tape casting with an industrial tape caster (KEKO, CAM M1-H). The tapes exhibit a high homogeneity and quality. A summary of the sintered AlN ceramic properties is given in Table 1.

Table 1: Summary of the measured AlN properties

Definition	Symbol (units)	Value
Density	ρ (g/cm ³)	3.30
Porosity	P (%)	<0.20
Thermal conductivity	λ (W/(m*K))	150
Roughness	R _a (μm)	1.30
Waviness	W _z (μm)	3.00

The starting powders were commercially available AlN powder (Grade M, H.C. Starck), Y₂O₃ (Grade C, H.C. Starck) and tungsten metal powders (HC 150S (average particle size 2.2 μm), HC 70S

(average particle size 1 μm), H.C. Starck; WP 80 (average particle size 12.3 μm), WP 08 P (average particle size 1.3 μm), Treibacher Industrie AG).

All tungsten metal powders and the AlN powder were proven regarding oxygen and carbon content by gas chromatography (LECO Corporation, TC 600 and CS 230). The obtained data are given in Table 2.

Table 2: Summary of oxygen and carbon content in used powders

Powder	Oxygen (wt.%)	Carbon (wt.%)
WP 80	0.05 ± 0.01	0
WP 08 P	0.36 ± 0.02	0
HC 150S	0.26 ± 0.01	0
HC 70S	0.61 ± 0.03	0
AlN	1.21 ± 0.01	0.02 ± 0.01

The tungsten metallization pastes formulations were diversified by variation of the tungsten metal powders, the mono- and bimodal particle size distribution, the tungsten-AlN- Y_2O_3 distribution and the paste solids content.

After sieving down to <63 μm , the tungsten metal powders were mixed with AlN and Y_2O_3 and homogenised for 1 h in a shaker-mixer (Willy A. Bachofen AG, Turbula). Following the binder was added to the mixed powders. To homogenise the tungsten pastes a roll mill (Exakt) was used. For sample preparation it was necessary to dry the tungsten metallization pastes for several hours under air. After drying, the paste powders were pressed into circular cylinders (4 mm in diameter and circa 4 mm in height) under 2.5 kN for 5 s using stainless steel dies. Single AlN green tapes were stacked to a laminate of a thickness of 1.2 mm. To measure the shrinkage of pure AlN laminates measuring crosses were marked on the top and bottom side with laser treatment.

The pressed tungsten bodies from paste powders and the pure AlN laminates were debindered under H_2 flow and sintered in a tungsten resistance furnace under N_2 flow (both furnace MUT Advanced Heating GmbH). By interrupting the sintering at temperatures of 1200, 1400, 1600 and 1700 $^\circ\text{C}$ the sintering process were aborted. In comparison with these sintering interruption experiments a sintering at 1830 $^\circ\text{C}$ were completed.

Checking the dimensional variation before and after sintering an optical microscope (Nikon, Measuring Microscope MM800) was used. With this data the linear shrinkage was obtained and volume shrinkage calculated.

Analyzing the phase compositions by X-ray diffractions all samples were milled and analysed with an X-ray diffractometer XRD 7 (Seifert-FPM, XRD 7).

The density of the sintered tungsten metallization samples were measured according to the

Archimedes method and the porosity calculated using theoretical density values.

Results and discussion

Reduction of residues of carbon

Several pure AlN substrates were prepared to investigate the debinding process by changing the debinding atmosphere. Furthermore, a variation of the debinding plateau temperatures, dwell time, peak temperature and debinding time was investigated. By changing atmosphere from inert to reducing one a decrease of residues of carbon was observed. Oxygen and carbon analysis of debindered AlN substrates in comparison to pure tungsten paste cylinders are shown in Table 3.

Table 3: Carbon and oxygen analysis results of debindered AlN substrates and tungsten paste cylinders

Atmosphere	Oxygen (wt.%)	Carbon (wt.%)
AlN		
N_2	1.82 ± 0.02	0.29 ± 0.004
Vakuum	1.80 ± 0.02	0.24 ± 0.008
Forming gas	1.77 ± 0.01	0.24 ± 0.004
H_2	1.76 ± 0.03	0.18 ± 0.004
Tungsten paste		
H_2	0.31 ± 0.01	0

The lowest value of residual carbon in the debindered tape was reached by hydrogen debinding. Comparing the amount of residual carbon of AlN substrate (0.18 wt.% carbon) and dried tungsten paste (0 wt.% carbon) the completely removal of organics could be easily achieved in the tungsten paste cylinders. According to Iwase et. al. [10] the amount of carbon after hydrogen debinding of the AlN substrate is over 3 times higher than the 0.05 wt.% limit for tungsten carbide formation. Thus the AlN substrate represented the carbon reservoir for the tungsten carbide formation in AlN/ W multilayer ceramics. The XRD-pattern shows in Figure 1 the formation of tungsten carbide during cofiring.

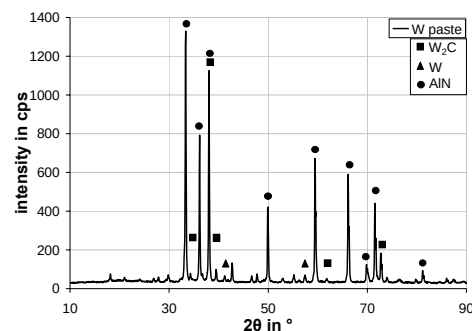


Figure 1: XRD-pattern of an AlN/ W multilayer ceramic

The W_2C formation influenced negatively the shrinkage of the AlN/ W multilayer ceramic. The tungsten metallization areas are disabling to shrink in time with the AlN substrate. It led to a bending. As mentioned additionally the carbothermal nitration takes place. The theoretical calculated phase distribution of yttrium-aluminium garnet (YAG) and yttrium-aluminium perovskite (YAP) were changed by reducing the Al_2O_3 amount to YAP and yttrium-aluminium monoclinic (YAM).

As Wu et. al. [13] reported the residues of carbon can be reduced by a two-step debinding process under several atmospheres. Decrease of residues of carbon was achieved by modification in temperatures and debinding conditions using oxidising and reducing atmosphere in combination. For pure AlN substrate the result of the residual carbon analysis was 0.03 ± 0.003 wt.%. But because of the oxidation behaviour of tungsten this kind of debinding technique was not useable for tungsten samples as shown in Figure 2.

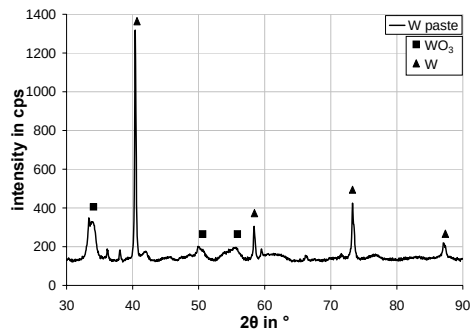


Figure 2: XRD-pattern of a tungsten paste powder in a two-step debinding

AlN/ W shrinkage investigation

Preparing dried tungsten metallization paste cylinders these investigations had key benefits because of the pressureless shrinkage and no influences by the tungsten carbide formation. It was an approximation to the multilayer fabrication process by reason of simulating the screen printing process by reading the same green density of the printed tungsten metallization layers. Therefore all dried tungsten pastes were pressured with the equal parameters, which were investigated in preliminary tests. A key factor for cofiring AlN/ W multilayer ceramics were the proper adaption of the shrinkage behaviour of AlN and tungsten metallization paste to realize multilayer components with a low warpage.

Starting with the tungsten metal powders from H.C. Starck the variation of solids content in paste was observed. The sample labels are given in Table 4 and the Figure 3 showed the shrinkage values with increasing temperature. All samples showed a rapid start in shrinkage at 1200 °C until 1830 °C in opposite to AlN. Because the average grain sizes of the tungsten metal powders of 1 and 2.2 μm is very

fine. Between 1400 and 1700 °C the greatest sintering mismatch of 10 until 20 % has been noticed. As a result there was not significant influence in variation of the tungsten solids content in the pastes. Increasing the solids content the shrinkage curve fitted near the AlN shrinkage curve. Switching the beginning of sintering to higher temperatures was necessary and can be achieved by using coarse grained tungsten metal powders.

Table 4: Summary of the solids content of tungsten paste using H.C. Starck tungsten metal powders

Paste	Paste solids content (vol.%)	W solid content (vol.%)
Paste A	10	80
Paste B	15	80
Paste C	20	80
Paste D	25	80

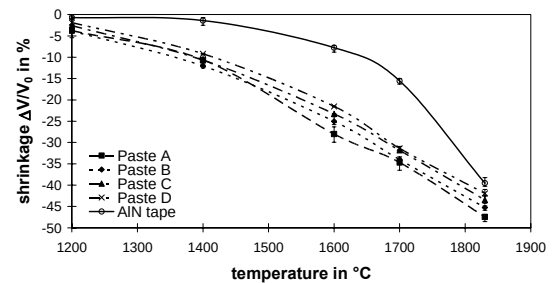


Figure 3: Shrinkage behaviour of tungsten metallization pastes in addition of solids content

Investigating the shrinkage behaviour by variation of coarse (12.3 μm) and fine (1.3 μm) grained tungsten at equal paste solids content of 20 vol.% tungsten metal powders were used. A summary of this paste series is given in Table 5 and the results are presented in Figure 4. Increasing the coarse grained tungsten metal powders by an equal ceramic component fraction a decreasing in the shrinkage mismatch between tungsten metallization and AlN can be observed. In the temperature range of 1400 until 1700 °C the paste 4 showed a shrinkage mismatch of 5 %. A mixture of 50 : 50 (coarse : fine) tungsten metal powders seemed to be optimal. According to Figure 3 the shrinkage behaviour of the tungsten metallization pastes were dominated by the variation of the tungsten metal powders.

Table 5: Summary of the coarse and fine grained size variation of used tungsten metal powders

Paste	Variation of coarse : fine W	W solid content (vol.%)
Paste 1	0 : 100	80
Paste 2	10 : 90	80
Paste 3	25 : 75	80
Paste 4	50 : 50	80
Paste 5	100 : 0	80

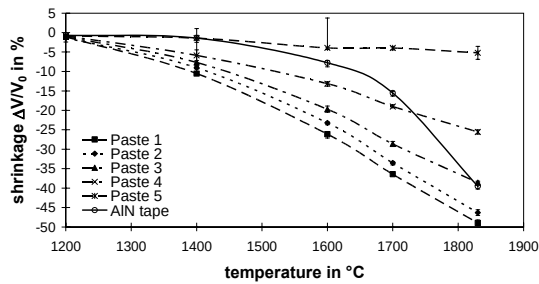


Figure 4: Shrinkage behaviour of tungsten metallization pastes in addition of the variation of coarse and fine grained tungsten metal powders

To minimize the shrinkage mismatch at 1830 °C increasing the amount of ceramic components (AlN and Y_2O_3) was advantageously. According to the theoretical consideration of liquid phase sintering of AlN with Y_2O_3 the tungsten pastes show an increase in shrinkage above 1700 °C. By rising the amount of ceramic components from 20 to 40 vol.% at equal paste solids content the paste formulation from paste 4 was modified. As shown in Figure 5 the increasing of the ceramic components led to improvement in shrinkage. Starting at 1200 °C the shrinkage curve of paste 6 fitted near the AlN shrinkage curve as paste 4. Between 1400 and 1700 °C the sintering mismatch of 2 until 4 % can be noticed and the curve shape is similar to AlN. It indicated that the shrinkage of paste 6 is influenced by the ceramic components. In comparison to paste 4 a decrease in sintering mismatch at 1700 °C can be observed. The liquid phase sintering of AlN and Y_2O_3 took place. At 1830 °C the mismatch were 14 % (paste 4) and 10 % (paste 6) respectively.

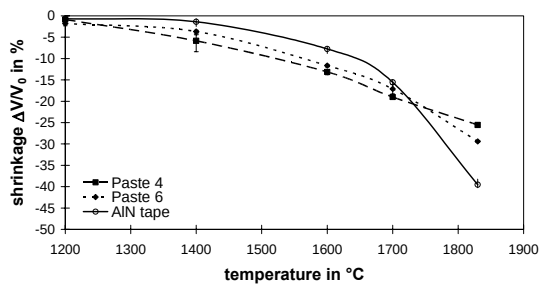


Figure 5: Shrinkage behaviour of tungsten metallization samples in addition of the AlN and Y_2O_3 addition

By measuring the dimensions of tungsten paste cylinders the density of the samples at several temperatures were calculated and the results are given in Figure 6. With increasing temperature the porosity of sintered tungsten paste samples decreased. At 1830 °C paste 6 offered a better densification than paste 4.

For manufacturing AlN/ W multilayer ceramics the residual porosity of tungsten metallization can be used to reduce the shrinkage stresses in

multilayer. The calculated porosity is shown in Table 6. If the amount of porosity is higher than the shrinkage mismatch, a densification of the tungsten metallization can take place and the shrinkage mismatch is reduced to zero.

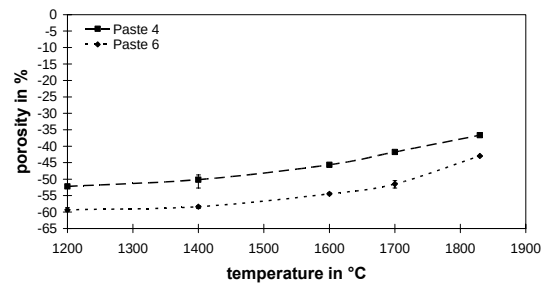


Figure 6: Porosity as a function of sintering temperature

Table 6: Summary of shrinkage mismatch and porosity of sintered tungsten paste samples

Paste	Shrinkage mismatch (%)	Porosity (%)
Paste 4	14	37
Paste 6	10	43

Conclusion

The work presents results of the development of thick film tungsten metallization pastes for AlN/ W multilayer manufacturing. The variation of tungsten average grain sizes and the content of AlN and Y_2O_3 in paste are the keys to minimize the shrinkage mismatch between tape and paste. The mixture of AlN/ Y_2O_3 with tungsten powder and use of coarse tungsten powders allow to match the sintering behaviour of the paste to that of AlN tape. However the content of carbon after tape debinding was too high to prevent the formation of tungsten carbide during sintering and should be further reduced by tape development to obtain perfect multilayer structures.

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