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Deposition of Thin Film of Titanium on Ceramic Substrate Using the Discharge for Hollow Cathode for Al_2O_3/Al_2O_3 Indirect Brazing

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Thin films of titanium were deposited onto Al_2O_3 substrate by hollow cathode discharge method for the formation of a ceramic-ceramic joint using indirect brazing method. An advantage of using this technique is that a relatively small amount of titanium is required for the metallization of the ceramic surface when compared with other conventional methods. Rapidly solidified brazing filler of $Cu_{49}Ag_{45}Ce_6$ in the form of ribbons was used. The thickness of deposited titanium layer and the brazing temperature/time were varied. The quality of the brazed joint was evaluated through the three point bending flexural tests. The brazed joints presented high flexural resistance values up to 176 MPa showing the efficiency of the technique.

Keywords: *indirect brazing, Al_2O_3, metallization, hollow cathode technique*

1. Introduction

With the development of high technology ceramics, it was necessary to create a process to allow the union of these materials. The most used process since the Second World War until now is the brazing process.[1,2]

Brazing is a process that allows the union of materials through the fusion of the filler metal inserted between the materials without the fusion of the base materials. It can be classified as direct brazing when the active metal is included in the filler metal or as indirect brazing when the active metal is previously deposited at surface to be brazed.

In the ceramic-ceramic brazed union by direct or indirect method, a subject thoroughly studied is the percentile of active metal necessary for the brazing process. If the amount is insufficient, the wetting of the ceramic substrate cannot be achieved and if the amount is excessive, the formation of intermetallic compound and oxide can lead to brittleness of the joint[3].

AgCuTi alloys are the most widely used filler alloys for Al_2O_3 brazing, with Ti acting as active metals promoting the union by forming a reaction layer at the ceramic surface increasing the wetting behavior.[4-6]

In the case of the indirect brazing, the previous metallization allows the wetting of the ceramic substrate without the introduction of an active metal in the filler alloy. This leads to a reduction of the processing cost. In metallization Ti dissociates alumina forming oxides at the ceramic surface which allows the wetability[7]. The metallization of the ceramic surface can be achieved by several processes, including Moly-Mn, bath of salts, mechanical metallization, and magnetron sputter deposition of thin film[8].

In this work, a Hollow Cathode Discarge – HCD sputtering technique was used to introduce Ti as the active metal on the Al_2O_3 surface for indirect brazing process. To verify the performance of this deposition technique, the mechanical resistance of the brazed joint was evaluated by a three-point flexural test.

2. The Hollow Cathode Discharge Sputtering Technique

The metallization of ceramic surfaces can be achieved by plasma and it is divided into a chemical process (Plasma Chemical Vapor Deposition - PECVD); and a physical process (Plasma Physical Vapor Deposition –PEPVD). The PEPVD processes involve the generation and deposition of the metallic vapor species from a solid target. These processes include ion plating and sputtering. By varying the plasma parameters, these processes offer the possibility to vary the properties of the films[9].

During the sputtering process, an electrical potential (e.g. 1-2 kV) is maintained between the target (anode) and substrate (cathode) in a vacuum chamber filled with inert gas and maintained at a pressure of 2×10^{-2} mbar. The electrical potential across the target and substrate causes the inert gas atoms to form ions, which are accelerated towards the cathode, removing superficial atoms (sputtering) from the target. These sputtered atoms are then deposited onto the substrate[10]. One of the techniques used to produce a ion source for sputtering is known as the Hollow Cathode Discharge - HCD.

The HCD technique is applied using two plates separated by a specific distance and polarized as cathode. The electron is repelled successively before leaving in its interior. Several collisions will happen due to oscillation in that area, forming a sector of ionized particles. This effect is called hollow cathode[10]. Different forms of hollow cathode can be used and its chemical composition is chosen according to those of the film.

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3. Experimental Method

Ti films were deposited onto cylindrical samples of commercial alumina of 99.8% purity with 5.00 of diameter and 100 mm of lengths. The deposition process was done using equipment developed at Lab-Plasma, UFRN. The brazing were accomplished in temperatures of 1110, 1070 and 1150 °C in a various furnaces using the following heating and cooling cycles: (1) heat from room temperature to 300 °C at 5 °C/min and heat up to the brazing temperature at 20 °C/min; and (2) cool from the brazing temperature to 300 °C at 10 °C/min and cool to room temperature at 5 °C/min. The brazing times were 20, 30 and 40 minutes. Ribbons of amorphous Cu49Ag45Ce6 alloy were obtained by melt-spinning and they were used as the filler material during the indirect brazing.

4. Hollow Cathode Technique

The cathode was composed of a cylindrical pin of stainless steel with 12.00 mm diameter and with 54.00 mm length. In the inferior part of the cylinder, there is a cylindrical hollow made of titanium. In Figure 1 is showed with HCD titanium inserted where happens the titanium sputtering.

The following process parameters were used in the deposition: work current: 0.4 A; work pressure: 6 × 10-3 mbar; distance between the cathode and the deposition surface: 30 mm; the position angle 90° and the gas flow: 6 cm^3/s. As the film thickness depends on the deposition time. Three different deposition times such as 60, 90 and 120 minutes were used to produce 18, 10 and 18 deposited samples, respectively.

The filler metals were then positioned between the metalized samples and submitted to 3 points flexion test with 0,1 mm/min of advance speed

5. Results and Discussion

The layer of titanium deposited on the ceramic substrate was quantitatively characterized by using of X-ray diffraction technique. A glass plate was metalized by titanium and the film thickness was measured to evaluate the deposition at alumina substrate. The deposition on glass plates had the objective of serving as comparison and it followed the same orientation used by Almeida.[11] After the deposition, the glass plates were cut, glued amongst themselves and sanded. After this, each layer was analyzed by SEM in the traverse section. Figure 2 shows the electronic micrograph of samples for three different times.

The thickness of the layers had average values of 1.74, 1.10 and 0.48 µm, in the central area of the sample deposited for 120, 90 and 60 minutes, respectively. The average rate of deposition was around 2.42 E^{-4} µm/s, 2.04 E^{-4} µm/s and 1.33 E^{-4} µm/s for depositions times of 120, 90 and 60 minutes, respectively. The deposition rates variations are associated to the parameters of the process and also to the cathode wear process.

The efficiency of the deposition of the films was confirmed by the good flexural resistance values of the brazing joints in all of the samples. To verify the influence of the variables on the flexure resistance, a factorial planning, using film time deposition, brazing temperature and brazing time as input variable was used. Table 1 presents the results of flexure resistance for each condition

The greatest value was 176.8 MPa and happened for the highest deposition time, shortest brazing temperature and brazing time. This value can be considered satisfactory as compared to those obtained in the literature where the average mechanical resistance of brazed joints are around 120 MPa[3,4,12,13], and the greatest value reached

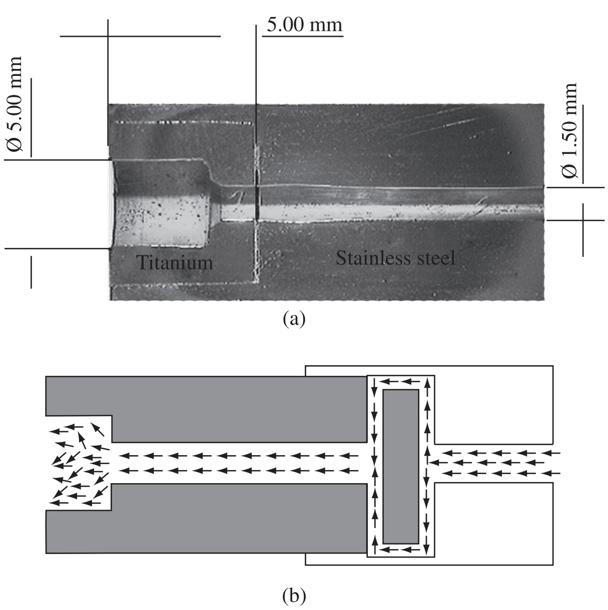

Figure 1. Titanium set in the inox cathod where happens the effect hollow cathode compounds by the small amount of Ti deposited (a) and a schematic representation of the way of the gas passing to the hollow cathode (b).

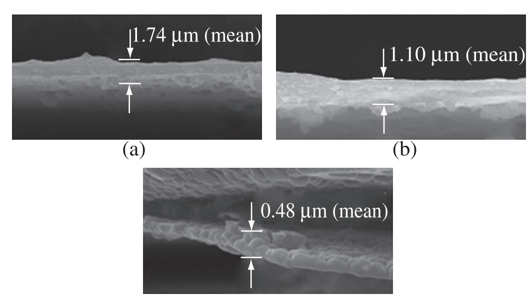

Figure 2. Thickness of the films deposited for (a) 120, (b) 90 and (c) 60 minutes.

Table 1. Input variable and flexure resistance values.

Test	Ti Layer thickness (µm)	Brazing temperature (°C)	Brazing time (minutes)	Flexure resistance (MPa)
1	1.74	1150	40	120.3
2	1.74	1150	20	134.5
3	1.74	1070	40	176.8
4	1.74	1070	20	136.5
5	0.48	1150	40	167.8
6	0.48	1150	20	154.7
7	0.48	1070	40	126.9
8	0.48	1070	20	135.3
9	1.10	1110	30	136.0
10	1.10	1110	30	134.0
11	1.10	1110	30	145.9

for 3-point flexural test obtained by Mori[12] was 189 ± 27 MPa for Al_2O_3-Al_2O_3 joint.

By Figure 3, it is verified that the higher values of the flexural resistance happen when the values of the layer thickness or brazing temperature reached their highest values, in an inverse combination of less layer thickness and greatest brazing temperature or lowest temperature and greatest deposition time. These results can be analyzed by the following way: the greatest layer thickness would results in the formation of a larger titanium deposits, increasing the wetting of the ceramic surface for the addition metal favoring the union. This happens in lower brazing temperature values when the formation of intermetallic compound, harmful to the union, do not occur. On the other hand, in less layer thickness, when the Ti amounts are smaller, high temperature would favor the union by the diffusion of the metallic elements in the alumina, without forming intermetallic compounds. The decrease of Al_2O_3 / Al_2O_3 brazed joint resistance with the increase of brazing temperature was also identified by Hongqi[6] who identified an increase from 1.2 up to 8.6 μm on the interfacial reaction layer thickness in Al_2O_3 brazed joint, increasing intermetallic compound when the brazing temperature increased from 1123 to 1323 K.

Mandal[4] also identified that brazing temperatures above 950 °C can reduce the thickness of the residual Ag-Cu which can avoid crack nucleation in Al_2O_3 brazed joint.

Figure 4 presents the higher FR increase values (from 127 to 177 MPa) which occurred when layer thickness was increased from 0.48 to 1.74 μm at 1070 °C showing that the Ti amounts is the most important variable to improve the joint resistance by increasing the wettability of Ti/O by copper when brazing temperature is not too high to form intermetallic compound[14].

The efficiency of the Ti layer thickness was indirectly proved by Janickovic et al.[5] who obtained an increase above 50 MPa in shear strength of alumina joint when he used two layers of Ag-Cu-Ti ribbons with 50-100 μm instead of one as filler metals in direct brazing process

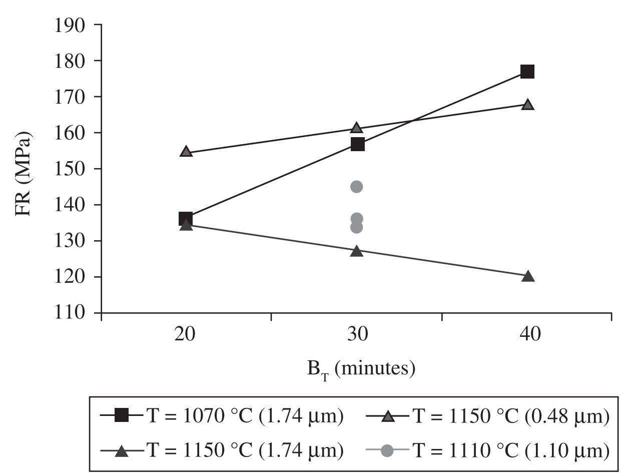

Figure 3. Flexural resistance value (FR) as a function of the Brazing time (BT) for different Brazing Temperature (T) and Ti layer thickness.

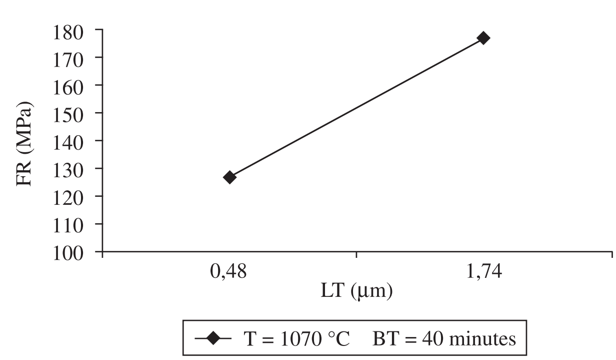

Figure 4. Flexural resistance (FR) as function of Ti layer thickness (LT) for brazing temperature (T) of 1070 °C and brazing time (BT) of 40 minutes.

6. Conclusions

- The use of the HCD technique for the alumina metallization with titanium was approved, making it possible to vary the thickness of the film while maintaining the parameters of the plasma fixed;
- The measurement of the film thickness directly on the alumina surface by electronic microscopy was not possible. However, the measurement by comparison with deposition on glass plates with the same parameters of the plasma was possible, supplying satisfactory results;
- The greatest flexural resistance value of the brazed joint was 176.8 MPa and happened for greater deposition time, shorter brazing temperature and brazing time which presented a interface without pore or discontinuity

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