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Cofired Platinum /Alumina Microsystems for Implantable Medical Applications

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Abstract: With the desire for reduction in size and increased requirements for higher input/output (I/O) for implantable microsystems, cofired platinum/ high temperature alumina cofire ceramic (HTCC) is emerging as a technology of choice due to the long reliable history of Pt wire /alumina ceramics use as feedthrough structures in pacemakers. The new developments require the development of brazing processes to attach a titanium seal ring to develop a hermetic enclosure and feedthrough requirements into the hundreds of I/Os for neurostimulator applications. This work evaluates the development of a cofired Pt/Alumina materials system, including interconnects and high density via structures. Reactions previously unreported have been investigated, including the catalytic reaction with organic binders, the reduction of alumina with platinum into PtAl3 and the reduction of the melting point of platinum 300o C below its melting point, independent of the particle size (nano to micron size particles) or particle morphology. Firing atmosphere (air, hydrogen, inert), firing profiles and additives to control thermal expansion was evaluated to minimize exothermic reaction using high temperature X-ray diffraction, FIB nano-machining, SEM with EDS analysis and TEM for each of these conditions.

Key words: High density feedthrough, HTCC, cofired platinum- alumina

Žgani mikrosistemi platina/aluminijev oksid za implantacijske medicinske naprave

Povzetek: Z zahtevami po zmanjševanju velikosti in povečevanju vhodno/izhodnih (I/O) zahtev implantacijskih naprav se je, zaradi že dolgo uporabljene keramike z žico iz platine / aluminijevim oksidom v vzpodbujevalcih srca, pojavila možnost uporabe žgane platine / žgane keramike z visokotemperaturnim aluminijevim oksidom. Nov razvoj zahteva uporabo procesa spajkanja titanovega tesnilnega obroča za izdelavo hermetičnega sistema s številnimi I/O prehodi za uporabo v nevrostimulatorjih. Delo ovrednoti razvoj žganih Pt/aluminijev oksid materialov skupaj s povezavami in veznimi strukturami visoke gostote. Še neobjavljene reakcije so raziskane skupaj s katalitično reakcijo organskih vezi, redukcijo Al oksida s platino v PtAl3 in znižanjem točke taljenja platine 300°C pod njegovo točko talitve neodvisno od velikosti delcev (nano do mikro velikosti) ali morfologije delcev. Atmosfera žganja (zrak, vodik, inertni plin), profil žganja in aditivi za kontroliranje termičnega raztezanja so obravnavani v smislu minimiziranja eksotermične reakcije z uporabo visokotemperaturne difrakcije x-žarkov, FIB nano strojno obdelavo, SEM skupaj z EDS analizo in TEM za vsako od opisanih okoliščin.

Ključne besede: pretok visoke gostote, HTCC, žgana platina/aluminijev oksid

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1. Introduction

Platinum metallization is finding increases applications in implantable systems, especially in neural stimulator. Platinum has a long history as a conductor wire feedthrough materials for low input/output devices like pacemakers and implantable defibrillators or as feedthroughs and leads [1, 2] in higher output neural stimulator devices such as implantable cochlea, retinal implants and deep brain and muscle stimulators. Platinum is readily weldable and solderable, leading to easily second level assembly processes for microelectronic modules within the hermetic enclosure or attachment of micro lead structures. With the development of medical devices such as the implantable retina, the possibility of having I/O structures in the 300 to 1000 range is becoming a possibility. Additionally, neurological implants often require a much smaller device configuration footprint to minimize physiological interaction and external, RF coupled power coupling configurations to minimize the size of the device. As an example, the housing for one implantable retina under development is small enough to be attached to the eye to allow the microelectronics assembly to rotate with

eye movement. The combined demands of small size, high I/O count, hermeticity and biocompatibility has pushed the development of a new class of cofired platinum / alumina feedthrough, leads [3] and microcircuit structures with I/Os in excess of 40/mm^2, gold brazed to a titanium housing which is welded to provide a hermetic enclosure capable of meeting the hermeticity requirement of 1 X 10^{-9} cc He/sec/atm , currently found in FDA approved medical devices [4, 5].

The bonding mechanism between platinum and alumina is believed to be by solid-state ceramic-metal diffusion bonding. However, despite different reaction mechanisms and products that have already been reported for the Pt/Al_2O_3 system, the exact bonding mechanism between them is not clear [6-9].

The glass phase of the alumina-glass ceramic plays several important roles in ceramic/metal bonding. It anchors the metal to the ceramic by a combination of mechanical interlocking and chemical bonding and ensuring the hermeticity by filling the porosity in the metal [10]. During sintering of the substrate, a silica based liquid is formed between the alumina grains and penetrates the porous, fine-grained metallization layers. This occurs because of the capillary pressure difference between the porous alumina layer and the porous metal layer due to the smaller grain size of the latter and difference between their surface tension [11]. The contact angle of glass/ceramic is almost constant over the range of temperature and is about 30°. However, with refrectory metals such as Mo and W, the contact angle of the glass/ metal interface decreases with increasing firing temperature in a hydrogen atmosphere [10-12]. The contact angle of glass/platinum does not change uniformly with temperature. It decreases with increasing the temperature up to about 1150° C and then increases. This change of behavior can be due to the change of surface properties of platinum with temperature [13]. This change of behavior can change the effect of the glass in metal/ ceramic binding.

Recently, Lu et al. [14] and Suppel et al. [15] showed that the strength of direct bonding Pt/Al_2O_3 depends basically on the crystal orientation of platinum and alumina. When the orientation is suitable for semi-coherency, the interface has a strong driving force to adopt direct metal-ceramic bonding; when the orientation is not suitable for coherency, then a weaker metal-glass-ceramic bond is favored since the covalent bonds in the glass and alumina are more conducive to mutual bonding.

In the current paper, the effect of glass migration mechanism and effect of the via diameter are studied initially, then the evaluation of the pt/alumina reation and effect of temperature on the microstructure and diffusion processes.

2. Experiments

Conventional high temperature cofired ceramics (HTCC) processing was used to develop the feedthrough [16]. 92% ceramic alumina tape (AdTech Ceramics Co.) and two different platinum powder, a spray dried and sintered Pt black platinum (Heraeus Inc. PM-100-10) and a spherical Pt (2 µm) from Alfa Asar were used as the primary materials. The inks were mixed on a Hoover Color Muller parallel plate mixer. The ceramic tape was punched with a Keko PAM mechanical punch machine and punched vias were filled with platinum ink by the means of a PTC vacuum assisted bladder filler. Filled tapes were stacked, isostatically laminated and fired up to the temperature range of 1050-1550° C in different atmosphere.

Shrinkage of platinum powder and ceramic alumina tape was measured by the Horizontal optical dilatometer Misura® ODLT. TA Q600 SDT machine was used to measure the colorimetric behavior of the platinum in high temperature. JEOL JSM-6330F FE/SEM was used to capture the secondary electron image of the samples. Siemens x-ray system with MoKa (λ = 0.71073Å) radiation was used to measure the crystal structure of the samples. High temperature *in-situ* X-ray diffraction experimnts were conducted on the beam line B-2 (λ = 0.485946Å) of the Cornell High Energy Synchrotron Source (CHESS). Diffracted x-rays were collected between Bragg angles of 2θ=5° and 2θ=25° using a MAR3450 imaging detector.

3. Results and Discussion

3.1. Effect of Heating Rate

Figure 1 showed the densification behavior of nano platinum and alumina tape with temperature with the heating rate of 5°C/min up to the temperature 1500 °C.

As it can be seen in about 1500 C the density of nano platinum increased about 35%, while alumina's was increased only about 17%. The high difference in densification and sintering kinetics of platinum and alumina could create defect like cracks and camber in the final multilayer assembly. However, densification behavior of the platinum and ceramic could be controlled by the heating rate. Basically higher densification can achieve by lowering the heating rate [17].

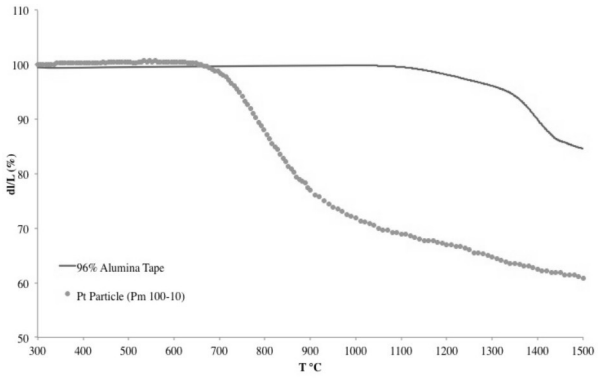

Figure 1: The nonisothermal densification behavior of platinum powder and alumina tape.

SEM images of feedthrough assembly fired in four different heating rates are showed in figure 2 and a summary of their densification results are also showed in table 1. Each measurement in the table 1 is the average of the 5 – 10 platinum via in one sample.

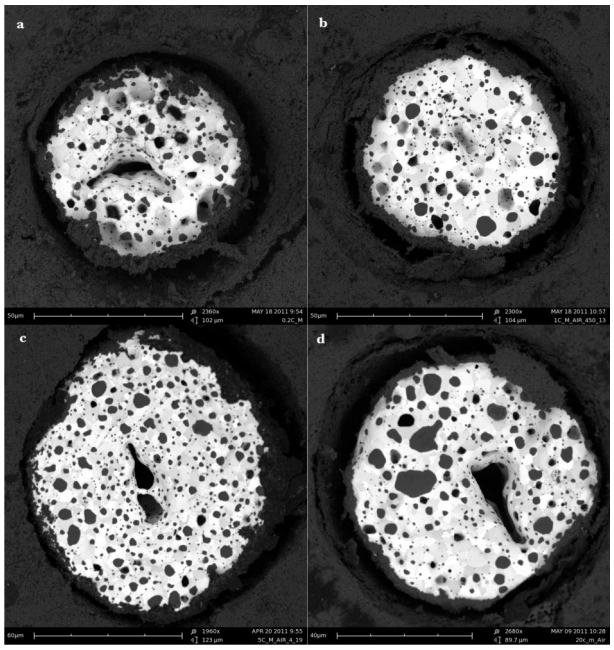

Figure 2: Backscatter SEM image of the platinum via fired in different heating rate. a) 0.2 °C/min, b) 1 °C/min, c) 5 °C/min and d) 20 °C/min.

As it can be seen in the pictures all of the four samples showed delamination of metal from ceramic and camber generation. Still, the results in table 1 showed that the minimum difference between platinum and alumina archived with the heating rate around 5 °C/min.

Table 1: Densification behavior of platinum and alumina in different heating rate.

Heating rate (°C/min)	Platinum (μm)	Alumina (μm)	Difference (μm)
0.2	64.068	86.891	22.822
1	66.287	87.707	21.42
5	68.36	82.37	14.01
20	69.775	88.043	18.268

Diameter of platinum via metallization is decreased by decreasing the heating, while we cannot see such behavior for alumina. Decreasing the heating rate increases the shrinkage of the alumina. On the other hand the interaction of platinum and alumina can increase the adhesion force between them. The strong metal support interaction that was observed several times in the platinum supported catalyst, could describe this interaction. Hwang et. al. [18] and Luo et. al. [19] showed that platinum aluminate (i.e. $Pt_xAl_yO_z$) structure could be formed in the process of sintering Pt/Alumina mixture; in addition to that low heating rate can increase the diffusion of platinum to alumina and alumina to platinum and increase their physical adhesion. In result of such interaction, platinum tries to pull in alumina with itself. However the interaction force is not enough, which makes ceramic to tear apart in the interface area as it can be seen in the figure 2.

It should be noted, that the hole which can be seen in almost all of the samples could be attributed to the formation of volatile platinum oxide which is usually formed in temperatures above 650 °C [20].

3.2. Glass migration beahviour

As shown previously, camber developed in the via and the platinum delaminated from the ceramic wall due to the difference in densification behavior of metal and ceramic tape In the sintering process of alumina-glass ceramic, the melting of glass enhances the sintering of alumina at lower temperatures due to liquid phase sintering. The flux of glass from the alumina to refractory metals increases the addhison of the metal/ceramic joint. In contrast to refractory metals, in the Pt/glass system, due to the complex surface tension behavior, increasing the temperature increases the flow of glass at first but the decrease in the Pt/glass surface tension decreases the flow and causes the seperation of the glass from the Pt as shown in figure 2.

Point 3 in figure 3 shows the average composition of the via. It is mostly occupied with platinum and has aluminum, carbon and oxygen as impurity. Presence of carbon could be attributed to an incomplete burn-out

process. Aluminum and oxygen could be from the diffusion of alumina in the platinum in high temperature. However, the presence of all three elements could also be due environmental contamination and experimental error.

The elemental analyses of point 1 and 2 indicated the presence of Si, Mg and Ca in addition to Pt, Al, C and O. This elemental composition implies the formation of the glass on the surface of platinum via. Glass particles usually have the flake-like structure with the average size of 10-20 μm, but the glass particles shown in figure 3 have spherical shape with size of 5 μm. This indicates the melting of glass at high temperatures. At high temperatures, melted glass failed to wet the platinum and floated to the surface of the via, and solidified into the spherical shape in the cooling process. In the cool down process, the temperature of the surface of platinum is less than the bulk. This temperature gradient could differentiate the glass/metal surface tension and produces capillary force to push the molten glass out of the metal. This mechanism can explain the formation of glass on the top surface of platinum via.

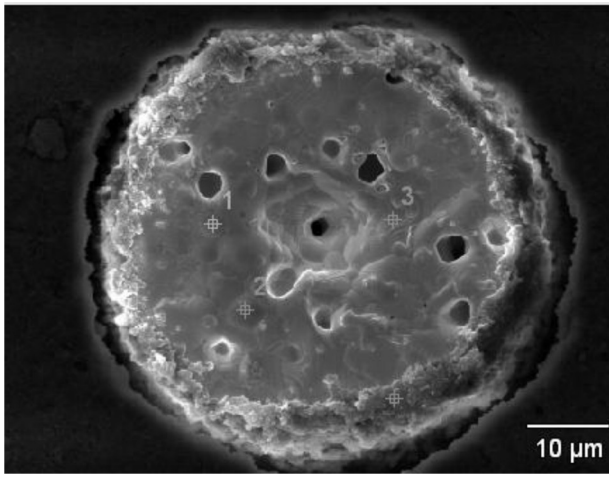

Figure 3: Backscatter image of Platinum Feedthrough fired in Air

3.3. Via diameter

Similar to glass particles, metal oxide materials, such as alumina powder, which are used to decrease the shrinkage of the ink, could also migrate to the surface of the via due to the capillary force. This migration increases by increasing the aspect ratio of the via. Via diameter could control the migration of the light oxide material to the surface since increasing the via diameter decreases aspect ratio. Results of the application of 20% volume fraction of Al_2O_3 in the platinum ink, for the vias with different diameters fired in air atmosphere, are shown in figure 4.

As depicted in the figure 4, increasing the via diameter decreases the migration of the oxide to the surface. The surface of the 100 μm via diameter completely covered with recrystized ceramic. The EDS results show that the ceramic has the composition of the alumina.

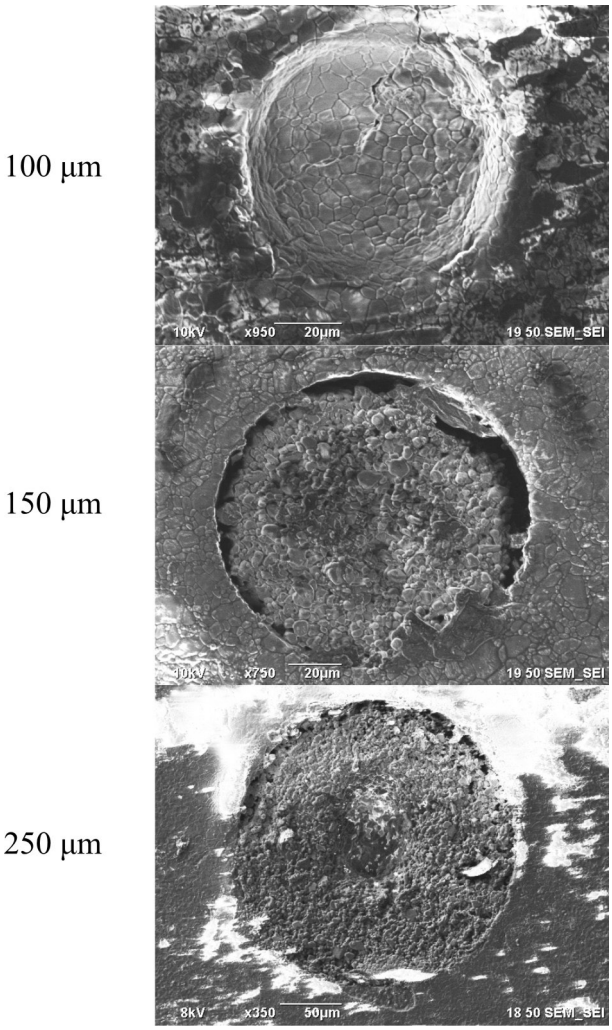

Figure 4: Microstructures of Platinum via with, 20% Al_2O_3 in different via size

3.4. Effect of Atmosphere

Atmosphere condition is the most important factor to control the interface of platinum and alumina. In addition to that replacing air with neutral atmosphere, such as argon, could eliminate evaporation of platinum. SEM image of sample fired in the air and Ar atmosphere with heating rate of 5 °C/min are showed in figure 5.

As it can be seen that platinum densified in Ar more than air. This behavior of platinum could be attributed to the decomposition of platinum dioxide and desorption of oxygen from the bulk of platinum. This oxygen layer is adsorbed on the layer of platinum below the surface and it is almost inert in temperature below 800

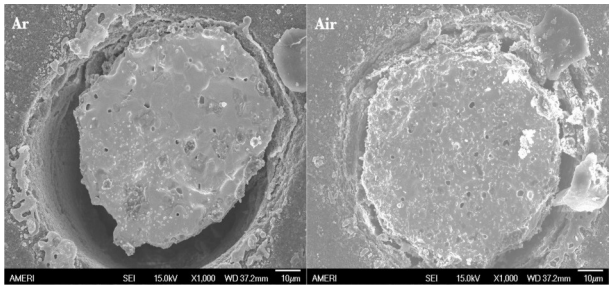

Figure 5: Secondary electron SEM image of feedthrough fired in air and argon atmosphere.

°C [21]. The results of DSC experiments of sintering of platinum are shown in figure 6. The colorimetric experiment followed the same condition was used in firing of feedthrough. As it can be seen, the exothermic reaction of decomposition occurred around 1000 – 1200°C. Heat generation in neutral atmosphere is more than air, which could result in local super heating in sample and increase the shrinkage of the platinum.

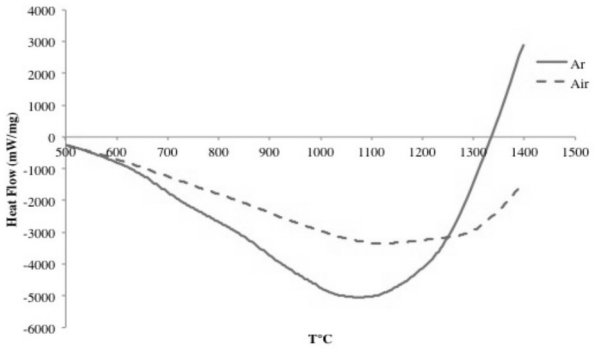

Figure 6: DSC analyses of the platinum powder in air and argon.

3.5. Pt/Alumina reaction

The reaction of Pt/Al_2O_3 could be enhanced in a reduced atmosphere due to Pt-Al alloy formation [15, 22]. Hydrogen can reduce alumina and the major product of this reaction is Pt_3Al. The X-ray diffraction pattern

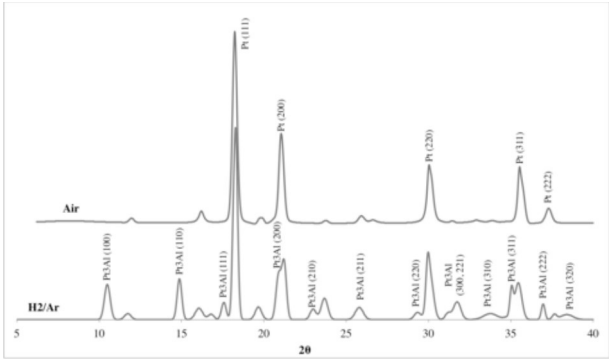

Figure 7: X-ray diffraction pattern of Platinum/ Alumina combination heated in two different environments in 1400°C

of reaction of the 25% Vol. powder mixture of alumina/platinum in the hydrogen and air atmosphere in 1400°C is shown in figure 7.

As is seen form figure 7, the first peak of Pt_3Al appered in 2θ=10.40° in a hydrogen atmosphere, which indicates the reation between platinum and alumina. To better understand the reaction of Pt/Alumina, a high temperature X-ray diffraction technique was utilized, using carbon as reducing agent. The result of the reaction of Pt/Alumina in the prescence of carbon is shown in figure 8.

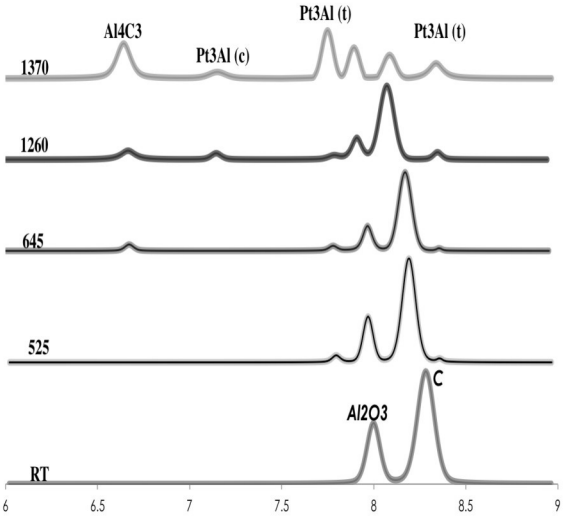

Figure 8: High temperature diffraction data of Pt/Alumian system

The first two peaks in 2θ=7.77° and 8.35° appeared at the temperature about 530 °C. Those peaks are related to tetragonal Ir_3Si structure. Pt_3Al in temperatures lower than 400 °C exhibit a tetragonal crystal structure [23]. By increasing the temperature up to 650 °C, another peak appeared at 2θ=6.65°. That peak is attributed to the formation of rombohedral structure of aluminum carbide [24]. In the temperature above 1250 °C, a new peak appeared at 2θ=7.15°, which corresponds to the cubic Pt_3Al structure. The Ir_3Si tetragonal structure could transform to cubic Cu_3Al easily. The Pt_3Al was formed with the tetragonal structure at low temperature and the crystal structure transformed to the cubic structure at high temperatures. From the results showed in figure 7, the equilibrium structure of the Pt_3Al is cubic, with sufficient amount of time and hydrogen concentration, the tetragonal structure transforms completely to the cubic structure.

A common firing profile consists of heating and soaking in temperature below 450 °C to burn-out the organic. During this portion of the profile, polymeric binder produces a fair amount carbon, which could

evaporate from the sample. Different burn-out process could change the carbon evaporation behavior and subsequently change the possibility of the reaction in platinum/carbon/alumina system. The results of firing of platinum feedthrough with two different burn-out process is shown in figure 9.

It could be seen that the thickness of ceramic layer around platinum decreases with increasing the time of burn-out process. Fast burn-out process could decrease the evaporation of the carbon from the system and increase the reaction between platinum and alumina.

TEM image of the platinum/alumina interface showed in figure 10. The intfrace shows strong bonding between platinum and alumina, which is due to the rduction reaction of alumina nd formation of $PtAl_3$.

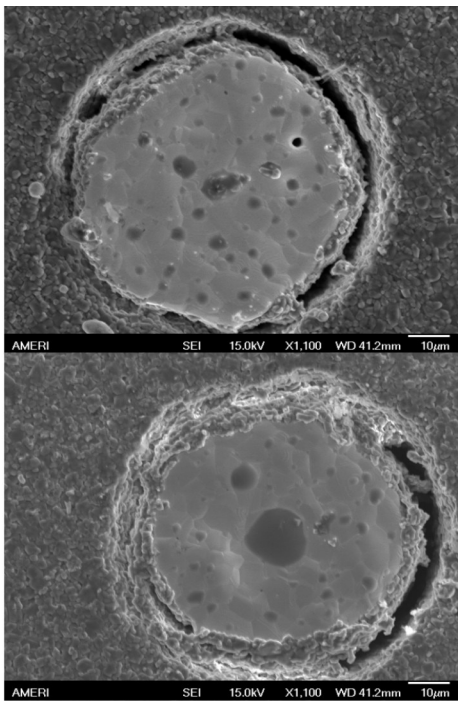

Figure 9: SEM image of the platinum particle via fired in different burn-out prcosee

3.6. Firing temperature

In addition to the reaction products, temperature could control the final microstructure of the feedthrough sample as well. The effect of firing temperature on the properties of the Pt-100-10 nano platinum powder feedthrough in a reduced atmosphere is given in figures 11. After the burn-out process, each feedthrough was heated up to the desired temperature at the heating rate of 10 °C/min, maintained at that temperature for an hour and was rapidly cooled down. Firing was done in the H_2 – Ar (25-75) atmosphere.

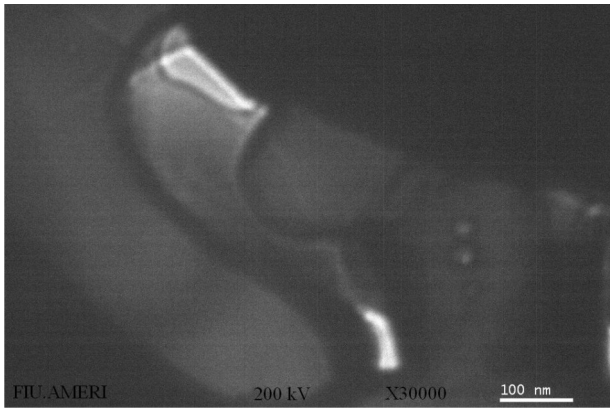

Figure 10: TEM image of the interface between platinum via nd ceramic particle.

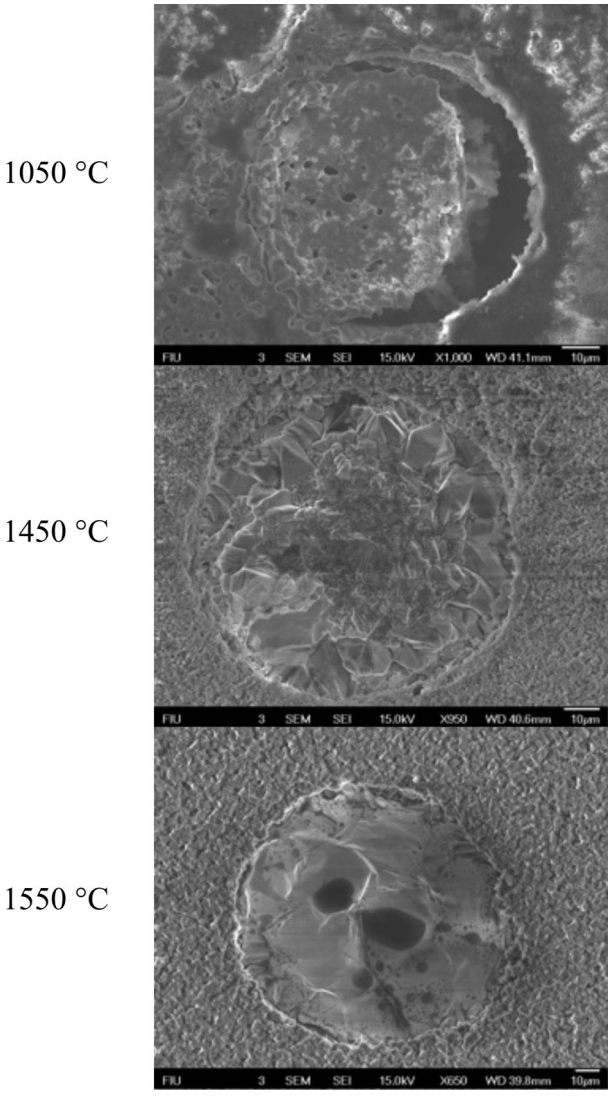

Figure 11: SEM image of the platinum particle via fired in different temperature

The behavior of platinum powders starts to change after the temperature reaches 1350 °C. In the range of 1350 – 1550 °C, by increasing the temperature, platinum starts

to expand and fill the via. In the temperature range of 1350 – 1450 °C, a coating of alumina covers the surface. In this temperature range, platinum dissolves some of the ceramic from the sidewalls and the alumina is transported to the top surface. At 1450 °C, the alumina covers the surface completely with a large grain structure. At the highest temperature, platinum completely dissolves the ceramic and there is no sign of it on the surface. A large droplet shape ceramic also appears on top of the platinum via, but it does not have a grain structure. The ceramic structure is more like a solidified glass, which was confirmed from the EDS results.

The results of the microsized platinum powder feedthrough fired in 1550 °C in the same condition is showed in figure 12 for comparison.

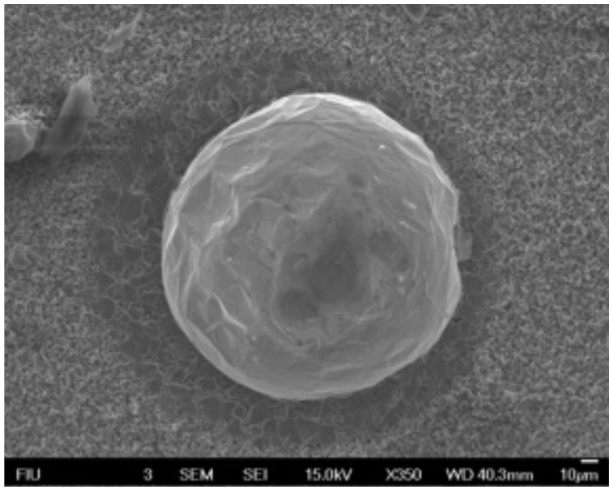

Figure 12: SEM image of the micron-sized platinum particle feedthrough via fired in 1550°C

By increasing the platinum particle size, platinum starts to expand and ultimately makes a dome-like structure above the via. As is seen from figure 12, the ceramic around the platinum disappears and creates a recessed structure. At 1550 °C, the platinum via is 150 μm in diameter and the recessed area around the platinum increased up to 200 μm. Platinum dissolves alumina and glass from the surrounding area and expands. By the introduction of alumina and glass particles into platinum, platinum starts to expand up to 150 μm and creates a dome structure. Platinum powder dissolves alumina at high temperatures, however, different final microstructure of the two platinum particles could suggest that smaller size particles wicks the alumina and push it to the top surface by capillary action.

Figure 13 shown the concentration gradient of different elements in platinum for the micrion-sized platinum powder via fired at 1550 °C, detremiuned by EDS analyses. It is obvious that silicon diffuse through the entire width of the via. The weight concentration of the silicon is almost constant and is about 3.5%. Pt-Si phase diagram [25] does not show any solid solution of silicon of silicon in platinum. Therefore, the 3.5% concentration of silicon in platinum suggests the reaction of SiO_2 with platinum and the creation of a Pt_3Si phase. Silicate compounds, which are used mostly as the glass phase in HTCC ceramic tape formulation, could be the source of SiO_2 for reaction. Aluminum is foundin the first few microns from the interface. The concentration of aluminum in platinum is about 1.5 Wt.%, which is equal to the solubility of aluminum into platinum [26]. After about 8 microns from the interface, the concentration of the alumina dropped drastically and it is almost negligible. This behavior could suggest that silicon prevents diffusion of aluminum into platinum.

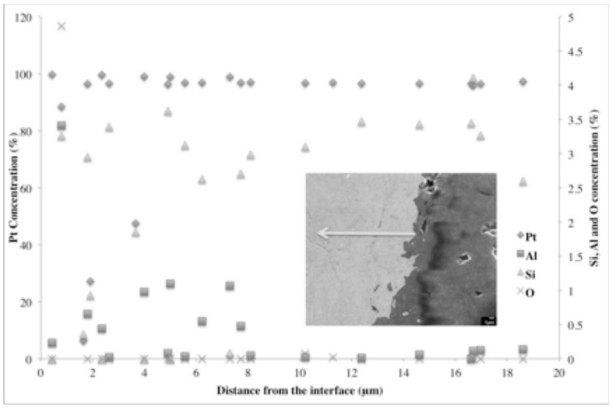

Figure 13: Concentrations gradient of different elements in platinum for the micron-sized platinum powder. Feedthrough fired in the H_2 – Ar (25-75) atmosphere at 1550 °C

To minimize the effect of silicon on the diffusion of the aluminum, the 99.9% HTCC ceramic tape were use to develop a feedthrough and the concentration gradient of different elements are shown in figure 14.

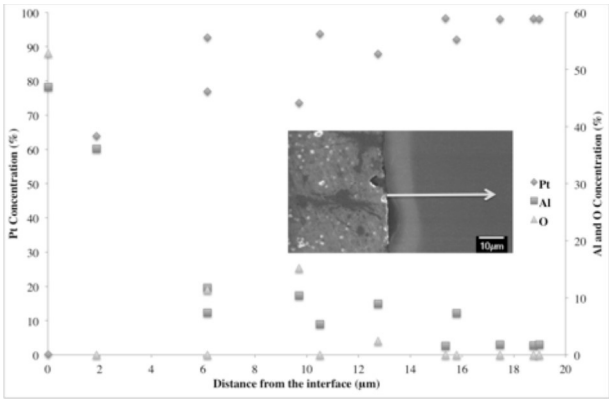

Figure 14: Concentration gradient of different element in platinum for the micron-sized platinum powder and 99.9% HTCC ceramic tape. Feedthrough fired in the H_2 – Ar (25-75) atmosphere at 1550 °C

It is clear that the concentration of the aluminum gradually decrease, however the final concentration is about 5 Wt%, which is more than the solubility limit of the aluminum in platinum. This behavior promotes the formation of Pt_3Al phase. The concentration of oxygen shown in Figure 7 and 8 is almost zero in all cases, which is due to the reduction of alumina and silica in the reduced atmosphere. It should be noted that the EDS does not show any trace of platinum in alumina, which indicates that diffusion only occursfrom the alumina side to the platinum.

At high temperatures, platinum absorbs the ceramic grains and glass from the sidewalls and that expands the structure. Platinum dissolves silicon and cannot maintain the solubility of the aluminum, thus the aluminum moves to the surface as alumina. Based on the temperature, alumina could recrystallize to large grains or small grain size. However, at temperatures above 1500 °C, it dissolves into the platinum and remains as a reaction product. This could be due to the formation of a Pt-Al compound as a second phase in the platinum-alumina interface.

4. Conclusion

The results of firing of feedthrough assembly in different conditions showed that glass migration mechanism is complicated in Pt/Al_2O_3 system and glass is not very useful in improving the metal/ceramic joint. Introducing some metal oxide powder as a shrinkage control agent to the formulation of the platinum ink also could improve the sintering kinetics of platinum and improve the properties of feedthrough assembly. However, the oxide material could float to the surface of the via. Decreasing the via diameter increases the migration of the ceramic powder to the top surface of the via. Mixture of hydrogen and argon is the best possible environment for firing the feedthrough. In addition to that, pt/alumina mixture starts to react in temperature as low as 550 °C. The tetragonal Pt_3Al forms in low temperature and transforms to the stable cubic structure in high temperature. In reduced atmospheres, the firing temperature could be adjusted by the size of platinum particle. Larger platinum particles could be fired in temperatures lower than 1550 °C.

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References

1. Brummer S, Turner M. Electrochemical considerations for safe electrical stimulation of the nervous system with platinum electrodes. Biomedical Engineering, IEEE Transactions on. 1977(1):59-63.
2. Schuettler M, editor. Electrochemical properties of platinum electrodes in vitro: comparison of six different surface qualities2007: IEEE.
3. Suaning G, Lavoie P, Forrester J, Armitage T, Lovell N, editors. Microelectronic retinal prosthesis: III. A new method for fabrication of high-density hermetic feedthroughs2006: IEEE.
4. Guenther T, Dodds C, Lovell N, Suaning G, editors. Chip-scale hermetic feedthroughs for implantable bionics2011: IEEE.
5. Karbasi A, Kinzy Jones W, editors. Evaluation of co-fired platinum/alumina high density feedthrough for implantable neurostimulator applications. 18th European Microelectronics and Packaging Conference (EMPC); 2011 12-15 Sept. 2011; Brighton, UK: IEEE.
6. Becher PF, Murday JS. Thick film adherence fracture energy: influence of alumina substrates. Journal of Materials Science. 1977;12(6):1088-94.
7. Allen RV, Borbidge WE. Solid state metal-ceramic bonding of platinum to alumina. Journal of Materials Science 1983;18:2835-43.
8. Panfilov P, Bochegov A, Yermakov A. The Transition Layer in Platinum-Alumina. Platinum Metals Review. 2004;48(2):47-55.
9. Ivanova AS, Slavinskaya EM, Gulyaev RV, Zaikovskii VI, Stonkus ûê, Danilova IG, et al. Metal-support interactions in Pt/Al2O3 and Pd/Al2O3 catalysts for CO oxidation. Applied Catalysis B: Environmental. 2010;97(1-2):57-71.
10. Lazaroff JE, Ownby PD, Weirauch DA. Wetting in an Electronic Packaging Ceramic System: 1, Wetting of Tungsten by Glass in Controlled Oxygen Partial Pressure Atmospheres. Journal of the American Ceramic Society. 1995;78(3):539-44.
11. Twentyman ME. High-temperature metallizing, Part 1. The mechanism of glass migration in the production of metal-ceramic seals. Journal of Materials Science. 1975;10(5):765-76.

12. Behrens G, Heuer AH. Microstructural Characterization of Cofired Tungsten-Metallized High-Alumina Electronic Substrates. Journal of the American Ceramic Society. 1992;75(10):2815-24.
13. Selman GL, Spender MR, Darling AS. The Wetting of Platinum and Its Alloys By Glass I, Contact Angle Determination Between Glass and Pure Platinum. Platinum Metals Review. 1965;9(3):92-9.
14. Lu H, Svehla MJ, Skalsky M, Kong C, Sorrell CC. Pt-Al2O3 interfacial bonding in implantable hermetic feedthroughs: Morphology and orientation. Journal of Biomedical Materials Research Part B: Applied Biomaterials. 2011:n/a-n/a.
15. Suppel KP, Forrester JS, Suaning GJ, Kisi EH. A Study of the Platinum/Alumina Interface. Advances in Science and Technology. 2006;45:1417-22.
16. Gangqiang W, Folk EC, Barlow F, Elshabini A. Fabrication of microvias for multilayer LTCC substrates. Electronics Packaging Manufacturing, IEEE Transactions on. 2006;29(1):32-41.
17. Bernard-Granger G, Guizard C, Addad A. Sintering of an ultra pure α-alumina powder: I. Densification, grain growth and sintering path. Journal of Materials Science. 2007;42(15):6316-24.
18. Hwang CP, Yeh CT. Platinum-oxide species formed by oxidation of platinum crystallites supported on alumina. Journal of Molecular Catalysis A: Chemical. 1996;112(2):295-302.
19. Luo M-F, Ten M-H, Wang C-C, Lin W-R, Ho C-Y, Chang B-W, et al. Temperature-Dependent Oxidation of Pt Nanoclusters on a Thin Film of Al2O3 on NiAl(100). The Journal of Physical Chemistry C. 2009;113(28):12419-26.
20. Jehn H. High temperature behaviour of platinum group metals in oxidizing atmospheres. Journal of the Less Common Metals. 1984;100(Journal Article):321-39.
21. Gland JL, Sexton BA, Fisher GB. Oxygen interactions with the Pt(111) surface. Surface Science. 1980;95(2-3):587-602.
22. Klomp J. Ceramic-metal reactions and their effect on the interface microstructure. Ceramic microstructures '86: Role of interfaces; Proceedings of the International Materials Symposium; 28-31 July 1986; Berkeley, CA; UNITED STATES1987. p. 307-17.
23. Chauke HR, Minisini B, Drautz R, Nguyen-Manh D, Ngoepe PE, Pettifor DG. Theoretical investigation of the Pt3Al ground state. Intermetallics. 2010;18(4):417-21.
24. Foster LM, Long G, Hunter MS. Reactions Between Aluminum Oxide and Carbon The Al2O3—Al4C3 Phase Diagram. Journal of the American Ceramic Society. 1956;39(1):1-11.
25. Tanner LE, Okamoto H. The Pt-Si (Platinum-Silicon) system. Journal of Phase Equilibria. 1991;12(5):571-4.
26. McAlister A, Kahan D. The Al-Pt (Aluminum-Platinum) system. Journal of Phase Equilibria. 1986;7(1):47-51.

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