Active metal brazing of various metals on nitride ceramics

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The development of new materials for thermoelectric generators (TEG) with higher operating temperatures requires improved metallised substrates. Commonly used alumina substrates with copper metallisation show low thermal conductivity and low stability against thermal cycles. Aluminum nitride (AlN) and silicon nitride (Si_3N_4) are very attractive alternative substrate materials due to their high thermal conductivity, electrical resistivity and mechanical strength. However, it is important to realise reliable bonds between the nitride ceramics and metals like copper, nickel or refractory metals to ensure that AlN and Si_3N_4 can be practically used as substrates for the hot or cold side of a TEG. In this work, the interactions between two silver based active braze filler metals, nitride ceramics and nickel, tungsten and molybdenum have been examined. The microstructures of the ceramic-metal composites and the elemental distributions of the reaction products at the ceramic/braze and metal/braze interfaces were analysed using scanning electron microscopy and energy dispersive X-ray spectroscopy. In all cases the formation of a TiN reaction layer at the ceramic/braze interface was observed. Active metal brazing of nickel to AlN and Si_3N_4 was possible with both brazes, whereas the metallisation of the nitride ceramics with the refractory metals worked only in combination with AlN.

1 Introduction

Thermoelectric generators (TEG) are devices which convert heat directly into electrical energy through a temperature difference between the hot side and the cold side of a thermoelectric material, so called thermoelectric legs. Most common TEG are based on semiconductor materials like bismuth or lead telluride [1]. Usually alumina (Al_2O_3) ceramics metallised with copper are used for integration of the thermoelectric legs into the TEG. These Al_2O_3 substrates are widely used for circuit boards for power electronics (e.g. IGBT-modules, power inverter, switching power supplies). Also the applied soldering processes for the electrical and thermal interconnection of the thermoelectric legs are standard in electronic packaging. However, the maximum temperature of such a TEG is limited by the reliability of the metallised substrates and the solders and by the stability of the thermoelectric materials.

The development of new, low cost thermoelectric materials based on conducting ceramics for higher operating temperatures will lead to an increased efficiency of the TEG and will offer new applications. For this high temperature operation novel substrate materials and assembling techniques are required. As alternative insulating substrates the ceramics aluminum nitride (AlN) or silicon nitride (Si_3N_4) can be used due to their electrical resistivity and high thermal conducitivity of 180 W/m·K in the case of AlN and up to 80 W/m·K in the case of some recently developed Si_3N_4 [2]. Due to a higher bending strength and better thermal shock resistance Si_3N_4 represents the superior solution for applications with fast and frequent thermal cycles.

However, it is important to bond the nitride ceramics with metals like copper, nickel or refractory metals in order to ensure that AlN and Si_3N_4 can be practically used as substrate materials. For example, the bonding process of copper to Al_2O_3 and AlN can be realised by a process called direct copper bonding (DCB) without any additional interlayers. As an alternative bonding process active metal brazing (AMB) in vacuum or in a protective atmosphere can be used to join metal foils to ceramic substrates. In comparison to DCB substrates where a brittle ceramic bonding phase is formed, the joint strength and thermal shock resistance of AMB substrates is significantly higher as the active braze filler metal forms a ductile interlayer [3].

Due to its excellent electrical and thermal conductivity copper is the most widely used metallisation layer for both AMB and DCB substrates. However, as the thermoelectric modules require oxidation resistant metallised ceramic substrates the limited stability of copper at temperatures above 150°C suggests the application of more stable metallisation layers such as nickel or refractory metals. The application of temperature stable and oxidation resistant alloys like nickel-chromium-based superalloys or special ferritic steels (e.g. Crofer 22 APU) is not preferred because these materials have lower electrical conductivities and higher Young's moduli than the previously mentioned metals.

In the literature the AMB process is more often investigated for brazing of nitride ceramics to themself than for brazing of nitride ceramics to metals [4, 5]. Furthermore the dimensions of the investigated ceramic-metal composites refer more to geometric conditions where the thickness of the brazed joint is neglectable with respect to the dimensions of the joined materials [6-8]. Hence studies on plane metal to ceramic composites made by active metal brazing are rare and the available information are not sufficient for an evaluation of different material combinations [9, 10].

2 Manufacturing process

The manufacturing process for structured metallisation layers on ceramic substrates comprises of four steps, **Fig. 1**. First the active brazing paste is screen printed on one side of the ceramic substrate, followed by a drying step and a repetition of this process on the back side. The screen printed paste shows already the layout of the later metallisation

structure. After surface treatment and cleaning of the metals, the stacked assembly of ceramic substrate and metal foils is brazed under vacuum or in protective atmospheres. For structuring the metallisation layers an etch resist is screen printed on both sides of the substrate which has a congruent layout to the brazing paste. Finally the uncovered areas of the metallisation layers are etched by aqueous solutions and afterwards the etch resist is stripped by an organic solvent.

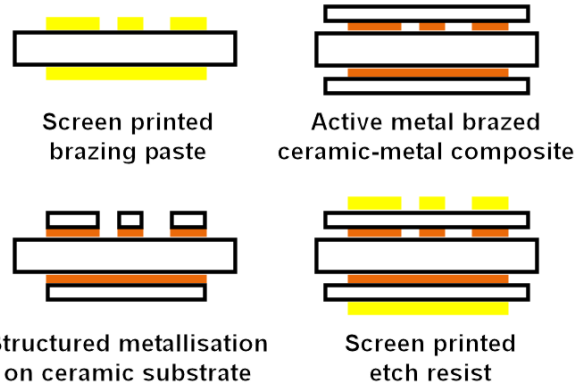

Fig. 1. Process scheme for manufacturing of structured ceramic-metal composites by active metal brazing.

Ground AlN and Si_3N_4 ceramic substrates with a thickness of 1.5 and 1.0 mm, respectively, were used for the manufacturing of ceramic-metal composites. Copper, nickel, molybdenum and tungsten foils with a thickness of 0.2 to 0.3 mm for Cu and approx. 0.1 mm for all others were used as metallisation layers. Two different active braze filler metals were used as brazing pastes: One paste is based on silver with 10 % titanium while the second paste contains silver and copper with a lower titanium content and an excess of copper compared to the eutectic.
The brazing process was done in a vacuum furnace with a vacuum pressure $< 1 \cdot 10^{-5}$ mbar. The brazing temperature of 900°C for the Ag-Cu-Ti braze and of 1050°C for the Ag-Ti braze was held between 10 and 30 minutes. Note, that during the brazing process various failures can occur such as pore formation, delaminations or spreading of the molten braze causing short circuits of conductor lines on the metallised substrates. Therefore a careful selection with respect to the furnace temperature profiles, the surface quality of the ceramic substrates, the surface treatment of the metal foils and finally the content of the active element titanium in the brazing pastes results in defect free ceramic-metal joints, as it was shown earlier for brazed composites of nitride ceramics with copper [11].
The microstructure of the brazed joints was analysed in cross sections with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

3 Metallisation with copper and nickel

Active metal brazing of copper to AlN and Si_3N_4 with Ag-Cu-Ti braze filler metals is well known. While brazing of AlN a thin, homogeneous reaction layer of TiN is formed, the brazing process with Si_3N_4 leads to the formation of a very thin, but porous TiN layer and, depending on the brazing conditions, to the precipitation of titanium silicides in the braze matrix [11]. For both ceramic types the braze filler metal consists of areas showing the Ag-Cu euctectic structure and of Cu-rich areas towards the copper foil. In contrast, active metal brazing of copper with Ag-Ti results in the destruction of the copper foil due to the formation of the Ag-Cu eutectic, **Fig. 2**.

Fig. 2. Destroyed copper metallisation after active metal brazing of copper to AlN with the Ag-Ti braze.

After brazing of nickel to AlN with Ag-Cu-Ti, compared to copper-AlN composites, a similar 1 µm thick interfacial reaction layer comprising of Ti and N is found at the ceramic/braze interface, **Fig. 3a**. However in comparison with brazed copper-AlN composites the microstructure of the braze filler metal differs strongly. The brazing zone in the nickel-AlN composite shows Ag with up to 10 at.-% dissolved Cu as continuous interlayer close to the TiN reaction layer and a solid solution of Cu, Ni and Al with 40-45 at.-% Ni and < 3 at.-% Al. Therefore the diffusion of Ni into Cu is the driving mechanism for the decomposition of the original braze filler metal and answers the lack of a formed eutectic structure. Additionally in the solid solution the precipitation of spherically shaped Ni-Ti-Al particles with 1 – 3 µm diameter surrounded by remaining Ag of the braze was found.
Diffusion of nickel in the braze filler metal was observed also in the microstructure of nickel-Si_3N_4 composites brazed with Ag-Cu-Ti, **Fig. 3b**. At the interface ceramic/braze a very thin, < 0,5 µm thick TiN reaction layer is formed which is mostly covered with Ag. The remaining phases in the braze filler metal comprise of a Cu-Ni solid solution with up to 20 at.-% Ni and large areas of silver. Moreover towards the nickel foil many needle-shaped Ni-Ti intermetallic phases having a length up to 10 µm are formed. The composition of the Ni-Ti needles was determined by EDS to 20-23 at.-% Ti and 77 – 80 at.-% Ni, which is typical for $TiNi_3$. Additionally at the surface of the nickel foil cu is dissolved and a Cu-Ni solid solution with 40 – 45 at.-% Ni is formed.
The results of the microstructural analysis let one assume, that the decompositon of Si_3N_4 to Si and N and the subsequent formation of Ti-N and Ti-Si compounds is hindered due to the formation of the Ni-Ti needles which results in a very thin interfacial reaction layer. This in turn suggests that the reaction

of AlN with titanium and the formation of TiN-phases is more favoured within the brazing cycle than the analogous reaction of Si_3N_4 with titanium.

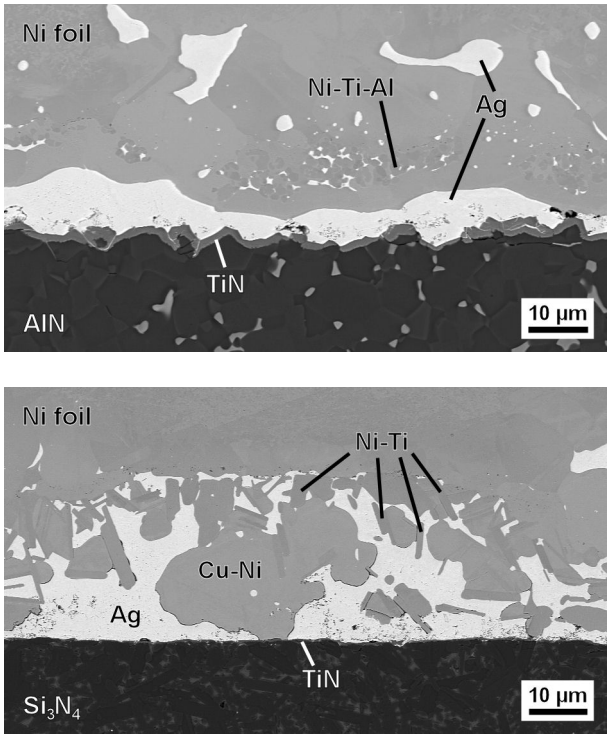

Fig. 3. SEM image of brazed microstructure of nickel to a) AlN and b) Si_3N_4 with Ag-Cu-Ti.

Fewer differences between AlN and Si_3N_4 were found after active metal brazing of nickel with the Ag-Ti braze, **Fig 4**. No clear interface layer between the Ag-based braze filler metal and the Ni foil can be distinguished. In both cases a thin interlayer containing Ti and N was formed at the interface ceramic/braze followed by a small strip of Ag and a thick Ni-rich ribbon. The Ni-rich band contains up to 92 at.-% Ni with 5 – 8 at.-% of dissolved Ti and < 2.5 at.-% Al in the case of AlN substrates and Si in the case of Si_3N_4. Near the TiN layer small TiO_2 particles and at the former interface metal/braze some larger areas of silver were found.

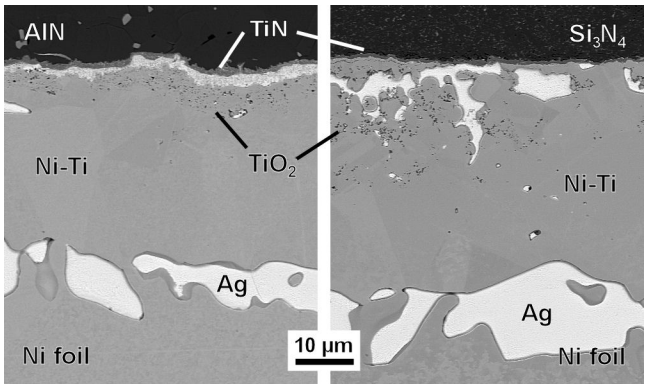

Fig. 4. SEM image of brazed microstructure of nickel to AlN (left) and Si_3N_4 (right) with Ag-Ti.

Hence in case of brazing nickel foils a limited reactivity between the nickel and the braze filler metals can be observed while the intensity does not result in a severe destruction of the metallisation layer. This is important with respect to the aspired application in thermoelectric generators. Only certain material combinations permit brazing processes of plane metal to ceramic composites with a good surface quality of the metallisation layers and without disadvantageous damages. Other combinations lead to strong reactions between the braze filler metals and the metal foils resulting in different interfacial layers or a destruction of the metallised layers.

4 Metallisation with refractory metals

Active metal brazing of tungsten and molybdenum to AlN with the Ag-Cu-Ti braze yielded in sound joints with no remarkable destruction of the metal foils. The brazed microstructure of W-AlN and Mo-AlN composites exhibit the formation of a 1 – 2 µm thick TiN interfacial reaction layer and the solidification of the braze filler metal as two phases, **Fig. 5**. One phase consists of the Ag-Cu eutectic composition; the other one is a Cu-rich phase with a small fraction of dissolved Ag. In both cases the precipitation of very small TiO_2 particles having a size between 50 and 300 nm was observed near the TiN layer and in the Ag-Cu eutectic structure. Though no reaction layer was found at the interface between the braze filler metal and the metal foil.
These results suggest, that composites of refractory metals and AlN can be made by active metal brazing. However the joint strength and the stability against thermal cycles has to be addressed in the future. At least fracture of the composites can occur from the brittleness of the refractory metals due to their high hardness and high Young's modulus. Also this effect could caused the fracture of the edge of the Mo foil during sample preparation as it is visible in the SEM image, **Fig. 5**.

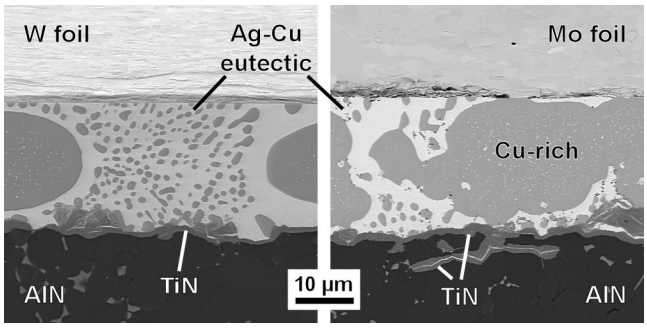

Fig. 5. SEM image of brazed microstructure after active metal brazing of tungsten (left) and molybdenum (right) to AlN with Ag-Cu-Ti.

The brazed microstructures of W and Mo to AlN with the Ag-Ti braze are in good agreement with our expectations, **Fig. 6**. During the brazing process a reaction layer of TiN with a thickness between 3 and 10 µm was formed at the ceramic/braze interface. In both cases the braze filler metal is composed of Ag with dissolved Al. During the brazing process also some Al_2O_3 particles are formed which are randomly distributed in the silver. The increase in thickness of the TiN layer can be attributed to the higher brazing

temperature of the Ag-Ti braze which results in a longer time period with a liquid braze and a more intense reaction between the active elements of the braze and the ceramic.

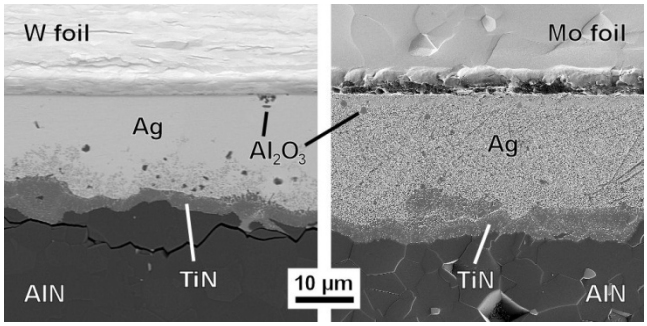

Fig. 6. SEM image of brazed microstructure after active metal brazing of tungsten (left) and molybdenum (right) to AlN with Ag-Ti.

In contrast to joining of refractory metals to AlN, active metal brazing of tungsten and molybdenum to Si_3N_4 led with both brazes to fracture-sensitive composites. Hence after preparation of SEM samples in all characterised W-Si_3N_4 and Mo-Si_3N_4 composites cracks were found along the brazed joint, **Fig. 7**. Depending on the composite layers the cracks propagate through the Si_3N_4 ceramic substrate or the refractory metals as well as along the interfacial reaction layers. As discussed above the high hardness and high Young's modulus of the refractory metals can be responsible for a crack formation though no cracks were found in AlN composites. These results suggest, that an additional aspect has to be considered in case of Si_3N_4 composites.

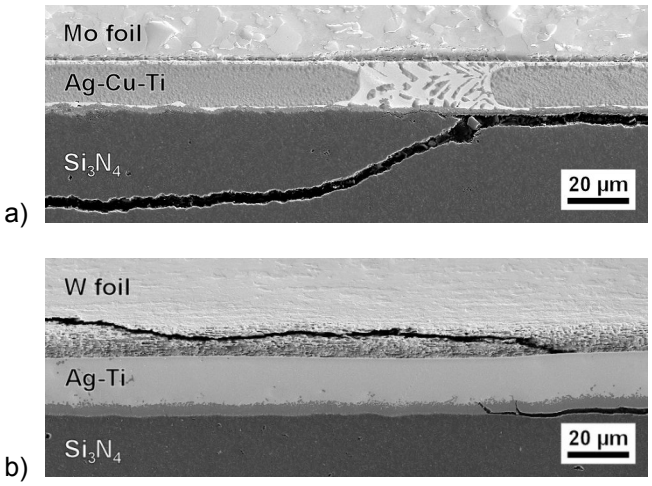

Fig. 7. SEM image of brazed composites of refractory metals and Si_3N_4 revealing cracks in the joined materials and the interfacial reaction layers.

The coefficient of thermal expansion (CTE) for Si_3N_4 is 3.0 to $3.5 \cdot 10^{-6} \cdot K^{-1}$ between 20°C and 1000°C whereas in the same temperature range the CTE of tungsten and molybdenum are 5.3 and $6.7 \cdot 10^{-6} \cdot K^{-1}$, respectively. These different CTE values will lead to high stresses inside the brazed joints when at the end of the brazing process the braze filler metal solidifies. Due to the high hardness and high Young's modulus these stresses can cause the formation of cracks and the fracture of the composites.

Cracks can also be found in the interfacial reaction layer of W-Si_3N_4 composites brazed with the Ag-Ti braze, **Fig. 8**. The high magnifaction SEM image captured with a backscattered electron detector shows two phases inside the reaction layer. A more detailed EDS analysis revealed, that point 1 consists of 52 at.-% Ti, 41 at.-% N and 7 at.-% Si and point 2 has a composition of 54 at.-% Ti, 28 at.-% N and 17 at.-% Si. Hence the reaction layer consists of a mixture of TiN and Ti_2Si. Therefore the observed cracks can be attributed to CTE mismatch between these phases and the Si_3N_4 ceramic substrate.

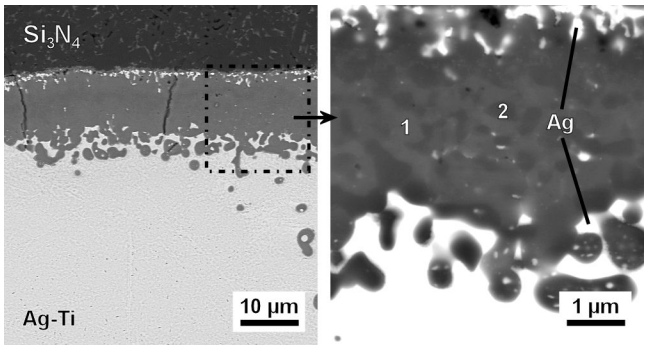

Fig. 8. SEM image of interfacial reaction layer of brazed composite of tungsten and Si_3N_4.

These results are somewhat surprising as it is possible to realise Si_3N_4 to Si_3N_4 joints using both types of braze filler metals, while the substitution of one ceramic part by a brittle refractory metal with similar coefficient of thermal expansion leads to severe damages in the brazed composites.

Furthermore the Ag-Cu-Ti braze seems to be more appropriate for active metal brazing of nitride ceramics, especially Si_3N_4, due to a lesser formation of brittle titanium silicides at the interfacial reaction zones. In case of the Ag-Ti braze a reduction of the titanium content could succeed in a reduced formation of silicides. However this could also lead to a lack of titanium at the brazing zone what in turn may result in an insufficient bonding strength.

5 Conclusions

The metallisation of plane nitride ceramic substrates with nickel and refractory metals using two silver based active brazes was demonstrated. In all cases the formation of a TiN reaction layer at the ceramic/braze interface was observed. While brazing at 900°C the TiN layer had a thickness of 1 – 2 µm, whereas increasing the brazing temperature to 1050°C results in an increase of the thickness up to 10 µm. Active metal brazing of nickel was possible with both brazes and to both nitride ceramics. Future work will investigate the influence of the formed intermetallic phases on the mechanical properties and the stability against thermal cycles.

The metallisation of AlN with tungsten and molybdenum worked well and offers opportunities for further tests to prove the reliability for microelectronic

packaging and manufacturing of thermoelectric generators. In contrast, the metallisation of Si_3N_4 with refractory metals was not successful due to mismatch in coefficient of thermal expansion and the high Young's moduli of the refractory metals. Finally it can be stated, that the metallisation of nitride ceramics with metals besides copper is possible but a careful selection of the right combination of ceramic, braze filler metal and metallisation layer is required.

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