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MICROSTRUCTURE OF METALLIC LAYERS SINTERED ON NITRIDE CERAMICS DEPENDING OF THE CHEMICAL COMPOSITION OF INTERLAYERS

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The effects of the oxygen and titanium contents in the reactive layer deposited on nitride ceramics on the wettability and sintering capability of the metallic layers were examined. The deposited metallic layers were standard Mo and Mn layers with the oxygen content ranging from 0 to 40 at.% and the titanium content from 0 to 8 at.%. The layers were sintered at a temperature between 1573 and 1653 K in a hydrogen atmosphere (dew point - 203 K). In the a transition layers, between the Al_2O_3 or AlN ceramic material and the metallic layer, a continuous glass layer is formed on the ceramic surface, which wets very well both the substrate and the metallic powders.

The microstructure of the metallic layers was examined using a scanning electron microscope and an electron probe. It has been found that both Al and Si migrate strongly to the interface layer. The microstructure of the metallic layers sintered on AlN differs from that of the layers sintered on alumina ceramics. In the interface layer formed between the ceramic material and the metallic layer, a continuous glass layer forms on the ceramic surface; the glass wets very well both the substrate and the metallic powders. The metallic layer is compact, and the solder does not flow in-between the grains. Based on the results of the microstructural examinations, the mechanisms of the sintering of Al and AlN ceramics are compared.

1. INTRODUCTION

Durable ceramic-metal joints are difficult to fabricate because of the considerable difference between the thermal expansion coefficients of the two materials. Moreover, when in a liquid state, metals do not wet ceramics. In order to ensure a high mechanical strength of the joints, with both nitride and alumina ceramic materials, it is advantageous to produce a metallic transition layer which improves the wettability and compensates the thermal stresses induced

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as a result of the differences in the thermal properties of the materials being joined. The literature reports on various methods of joining non-oxide ceramics with metals, especially nitride ceramics such as chiefly AlN [1]. Most frequently, non-oxide ceramic materials are joined using the same methods as those employed for joining oxide ceramics, and the process parameters are adjusted to suit the properties of the materials being joined.

The processes of metallization and joining of nitride ceramics are conducted in vacuum or in an atmosphere of protective gasess (nitrogen, hydrogen, argon) added with a small amount of oxygen (dew point below 203 K, ca. 1.5 ppm O_2). Standard metallic Mo, Mn or W, Mn layers on alumina ceramics are produced in an atmosphere of wet hydrogen. The presence of oxygen in the protective atmosphere ensures the formation of the phases necessary to achieve an appropriate adhesion between the metallic layer and the substrate.

At temperatures above 1423 K and in the presence of moisture, nitride ceramics decompose according to the reaction [1]:

$$AlN + 2H_2O = NH_3 + AlOOH$$

Based on this formula we assumed that the oxygen in the amount (at.%) required for the phase transformations should be introduced directly into the metallic layer, and that the process of sintering of the MoMn layers should be conducted in dry hydrogen (an oxygen content of 1.5 ppm).

2. EXPERIMENTAL PROCEDURE

The metallic pastes used for the experiments were composed of the mixtures:

A. 80 wt.% Mo and 20 wt.% of the Mn + FeSi75 mixture - intended for sintering in hydrogen with a dew point of 202 K,

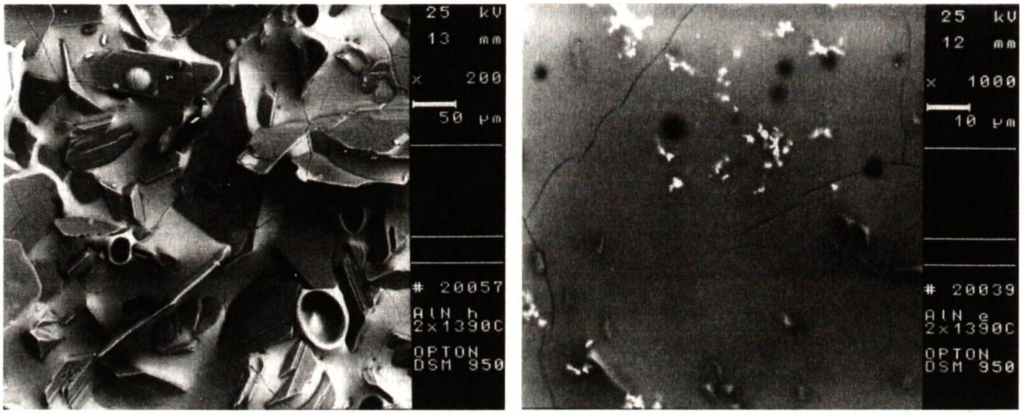
B. 80 wt.% Mo and 20 wt.% of MnO_2, FeSi75 and Ti mixtures with various oxygen and titanium contents - intended for sintering in a protective atmosphere with a dew point of 203 K.

The mixtures containing oxygen and titanium were prepared in the proportions:

a) 18.5 at.% oxygen, 0% titanium;
b) 31 at.% oxygen, 3.8 at.% titanium;
c) 40 at.% oxygen, 2 at.% titanium.

The oxygen mixtures (a,b,c) were spread on the surface of AlN plates and melted at temperatures of 1623, 1653 and 1673 K (1350, 1380 and 1400°C) in an atmosphere of nitrogen mixed with hydrogen (3 parts of hydrogen, 1 part of nitrogen) with a dew point of the mixture of about 203 K. The plates were maintained at the maximum temperature for 20 min. For comparative examination, an Mn(FeSi75)50 mixture was melted on a leucosapphire plate; this process was carried out in a hydrogen atmosphere with a dew point of 303 K.

The appearance of the layers produced on AlN ceramics in shown in Fig.1. In the layers containing 30 - 40 at.% of oxygen and about 4 at.% of titanium we can see a substantial amount of a vitreous phase, very fine crystalline precipitates of irregular structure and numerous large lamellar precipitates (Fig.1b). The glass covers uniformly the aluminium nitride ceramics. The layers produced from the mixture with an 18 at.% content and 0 at.% titanium contained a great number of the lamellar precipitates and a min amount of glass (Fig.1a). We can also see gas-induced craters.



a) b)

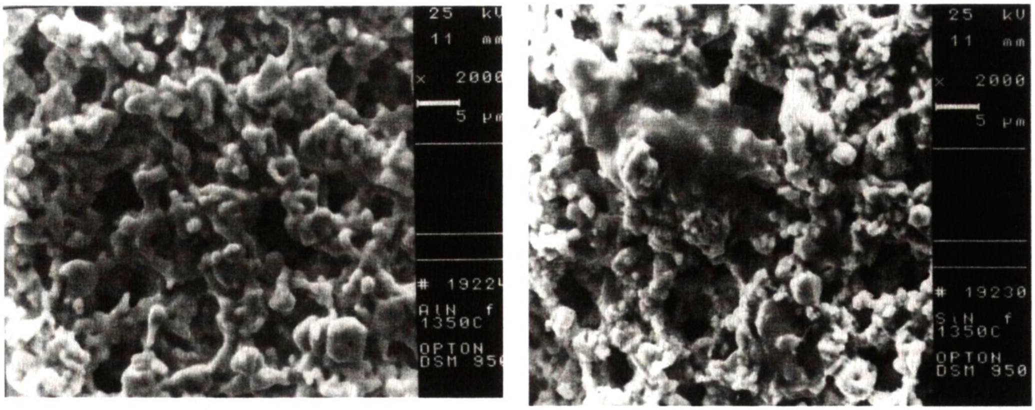
Fig.1. Layers of glass-forming mixtures melted on AlN ceramics: a) composition "a" (18.5% oxygen, 0% titanium), b) composition "b" (31 at.% oxygen, 3.8 at.% titanium).

The adhesion of these layers to the substrates is good, the layers are compact and suitable to be chemically nickel-plated.

The appearance of the metallic layers produced on various substrates is shown in Fig.2. The layers without oxide constituents show no adhesion to any of the ceramic substrates examined, and contain regions filled with various liquid metallic phases which do not wet any substrate, neither AlN nor Si3N4.

The oxygen-containing additives introduced into the metallic layers bring about changes in the appearance of the layer surfaces visible after the sintering process (Fig.2). The metallic layers are now homogeneous, and when sintering on the Si_3N_4 substrates, glass excess can be seen on the metallic grains (Fig.2b).

The adhesion of these layers to the substrates is good, the layers are compact and suitable to be chemically nickel-plated.



a) **b)**

Fig.2. Metallic layer "b" (31 at.% oxygen, 3.8 at.% titanium) sintered on AlN (a) and on Si_3N_4 (b).

3. MICROSTRUCTURAL AND IDENTIFICATIONS OF THE METALLIC LAYERS

The constituent phases of the melted glass-forming mixtures and sintered metallic layers added with these mixtures were identified using a scanning electron microscope, an X-ray diffractometer and an electron probe which permitted determining the maps of the Al and Ti distributions within the joints.

The glass-forming mixture (Mn, FeSi75) melted on a leucosapphire substrate at a temperature of 1663 K in a hydrogen atmosphere (dew point - 303 K), and the mixture of composition (b) melted on an AlN substrate at the same temperature (1663 K) in a hydrogen atmosphere (dew point - 203 K) were examined by the X-ray diffraction method using a PHILIPS PW 1840 X-ray diffractometer .

The phases identified on the surface of the melted layers were:

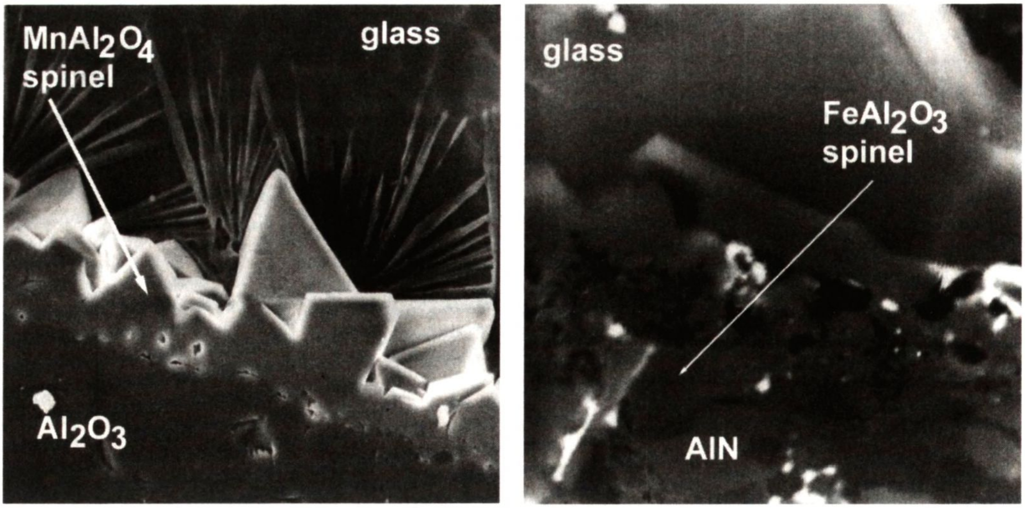
AlN substrate:

- oxide phases: corundum, $FeAl_2O_4$ spinel and silicates: Fe_7SiO_{10} ($5FeO.Fe_2O_3.SiO_2$) and Fe_2SiO_4 ($2FeO.SiO_2$),
- nitrides: TiN (osbornite), Fe_2N,
- intermetallic compounds: $MnAl_{0.75}Si_{1.25}$;

leucosapphire substrate:

- $MnAl_2O_4$ spinel,
- silicates: $MnOSiO_2$.

The microstructure of these layers on a cross-section perpendicular to the layer surface is shown in Fig.3.

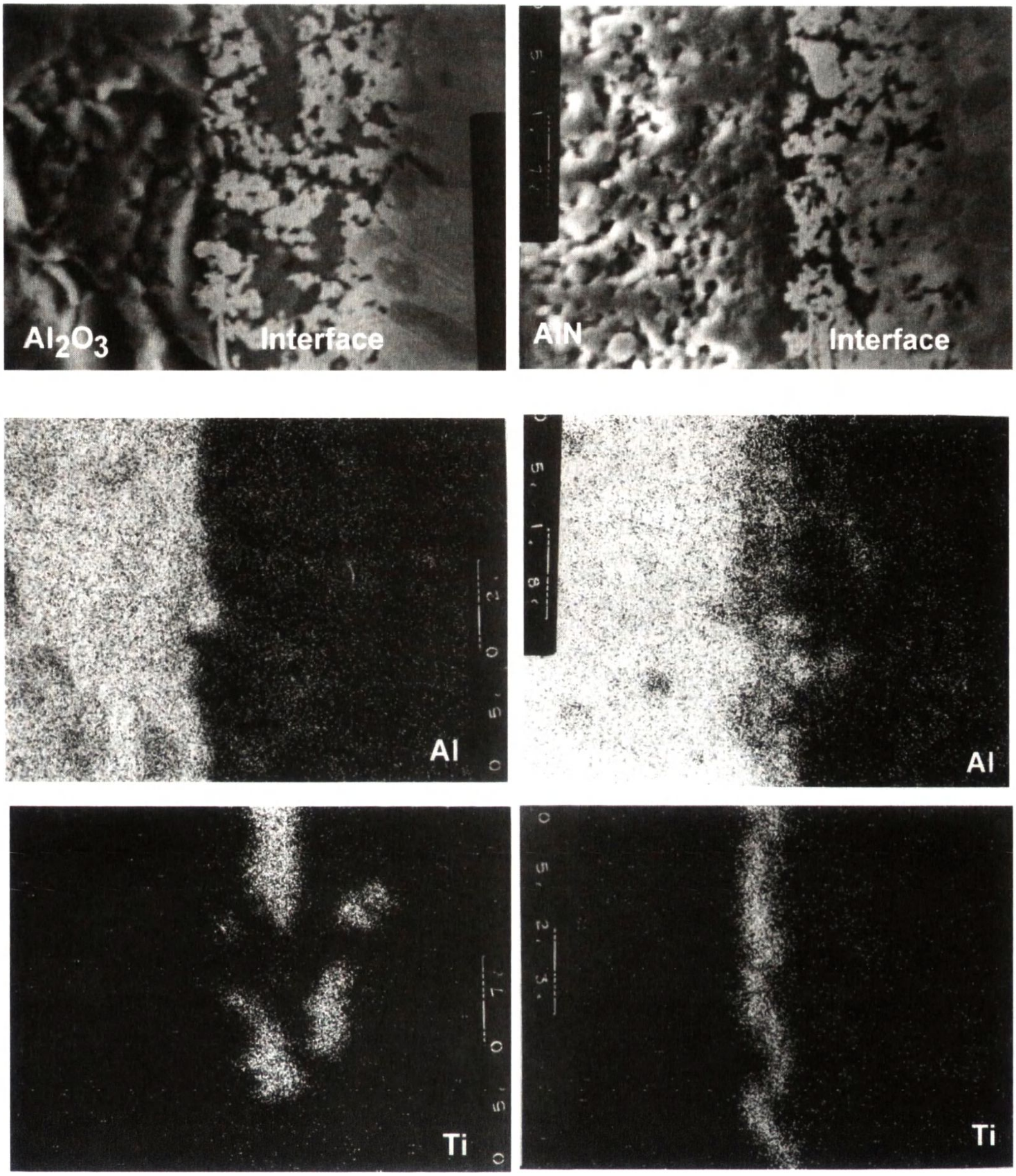


a) b)

Fig.3. Microstructure of the glass-forming mixtures melted on leucosapphire and AlN at a temperature of 1663 K for 60 min: a) Mn, FeSi layer sintered on leucosapphire in hydrogen (dew point -303 K i.e. +20°C), b) layer containing 31 at.% oxygen and 3.8 at.% titanium, sintered on AlN in hydrogen (dew point 203 K, i.e. 70°C) (mag. 2000x).

The microscopic examinations of the glass-forming mixtures sintered on leucosapphire and AlN show that the layers differ considerably as regards their continuity and adherence to the substrate. The transition layers formed on leucosapphire have compact and continuous microstructures, where as those on AlN show a considerable porosity, even though the X-ray diffraction analysis identified similar phases in both kinds of the layers: aluminium-manganese spinel and manganese silicates on leucosapphire and the aluminium-iron spinel and iron silicates on AlN.

The metallic layers (80% Mo, 20% mixture "b") sintered under the same conditions, namely, at a temperature of 1663 K and humidity of 203 K for 20 min, were examined using an electron probe (Fig.4). The results are shown in the form of maps of the surface distributions over a cross-section perpendicular to the layer. On leucosapphire, the interface is compact and no Al transition into the metallic layer is observed. Titanium occurs in agglomerations within the metallic layer, at a significant distance from the alumina interface. With the Al substrates, we observe a strong solubility at the interface. Aluminium penetrates deep into the metallic layer, where as titanium occurs on the ceramic surface where it is distributed evenly and uniformly.



a) b)

Fig.4. Surface distributions of Ti and Al within the metallic layer 'b' sintered on sapphire and AlN.

4. DISCUSSION

The present study was concerned with the joints brazed with metallic molybdenum-manganese layers produced on AlN ceramics by the powder metallization technique. For the sake of comparison, technological tests were also performed using alumina substrates.

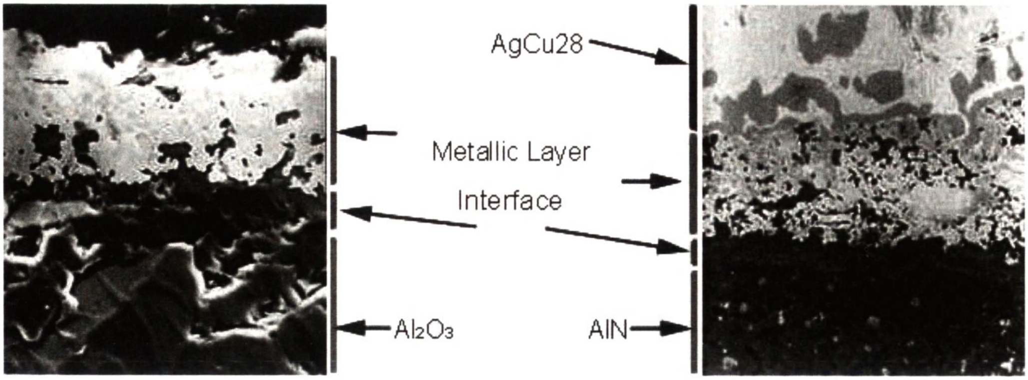
In view of the poor resistance of non-oxide ceramics to the action of moisture at elevated temperatures, the metallic layers were sintered in the atmosphere of dry hydrogen with a dew point of 203 K (-70°C), whereas oxygen necessary for the joining process was introduced into the components of the metallic layer. The oxygen content in the metallic layers was varied from 18.5 to 40 at.%. Another additive introduced into the metallic layers was titanium in the amount from 0 to 3.8 at.%. The metallic layers were sintered at temperatures of 1623 and 1663 K (1350, 1390°C). The metallic layers thus obtained have a satisfactory adhesion to the substrate, so that the joints can be brazed using the hard AgCu28 solder which guarantees a good mechanical strength.

The results of the microstructural examinations of the metallic layers and examinations of the glass-forming additives permit describing the sintering process of the molybdenum-manganese layers on AlN ceramics. The courses of this process on alumina ceramics and on AlN are quite similar. A good adhesion of the layers is achieved thanks to the reaction processes that proceed on the ceramic surface and to the vitreous phase formed during the sintering process (Figs. 3, 5). In both the ceramic materials we find spinel structures built into the substrate, but on the AlN substrates the layers are not as compact as they are on alumina (Fig.3).

Fig.5 compares the microstructures of the cross-sections of the 'standard' Mo,Mn layers sintered on alumina ceramics with the microstructures of the layers produced on AlN with the participation of specially modified MoMn, FeSi, Ti layers that contained 31 at.% of oxygen and 3.8 at.% of Ti.

The metallic Mo, MnFeSi layers on alumina ceramics were sintered in an atmosphere of wet hydrogen with a dew point of 303 K (+30°C). On AlN ceramics - the sintering process was carried out in dry hydrogen with a dew point of 203 K (-70°C), and the necessary oxygen (31 at.%) and titanium (3.8 at.%) were introduced together with the layer constituents. On the surface of the sintered layers, we can see a vitreous phase, which also fills the intergranular spaces in the layers. The metallic layers are compact, no solder flows can be seen in-between the grains of the metallic powders.

The mixtures of the glass-forming constituents melted on AlN ceramics show a high porosity, and the vitreous layer contains bubbles (the upper right corner of Fig. 3b). The pores observed in the transition layer and the bubbles in the glass layer can be attributed to the release of nitrogen.



a) **b)**

Fig.5. Comparison o the microstructures of the molybdenum layers produced on alumina ceramics: a) and AlN ceramics, b) mag. 1000X.

A similar effect of the nitrogen release from the AlN surface was observed by Wenjea, J.Tseng et al. [3] when they sintered 'soft' metallization layers (silver-palladium). Moreover, when examining the alumina layers produced on AlN, surface oxidised to form Al_2O_3, they found that the alumina layer adjacent directly to the AlN surface showed a high porosity. According to these authors, the highest porosity occurs on the interface between AlN and alumina. Entezarin and Drew [2], who joined AlN ceramics, surface-oxidised and non-oxidised, using the DCB technique, found that the mechanical strength of the joints decreased considerably with increasing thickness of the alumina formed on AlN prior to the joining process. According to these authors, the Al_2O_3 layer hinders the release of nitrogen from the AlN surface during the oxidation reaction. These authors also found that the great difference between the thermal expansion coefficients of alumina (8×10^{-6}/K) and AlN (4.4×10^{-6}/K) results in the microcracks being formed in the interface layer.

Our earlier studies [5] have shown that the high compactness of the metallic layer sintered on AlN was achieved thanks to titanium introduced into the metallic mixtures and to the 20 min sintering time at a temperature of 1623 K. Microscopic examinations have shown that titanium forms a continuous TiN layer, 6-7 μm thick, on the AlN surface.

When joining Si_3N_4 ceramics using active solders, Tillman et al. [4] identified a reaction TiN layer on the ceramic surface and determined its thickness using the simplified formula (derived from the diffusion laws):

$$x = kD^{1/2}t \tag{1}$$

where x is the layer thickness, D is the diffusion coefficient, k is a constant and t is the sintering time.

Having determined the layer thickness, they could calculate the activation energy from:

$$ln\,x = ln\,k'' - Q/2RT \tag{2}$$

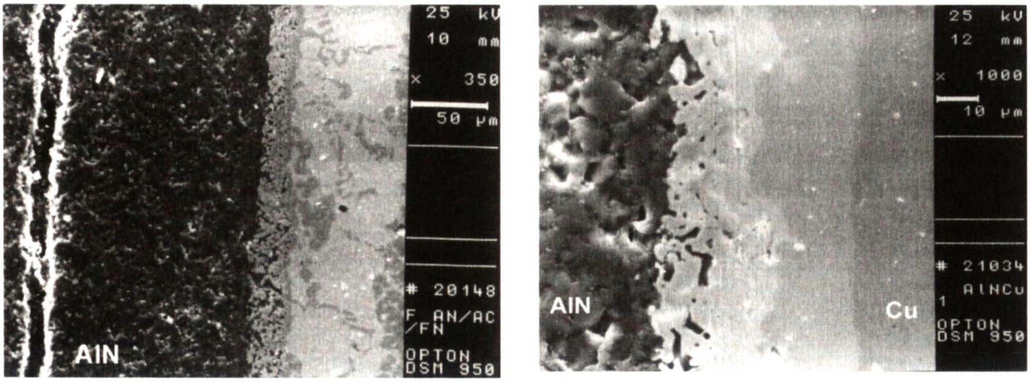
Substituting the sintering time and temperature employed, the activation energy of TiN was calculated to be 210.0 KJ/mol [4].

The results of our investigations with the use of controlled amounts of oxygen and titanium seem to confirm the Tillman et al. [4] suggestions that when joining nitride ceramics, a barrier TiN layer forms on the ceramic surface and that this layer is advantageous for the joining process. For the barrier layer to grow, it is necessary that titanium and nitrogen should be involved in the process; both these constituents contribute to the formation of the reaction layer. Because of its dimensions (its radius is 0.071 nm), the nitrogen atom probably moves most quickly. The reaction of TiN synthesis is however limited by the amount of Ti. In addition to the control of the oxygen additive, we can utilise this fact for the protection of the AlN surface against, for example, the oxidation of the interface layer during the reaction.

Fig.6 shows the microstructures of cross-sections of the two flat joints: AlN ceramics/FeNi42 alloy brazed with the AgCu28 solder at a temperature of 1093 K, and AlN/Cu of the same design brazed with the AuSn20 solder at a temperature of 553 K. We can see that both the hard solder (1093 K) and the soft solder (553 K) are suitable for brazing the metallic mixtures sintered on AlN ceramics.

In both the joints, the microstructure of the interface layer between the solder and the metallic layer (molybdenum added with mixture (b) sintered at a temperature of 1663 K in a gaseous atmosphere of a dew point of 203 K, observed on a cross-section perpendicular to the joint, is homogeneous. The Figs. show the interface layer formed on the ceramics. The microstructures of both the joints are compact and homogeneous.

The microcracks observed in the flat asymmetric FeNi42 joint brazed with the AgCu28 alloy result from the considerable difference in the thermal expansion coefficients of the joined materials (AlN - $\alpha = 4.4\text{x}10^{-6}$/K, the AgCu28 solder - $\alpha = 19 \text{ x } 10^{-6}$/K, and the FeNi42 alloy - $\alpha = 7 \text{ x } 10^{-6}$/K).



a) b)

Fig.6. Microstructure of asymmetric AlN joints: a) with the FeNi42 alloy brazed using the AgCu28 solder, b) with Cu brazed using the AuSn20 solder.

The lower bending strength of the AlN joints compared to that of alumina joints can be attributed to the poor adherence of the interface layer formed on the AlN ceramics. The bending strength achieved with the AlN bars (about 80 MPa) is however sufficient for most ceramic/metal joints subjected to exploitation loads.

5. CONCLUSIONS

1) On both AlN and alumina ceramics, the metallic layers should be sintered in the presence of a liquid phase which ensures a good wettability of both the ceramic and metal and thereby the compactness and good adherence of the metallic layer to the substrate.
2) Oxygen, in an amount of 30 to 40 at.%, contained in the metallic layer permits forming the phases necessary for the metallic layer to adhere well to the substrate, whereas the hydrogen atmosphere of a dew point of 203 K in which the sintering process is conducted protects the ceramic surface against moisture.
3) The barrier TiN layer formed during the sintering process ensures effectively the continuity of the microstructure between the layer being sintered and the substrate. The amount of titanium introduced during the sintering process must be precisely controlled since it affects the mechanical strength of the joint.

4) The AlN/Cu joints brazed with soft solders are free of microstructural defects and can be used for heat sinks in electronic devices.

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