INTERFACE BEHAVIOUR OF Al$_2$O$_3$/Ti JOINTS PRODUCED BY LIQUID STATE BONDING

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Abstract

The main objective of this work was to determine various aspects during brazing of Al$_2$O$_3$ samples to commercially titanium alloy grade 4 with biocompatibility properties, using a Au-foil as joining element. Al$_2$O$_3$ ceramic was previously produced by sintering of powder cylindrical shape at 1550°C for 120 minutes. Previously to joining experiments, the surface of Al$_2$O$_3$ samples were coating, by chemical vapor depositions (CVD) process, with a Mo layer of 2 and 4 $\mu$m thick and then stacked together with the Ti samples. Joining experiments were carried out on Al$_2$O$_3$-Mo/Au/Ti combinations at temperature of 1100°C using different holding times under vacuum atmosphere. The experimental results show a successful joining Mo-Al$_2$O$_3$ to Ti. Analysis by scanning electron microscopy (SEM) revealed that joining of Al$_2$O$_3$ to metal occurred by the formation of a homogeneous diffusion zone with no interfacial cracking or porosity at the interface. Results by electron probe micro analysis (EPMA) of Al$_2$O$_3$-Mo/Au/Ti combinations revealed that Mo traveled inside the joining elements and remained as solid solutions, however during cooling process Mo had a tendency to stay as a precipitate phase and atomic distributions of elements show a concentration line of Mo inside the joining element Au. On the other hand, well interaction of Ti with Au form different phases; like Ti$_3$Au and TiAu.

Keywords: metal/ceramic joining, alumina, titanium, brazing
1.- INTRODUCTION

In order to increase the practical use of advanced materials, bonding constitutes an alternative to produce metal/ceramic joints for medical applications; so it is necessary to develop simple techniques that allow us to link these materials. The appropriate selections of the bonding materials represent the technological key of this method, properties such as physical and thermodynamic compatibility, mechanical and physical properties, and thermal expansion coefficient of thermal expansion must be considered [Yong et al., 2006]. Alumina (Al\textsubscript{2}O\textsubscript{3}) is an important material used in a wide range of applications, including refractories, structural materials, electronic packaging, catalysts, and sensors. Alumina precursors, depending on the starting materials, processing route, presence of impurities, and heating conditions, undergo a variety of transitions until the most stable structure (\(\alpha\)-Al\textsubscript{2}O\textsubscript{3}) is formed at high temperature [Bahlawane and Watanabe 2000; Ebadzadehw and Sharifi 2008]. The manufacture of component shapes from monolithic engineering ceramics is difficult, and this has generated a continued interest in the use of joining technologies to produce complex configurations from assemblies of simple shapes. In most cases it is required to join these ceramics to metals with sufficient bond strength as metal can compensate for the poor workability and brittleness of ceramics.

There are three general categories or types of joining process. The first is \textit{mechanical} and is achieved through the use of mechanical interlocking of components. The second approach is \textit{direct joining}, in which components are bonded either by a solid-state process or by fusion. The third approach could be referred as \textit{indirect joining} in the sense that an intermediate layer of material, such as an adhesive, cement, or braze, is used to bond two components [Asthana and Singh 2009; He \textit{et al.}, 2006]. In metal-ceramic bonding, it is a common practice to introduce a metal interlayer between the components, producing a joint structure similar to that created by brazing but with higher temperature capabilities. The interlayer should be ductile so that it can deform readily to achieve intimate contact with both mating surfaces at various pressures and temperatures. Moreover, it will act as a stress relieving buffer layer should the thermal expansion of the metal and ceramic components differ significantly, and of course it must adhere and bond strongly to both the metal and ceramic.
Various techniques for joining ceramic to metal are available, some need an intermediate liquid phase, brazing, and others are produced by diffusion bonding [Liu et al., 2009; Firmanto et al., 2011]. One widely-used method for joining ceramics consists of brazing with a reactive metal alloy, however, the highest obstacle of successful brazing of ceramics to metals is the fact that most conventional brazing materials, in general, the first problem is the poor wettability of ceramics by most metals and alloys. The second problem is the difference in the physical properties between ceramics and metals which is manifested by extreme differences in the thermal expansion coefficients (α) and Young’s modulus. Brazing process increases contact between the materials promoting interfacial interaction through the liquid material. To improve wetting and adherence of filler metal with the surfaces in contact during the joining process it is essential the surfaces preparation (cleanliness) and/or state condition of the materials to be joint, i.e. an effective metallization (through wetting or flow) is required [Sugar et al., 2006; Lee et al., 2006]. In diffusion bonding chemical reaction takes place between the metal and the ceramics, and the properties of the reaction product layer dictate the usefulness of the bind and thus of the whole assembly at high temperature.

The reaction product layer should provide a strong bond between the two dissimilar materials, which means: i) it should accommodate for the thermo-mechanical mismatch resulting from differences in thermal expansion coefficients, and ii) the reaction product layer should not consist of compounds that have mechanical properties significantly inferior to those of the metal and the ceramic [He et al., 2010; Roy et al., 2009]. Al₂O₃ has been widely used as a very promising structural ceramics in variety of engineering applications due its excellent performance in various severe working environments [Walker and Hodges 2008; Nono et al., 2006]. The use of copper as a reactive system for joining metals to Al₂O₃ has significant potential as an active element, in particular for the active brazing. However, studies of the diffusion bonding kinetics, interfacial reaction and their effects on the properties of the joints are far from complete. The practical use of advanced ceramics depends on the reliability of ceramic/metal joining techniques and the properties of the resulting interfaces. Therefore, it is important to study the microstructure and mechanism of interface formation between the metal and ceramic. Therefore the main objective of this
work was to determine various aspects during brazing of Al$_2$O$_3$ samples to commercially titanium alloy grade 4 with biocompatibility properties, using a Au-foil as joining element.

2.- MATERIALS AND METHODS

The starting materials used were cylindrical monolithic Al$_2$O$_3$ samples, produced by isothermal sintering of commercial powders, $\alpha$-Al$_2$O$_3$, in a CARBOLITE furnace at 1550°C for 120 minutes, and commercially pure Ti-rod and Au-foil (99.98%), Aldrich Chemical Company, Inc. USA. The alumina samples were produced with the same diameter of the Ti rod (10 mm), and 3 mm thick. The success of diffusion bonding processes depends on a combination of factors, one of the most important is the surface preparation of the materials because it controls the initial contact area between the diffusion couples. From the above, the diffusion bonding experiments started with the preparation of the materials to be joined. Previously to joining experiments, the surface of Al$_2$O$_3$ samples were coating by chemical vapor depositions (CVD) process, with a 2 and 4 µm thick of Mo layer. Sandwich joints samples consisted of a block of Mo-Al$_2$O$_3$ mounted axially with a block of Ti and Au-foil in between, such that coating surface was in contact. The specimens to be joined were placed in a graphite die embedded in a boron nitride (99.5% pure) powder bed showed in figure 1. The purpose of the powder-bed was to avoid contact between the sample and the internal walls of the graphite die.

Figure 1.- Schematic representation of the samples assembly inside the graphite die.
The experimental apparatus used to join the sample combinations consist of a resistance furnace with a square chamber. Once the sample was assembled in the graphite die, it was positioned in the furnace and it was closed and fillet with argon prior to be evacuated to the vacuum joining atmosphere. After the joining environment was established, the furnace was heated up to the preset joining temperature. Joining experiments were carried out on Al$_2$O$_3$-Mo/Au/Ti sandwich-like combinations at temperature of 1100°C using different holding times for both, 2 and 4 µm thick of Mo-coating, under vacuum. The microstructural examination was performed in cross-section of polished experimental joined. Micrographs and analysis of the interfaces were obtained from a JEOL JSM-6400 scanning electron microscope.

3.- RESULTS

1.1.- Sintering of Al$_2$O$_3$

Cylindrical samples of 10 mm of diameter and 3 mm thick were produced by sintering at 1550°C for 120 minutes of high homogeneous commercial powder of Al$_2$O$_3$ of spherical shape with size distributions lower than 100 nm. Figure 2a shows a fracture Al$_2$O$_3$ sample consisting of grain formed by nanometric particles.

![Fracture image and ray-x diffractions pattern of Al$_2$O$_3$ samples sintered at 1550°C for 120 minutes.](image)

Figure 2.- a) Fracture image and b) ray-x diffractions pattern of Al$_2$O$_3$ samples sintered at 1550°C for 120 minutes.
It is possible observe some residual porosity because the relative density of this specimen is higher than 90%. X ray diffractions analysis carried out in alumina sample produced at high sintering temperature confirms the α-Al$_2$O$_3$ phase structure as it is shows in figure 3b. On the other hand, figure 3 shows a cross-section and surface of the alumina samples coated with Mo. It can be observed the estimated thickness of the surface Mo-coating of a) 2 μm and b) 4 μm, respectively.

![Surface coating](image1)

![Surface coating](image2)

Figure 3.- Cross-section and surface examination of a) 2 μm and b) 4 μm Mo-coating of Al$_2$O$_3$ samples sintered at 1550°C for 120 minutes.

1.2.- Metal/ceramic joint behavior

Diffusion bonding of sandwich-like samples of Al$_2$O$_3$/Ti was investigated by Al$_2$O$_3$-Mo/Au/Ti combinations joined at temperature of 1100°C in vacuum atmosphere and varying holding times for both, 2 and 4 μm thick of Mo-coating. In general, it can be observed successful joining of alumina to titanium, achieved at joining time of 2.5 and 5 minutes when the alumina surface was coating with Mo. However, in the case of samples treated without Mo-coating, separations during metallographic preparations process occurred for the
samples bonded at 1100°C. It could be associated to the low bonding strength of the sample produced by the diffusion process. On the other hand, in order to determine the interfacial interaction during the joint, a microstructural examination was performed in cross-section of polished experimental joined samples produced at 1100°C. Joints of Al₂O₃-Mo/Au/Ti combinations are formed through the formation of a reactive interface on the metal side of the sample as a result of diffusion and interaction of Au with Ti and Mo-coating. A cross-section of Al₂O₃-Mo/Au/Ti interface for samples joined at 1100°C for a) 2 µm of Mo-coating for 5 minutes and b) 4 µm of Mo-coating for 2.5 minutes are shown in figure 4.

![Cross-section of Al₂O₃-Mo/Au/Ti interface](image)

Figure 4.- Cross-section of Al₂O₃-Mo/Au/Ti interface for samples joined at 1100°C for a) 2 µm of Mo-coating for 5 minutes and b) 4 µm of Mo-coating for 2.5 minutes.

It can be observed in figure 4a that starting Mo-coating of 2 µm thick stay disperse inside the Au joining element even for joining time of 5 minutes; however when the staring Mo-coating increase to 4 µm thick, it is possible observe different Mo concentration inside the joining element. It can be observed that, when the joining time increase from 2.5 minutes (figure 4b) to 5 minutes the Mo concentration is observed along region forming a line close to alumina side, as is showed in figure 5. On the other side, interaction of Ti and Au produced by atomic diffusion generate the formation of Ti₃Au and TiAu on the interface along the bonding line with the metal size Ti. Electron probe microanalysis carrier out in the cross-section of the Al₂O₃-Mo/Au/Ti interface shows the main diffusion atomic elements during bonding. The analysis were performed on different points along the line illustrated at
the interface of the joint made at 1100°C for 5 minutes using Al₂O₃ with 4 mm of Mo-coating (figure 5) and the results are shown in the graphic in the same figure 5. The scan line was chosen to start on the Ti side of the sample through the bonding line interface passing through different interactions phases until the ceramic Al₂O₃.

Figure 5.- Line analysis across the Al₂O₃-Mo/Au/Ti interface bonded at 1100°C for samples with 4 μm of Mo-coating for 5 minutes.

The Ti signal reached its maximum at the metal side, however, Au signal reach its maximum the interface and the minimum inside the Ti metal and in the size in the interface where the Mo signal rich its maximum. It can be observed that the Mo signals is current inside all the interface.
4.- DISCUSSION

In general, when a ceramic is in contact with a metal a reaction is expected to occur. Joining temperature, time, and Mo-coating thickness were the main process parameters studies. Temperature is the most important one due to the fact that in thermally activated processes, a small change in temperature will result in a significant change in process kinetics compared with other parameters, and virtually all mechanisms including plastic deformation and diffusion are sensitive to temperature. Joints of Al$_2$O$_3$-Mo/Au/Ti combinations are formed through the formation of a reactive interface on the metal side of the sample as a result of diffusion and interaction of Au with Ti and Mo-coating and it can be explained since diffusion is more difficult in ceramics than metals [Lesage 1994]. Liquid formation plays an important role in the joining process, because it increases the rate of the interface formation, improving the contact area between the bonding materials, and consequently the interaction is higher, promoting rapid diffusion of the material, since liquid diffusion is much faster than the diffusion in solid-state [Lemus and Drew 2003]. The interface consisted of a homogeneous reaction layer produced by chemical interaction, as well as the high affinity of Au and Ti forming a Ti$_3$Au and TiAu phases. These results are in good agreement with the observation realized by [Kumar and Paul 2010]. It can be observed that the joints formed at the same temperature and different times exhibit similar microstructures with a continua and homogeneous interface free of crack and porosity. It can be observed that increasing the holding time from 2.5 to 5 minutes in samples joined with alumina, coated with 4 µm of Mo, did not significantly increase the interface thickness; however, it can be observed the formation of a region of Mo forming a line inside the reaction layer and close to bonding line with the Al$_2$O$_3$.

5.- CONCLUSIONS

On the basis of the results presented in this work, we had shown that it possible join alumina with a Mo-coating layer to titanium using a Au foil interlayer has joining element.
Successful bonding was observed at 1100°C under vacuum and Mo-coating. Joining of Al$_2$O$_3$ to Ti occurred through the formation of a homogenous diffusion zone on the metal side of the joint, with no several interfacial cracking or porosity. Diffusion of the Mo-coating inside the interface take place forming a continuous region line close to bonding line with the Al$_2$O$_3$ when 4 µm of coating and 5 minutes were used.

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