

## ALUMINA-FeNi42 FOIL AND AgCuTiIn ALLOY JOINTS AND THEIR HIGH THERMAL SHOCK RESISTANCE

Władysław K. Włosiński<sup>1,2)</sup>

Wiesława Olesińska<sup>1)</sup>

Study on technological and microstructural conditions for brazing of alumina ceramics and FeNi42 alloy, by means of filler alloys contain active elements, are presented. Diffusion of titanium into alumina ceramics within the area of intermediate layer between ceramics and Ag72,5Cu19,5Ti3In5 solder, was specially investigated. Effect of titanium on thermal stability of ceramic-to-metal joint was experimentally verified. Vacuum tight ceramic-to-metal joint having high mechanical strength was produced as a result of this study.

### 1. INTRODUCTION

It is well recognized that application of active braze alloys in the technology of ceramic-to-metal joints give rise to better mechanical strength of joints. However vacuum tightness of joint is decreased in comparison with those obtained with MoMn metallization [1]. It is assumed that this situation is caused by the following phenomena:

- lesser wettability of ceramic surface by active alloys,
- mechanical stresses within interlayer,
- microcracks within interlayer.

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1) INSTITUTE OF ELECTRONIC MATERIALS TECHNOLOGY,  
Wólczyńska 133, 01-919 Warszawa, Poland.

2) WARSAW TECHNICAL UNIVERSITY,  
Narbuta 85, 02-524 Warszawa, Poland

All this phenomena may be related to the high chemical activity of titanium. Wettability of alumina by solders containing active elements, which has been measured by wetting angles in brazing - had been investigated in temperature 1173K (900°C) by 60min under pressure of 0,8 mPa ( $6 \times 10^{-6}$  Tr) and partial pressure of  $O_2$   $10^{-11}$  Pa. Wetting angles were as follow:

1. Ag Cu28 (Cusil) -  $136^\circ$ ,
2. Ag62,25 Cu27 Ti1,25 In9,5 (Incusil) -  $15^\circ$ ,
3. Ag65 Cu33,5 Ti1,5 (Cusil ABA) -  $13^\circ$ ,
4. Ag68,8 Cu26,7 Ti4,5 (Ticusil) -  $6^\circ$  [2].

By increase of Ti content in alloy from 1.5 to 4.5% weight percent, we obtain better spreading of solder on the ceramics surface, but liquidus temperature of solder Ag Cu28 increase. Simultaneously with increase of titanium content, increase the probability of the chemical reaction between titanium and alumina. This is confirmed by several authors where during application of AgCuTi braze in the temperature of 1173K, nonstoichiometric  $TiO_x$ , Al and CuTi alloy were found [2] and during the diffusion bonding of alumina and Ti (1273K,  $10^{-4}$  Tr vacuum, 3.1 MPa bonding pressure) intermetallic compounds such as  $Ti_3Al$ ,  $Ti_2Al$  and  $TiAl$  have also been found [3].

His assumed that occurrence of intermetallic compounds within adjacent layer of alumina would negatively affect on physical features of joints, specially for vacuum tightness and thermal shock resistance.

A conclusion may be drawn that for better results, the brazing alumina ceramics through active solders, should be carried out with lower titanium content solders, which simultaneously have a lower melting point. Wettability of ceramics by solder may be improved by metallization with Ni or Cu. Also, metallic layer may limit titanium migration into ceramics. To verify the assumptions stated above a study was carried out on the properties of joints and intermediate layers produced during brazing by Ag72,5 Cu19,5 Ti3 In5 solder, two kinds of ceramics, uncovered and covered by Ni and Cu layers.

## 2. EXPERIMENTAL

### 2.1. Materials

Alumina ceramics with 97,5%  $\text{Al}_2\text{O}_3$  content was used. A different states of ceramics surface were prepared:

- 1) annealed at 1273 K ( $1000^\circ\text{C}$ ) in air,
- 2) etched and activated by  $\text{PdCl}_2$  and subsequent covered chemically by Ni layer,
- 3) covered by Cu layer by sintering and further reduction of  $\text{CuO}$  at nitrogen atmosphere with 40 ppm oxygen content. Sintering temperatures were about 1343, 1348, 1353K ( $1070, 1075, 1080^\circ\text{C}$ ).

Metallic parts of joints were made of FeNi42 alloy. Brazing was carried out by means of Degussa solder with Ag72,5 Cu19,5 Ti3 In5 composition.

### 2.2. Brazing conditions

Brazing of joints by active solder were carried out in the vacuum furnace to temperatures 1173K and 1193K ( $900$  and  $920^\circ\text{C}$ ).

The vacuum in the furnace was as high as  $1,33 \times 10^{-3} \text{Pa}$  ( $1 \times 10^{-5} \text{Tor}$ ).

Flat ring samples of alumina, solder and FeNi42 alloy were prepared and sandwich was made supported by graphite chasis. Through orifice a metal rod made of FeNi42 alloy was placed vertically (layout shown at Fig. 1).

### 2.3. Sample preparation for micro-structural investigations

Active solder Ag72,5Cu19,5Ti3In5 has been fused on alumina samples prepared as mentioned in 2.1 chapter, at the temperature 1193K ( $920^\circ$ ) according to the course presented at Fig. 1.

Samples were annealed by 3 hours.

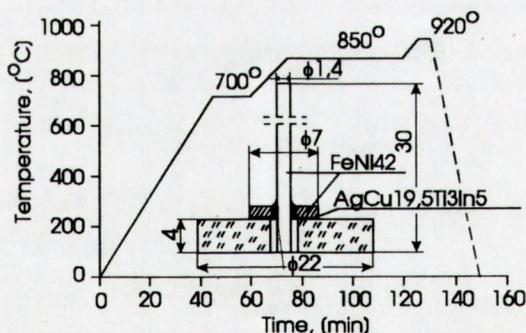


Fig. 1  
Assembling for testing and course of temperature for process brazing.

### 3. INVESTIGATIONS

#### 3.1. Tensile strength and vacuum tightness testing

Tensile strength was measured using Heckert testing machine. Machine grips were attached axially to the ceramics ring and Fe Ni42 alloy rod, in such a manner, that tensile force acts perpendicularly to the surface of joint. Strain rate was 3 mm/min.

Vacuum tightness of joints were examined with helium leak detector. Helium leakage limit is assumed to be about  $1,33 \times 10^{-8} \text{ Pam}^3 \text{ s}^{-1}$ .

Results are given at the Table 1. Joints brazed with Ag72,5 Cu19,5 Ti3 In5 solder at temperature of 1173K (900°C) had a low tensile strength - only 30% of joints was vacuum tight. Increase of temperature up to 1193K (920°C) caused about threefold tensile strength increase and number of vacuum tight joints grow to 80% of total population. Joints brazed with alumina covered by Ni and Cu layers were 100% vacuum-tight. Mechanical strength of joints brazed with Cu covered alumina was close to those brazed with pure alumina. The lowest strength has been observed for Ni covered alumina ceramics.

Table 1. Tensile strength and vacuum tightness results.

No	Brazing technology	Percent of the vacuum tight joints	Average tensile strength <sup>x)</sup> $\pm \sigma_{n-1}$ [N/cm <sup>2</sup> ]
1	Alumina-solder-FeNi42 Brazing temp. 1173K	30	443,3 ± 98,2 W <sub>2</sub> = 22,1%
2	Alumina-solder-FeNi42 Brazing temp. 1193K	80	1136,6 ± 157,6 W <sub>2</sub> = 14,3%
3	Alumina-solder-FeNi42 Brazing temp. 1193K	100	912,4 ± 136,8 W <sub>2</sub> = 15%
4	Alumina-solder-FeNi42 Brazing temp. 1193K	100	1144,6 ± 112 W <sub>2</sub> = 9,8%

x) results from 10 samples

### 3.2. Thermal shock resistance

The thermal shock resistance was evaluated within following temperature ranges:

- a) 218-428K (-55+155<sup>0</sup>C) in air; two cycles with three thermal shocks at chosen temperature range and, two cycles with ten shocks at chosen temperature (26 shocks total).

After thermal cycles all joints have shown helium leakage above safety limit,  $1,33 \times 10^{-8} \text{ Pam}^3 \text{ s}^{-1}$ .

- b) 293-973-293K (20-700-20<sup>0</sup>C) in nitrogen; temperature of samples was raised up to 973K by 15 minuts, then kept constant by next 15 minuts and after that dropped suddenly to the room temperature. The vacuum thightness of joints was set up as evaluation criteria. This was checked after every shock. The highest resistance for the thermal shock conditions within the temperature range 293-973-293K, have shown joints brazed with ceramics covered by sintered CuO.

An oxidation of metallic parts was a reason for deterioration of vacuum tightness for nearly 70% of total population of joints being tested. This happened after eight cycles; after six cycles 30% of population was out of order. Thermal shock resistance for joints brazed both with uncovered and Ni-layer covered ceramics was quite comparable - 60% of population lost the vacuum tightness after third thermal shock and remaining 40% was stable over five cycles.

### 3.3. Microstructure

The investigation of microstructure of joints was carried out means of scanning electron microscope and electron microprobe. Both polished surfaces of joints show similar distribution of elements (Fig. 2, 3 and 4). In both cases it is possible to distinguish a metallic layer composed of Fe, Ni and Ti. For joints with ceramics covered with Ni, this layer is several times thicker in comparison to those formed on uncovered ceramics. Metallic precipitates of this same composition may be observed throughout whole layer of solder. Copper and indium atoms concentrate around Ti, Fe, Ni metallic layer covering ceramics; on the counterwise silver atoms diffuse into FeNi42 alloy.

In both cases these same directions of penetration are observed, but concentrations along them are diferent. Titanium diffuse into ceramics if Ni and Fe are present. This is cofirmed by the fact, that thickness of layer composed of Ti, Fe and Ni on Ni covered ceramics, is about three times bigger then those on uncovered ceramics. On the contrary, concentration of titanium on the uncovered

ceramics surface (Fig. 2 and 6a) is much bigger than those on Ni covered ceramics (Fig. 6b).

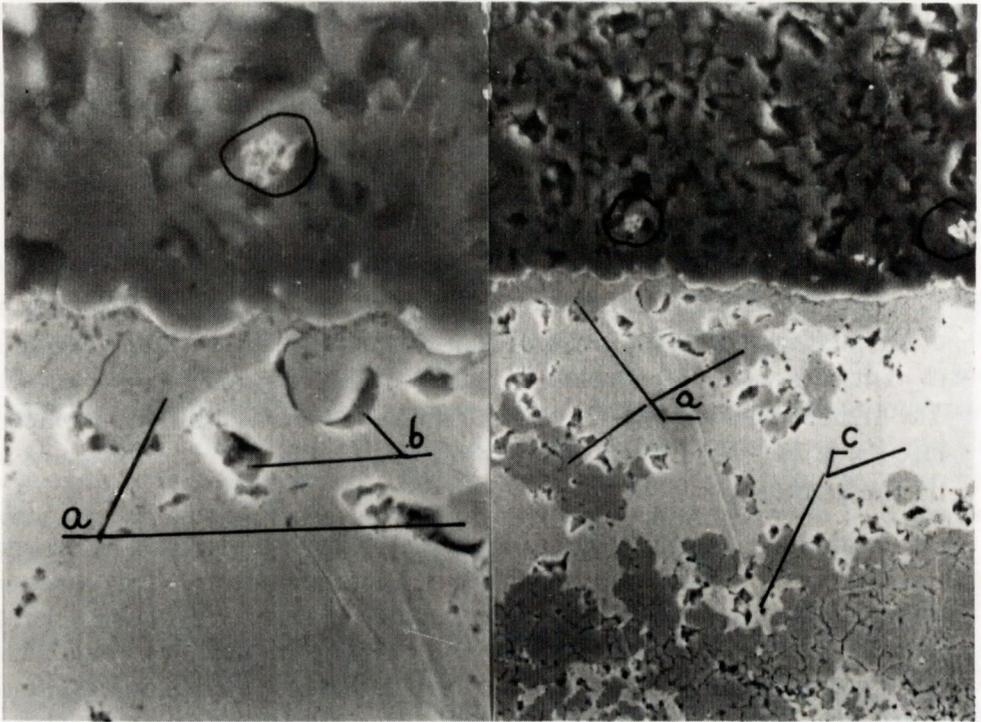


Fig. 2

Polished section of brazed alumina - solder - FeNi42 alloy SEM. 1500X, 200X.

a) Fe, Ni, Ti,    b) Cu, In,    c) Ag.

Penetration of Ag atoms to the FeNi42 alloy is also different for both cases. In the case of joint formed with Ni covered ceramics, Ag atoms concentrate near the surface at FeNi42 alloy, and then diffuse inside along grain boundaries (Fig.3). An irregular concentration of Ag atoms may be noticed within FeNi42 alloy (Fig.2) if joint is formed without metallic layer on ceramics.

Fracture surfaces and skew polished surfaces for demonstration of interlayers were exposed for observations. 90% of population of ruptured joints which were soldered with uncovered ceramics, have shown fracture surface going through ceramics, 1-2mm a way from soldered layers. For remaining 10% of population fracture surfaces were situated on ceramics-metal interface and on the

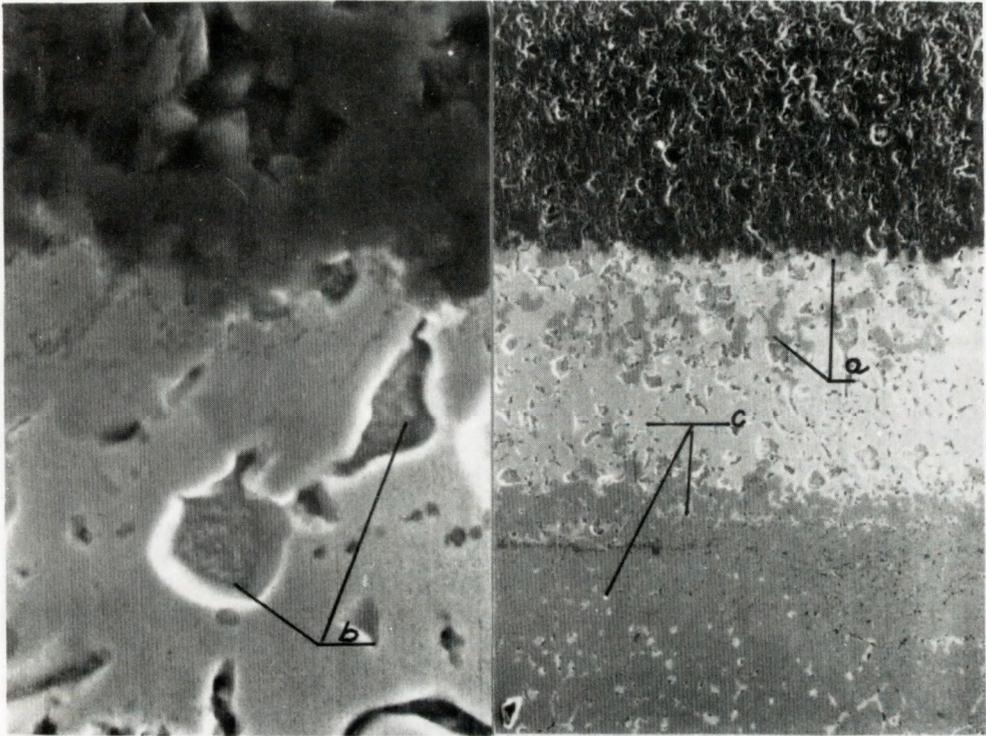


Fig. 3

Polished section of brazed alumina/Ni - solder - FeNi42 alloy SEM. 1500X, 200X.

a) Fe, Ni, Ti, b) Cu, In, c) Ag.

fracture ceramic surface one can observe a metallic precipitate (Fig.4 i 5), around which microcracks are quite visible.

It is interesting to note, that these microcracks, did not destroy the joint during technological process of its formation. Chemical analysis of precipitate area, carried out by electron microprobe have shown presence of Ti,Fe,Ni.

In the case of joints soldered with Ni and Cu covered ceramics, fracture surfaces were also situated exactly on the ceramics-metal interface and no metallic precipitates were found so far.

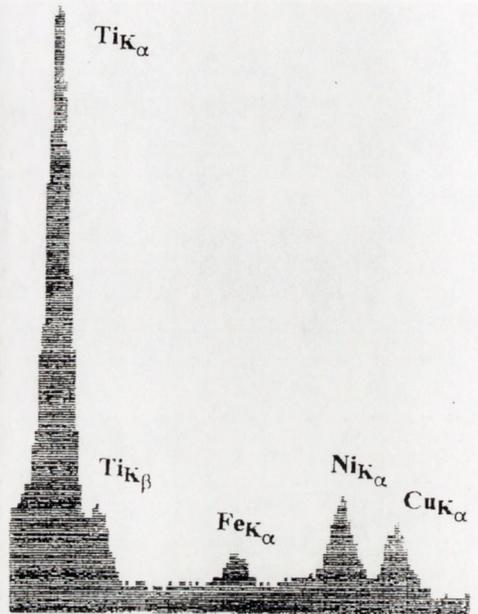


Fig. 4

Microstructure of ceramics side of fractured joint. Microcracks of ceramics and metallic residue of area of 35x30  $\mu\text{m}$  are visible. OPTON SEM, 1000X.

Fig. 5

Chemical composition of area presented on Fig. 4. Electron microprobe.

Surface distribution of titanium within the joints presented on Figures 2 and 3 is shown on Fig.6.

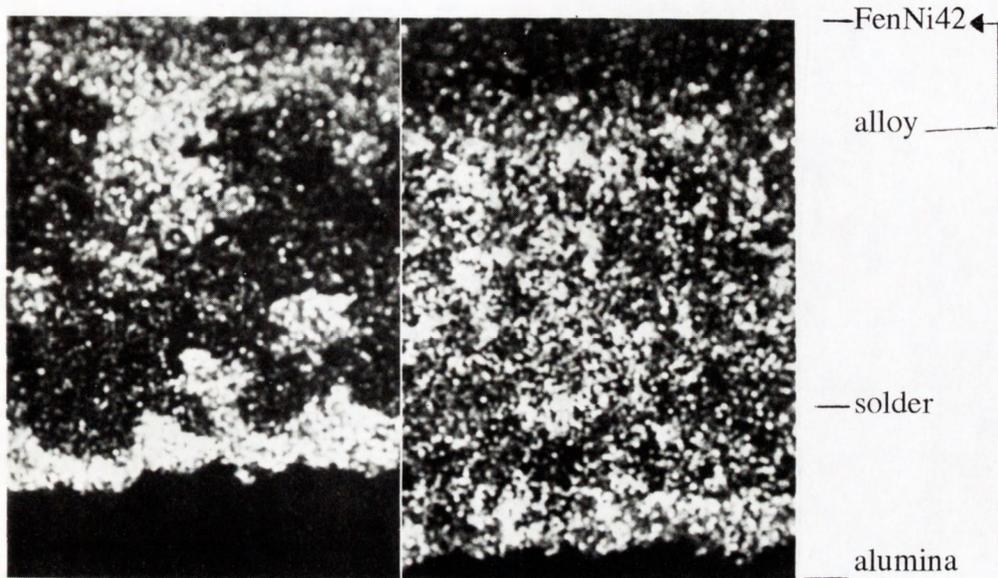


Fig. 6

- Surface distribution of titanium within the joints  
a) alumina - Ag72, 5Cu19, 5Ti3In5 - FeNi42,  
b) alumina/Ni - Ag72, 5Cu19, 5Ti3In5 - FeNi42.

In the case of joints formed on uncovered ceramics, titanium penetrates to the surface of ceramics, forming thin layer in there. Application of Ni on the surface of ceramics (Fig.6b) causes the homogenous distribution of titanium through layer of solder.

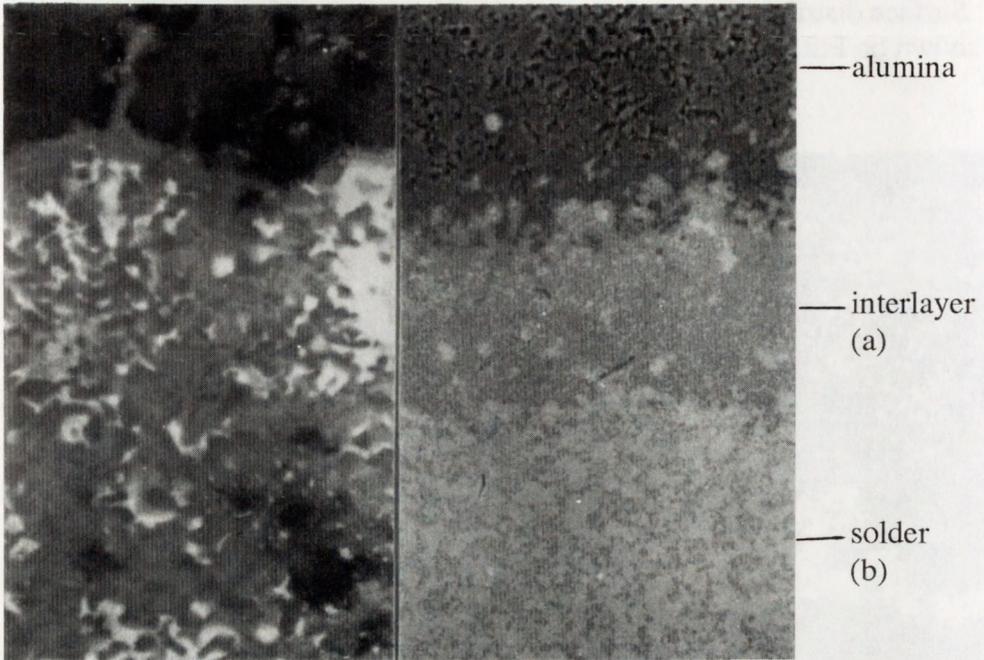


Fig. 7

Polished section of brazed alumina/Cu - solder - FeNi42 alloy. SEM 1500X, 200X.

a) Cu, Ti, Fe, Al

b) Ag, In, Ni.

Quite different microstructure is observed for joints brazed with Cu covered ceramics (Fig.7,8). One can distinguish an interlayer between ceramics and solder, which consist of Ti, Cu and Al mainly, and only traced amount of Fe. Within solder Ag, In, Ni and small amounts of Ti are homogenously distributed.

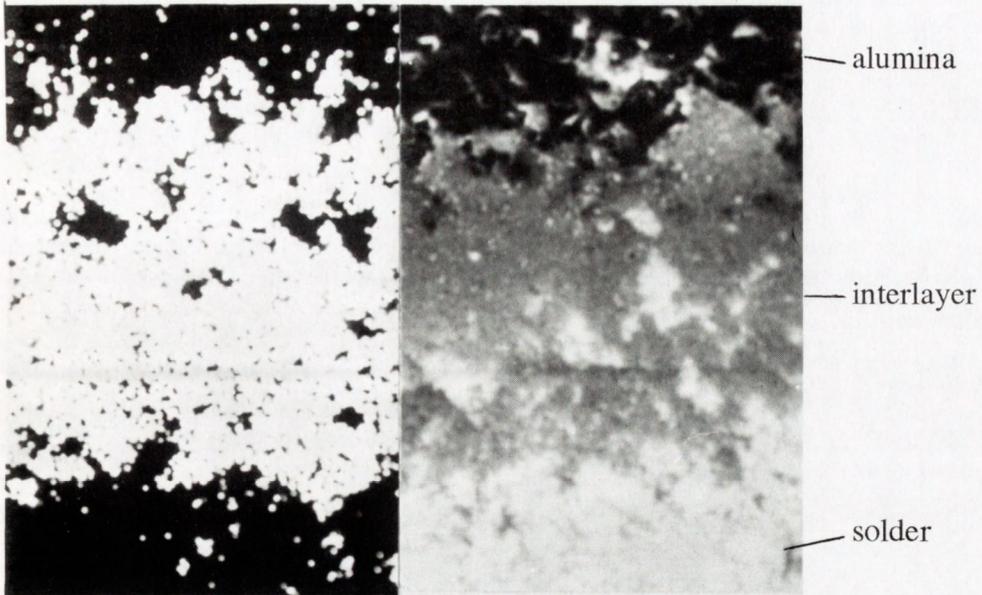


Fig. 8

Surface distribution of titanium and copper within the joints presented on Fig. 7.

## CONCLUSIONS

1. During active brazing of alumina ceramics with Ag72,5 Cu19,5 Ti3 In5 solder, migration of components may be described as follows:
  - » Fe, Ni and Ti penetrate through layer of solder to ceramics surface and form there homogenous interlayer several microns thick.
  - » Ag and Ti atoms diffuse into FeNi42 alloy.
2. Properties of joints produced by active brazing depend of composition and microstructure of interlayer. Homogenous interlayer having remarkable thickness was formed by Al, Cu, Ti and Fe.
3. Mechanical strength of joints increase with concentration of titanium on the ceramic surface.

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