

**THE STUDY INTO THE CERAMIC-TO-METAL SOLDERED JOINTS  
INTERFACE FOR Al<sub>2</sub>O<sub>3</sub> AND SiO<sub>2</sub> MATERIALS**

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**Abstract**

*The conditions of joining a ceramic-metal configuration by active metal soldering using tin-based (SnTi3) alloys are presented. Active metal (Ti) was alloyed in a low concentration of 3 weight percent. The joining process was carried out in a vacuum (10<sup>-2</sup> Pa) at a peak temperature of 860 °C with a short holding period (t = 9 min). The ceramic-metal soldered interface was examined using optical microscopy, scanning and transmission electron microscopy (SEM, TEM). The natures of the interfacial reactions and the reaction products were identified using X-ray diffraction (XRD). The thickness of reaction layers and X-ray maps of the same region were measured.*

**Key words**

*active soldering, oxide ceramics, reaction layers, intermetallic compounds, fracture surface*

**Introduction**

Combined engineering materials have been recently used in a wide range of technical applications. Their advantage is that their extraordinary properties can be used in demanding technical applications in a controlled or targeted manner. Ceramic and metal combined in the form of a soldered joint [2] are doubtlessly one of such combinations. From the perspective of joint production, the critical factor is the selection of suitable solder. The first condition for the production of a high-quality joint is the substrate's wettability with molten solder. The wettability of a ceramic material with common solders is difficult without having the substrate sufficiently coated with metal. Another solution is to use a solder with a small amount of an active element (Ti, Zr or Hf) that has a strong affinity to the ceramic substrate's anions. Inside molten solder, an active element migrates to the interface between the solder

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and the ceramic substrate where it generates intermediary compounds, thus catalyzing oxidation or reduction reactions [3]. By adding an active element into soft solder, the metal content of which offsets the differences in thermal expansivity of the parts being united, metals can be joined with various non-metallic materials such as quartz ( $\text{SiO}_2$ ), ceramics, carbon or the like [4-6]. Soldering ceramic materials by using an active solder alloy is therefore economically advantageous. Various methods of preparing ductile active solders, primarily the option to produce a solder of a desired composition during the soldering process, substantially extend the range of applicability of said technology.

The study analyzed the interface of a soldered joint between ceramic and solder attained by uniting a ceramic-metal combination using the active SnTi3 soft solder. The issue in question is whether the use of the SnTi3 solder is suitable in the context of soldering parameters optimization.

### Experiment Preparation

The combination of a soldered part studied in this study consisted of a ceramic substrate, the active SnTi3 solder, and a metallic pad. A metallic pad made of CrNi steel (18/8) 5 mm in thickness was used for the experiment, as well as two types of ceramic substrates: Corundum  $\text{Al}_2\text{O}_3$  and melted  $\text{SiO}_2$ . These materials were joined by using active Sn-based solder with an addition of 3 wt pct of active Ti (Fig. 1). The active SnTi3 solder was prepared by the Slovak Academy of Sciences' Institute of Physics, Bratislava, using the method of rapid cooling of the melt into the form of a tape 30  $\mu\text{m}$  in thickness. To produce a joint of the required thickness, four SnTi3 solder layers were used.

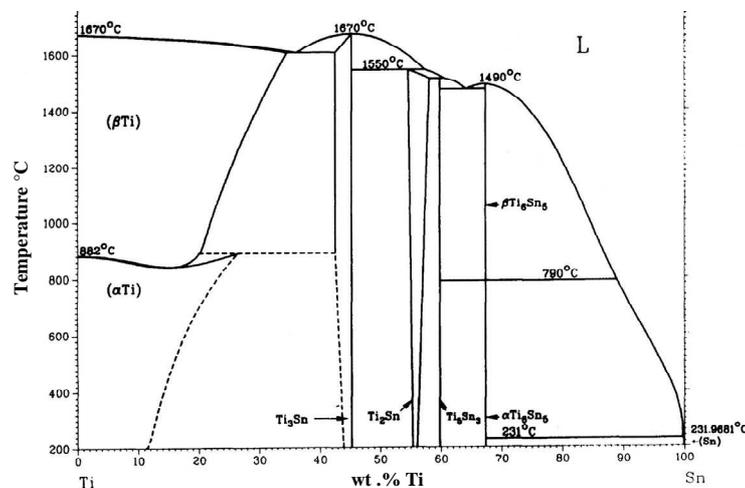


Fig. 1 Ti – Sn binary diagram

### Soldering Design and Performance

All samples intended for the study of the interface of soldered joints between ceramic-metal combined materials were prepared by soldering in a vacuum brazing furnace (TESLA PZ 803). Before being actually soldered, the joint components' surface layers were gently abraded and cleaned using an ultrasonic acetone bath. Shown in Table 1, the soldering process

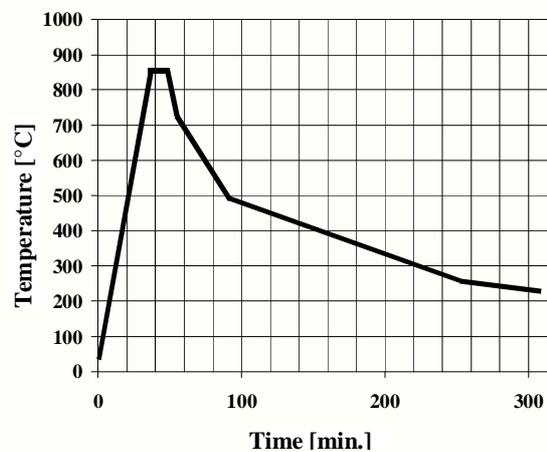
parameters were designed with respect to the wettability and diffusion capacity of the solder's active element at the given temperature.

#### VACUUM SOLDERING PARAMETERS AS DESIGNED

Table 1

Soldering temperature	860 °C
Working vacuum	10 <sup>-2</sup> Pa
Dwell time	9 min

The temperature cycle shown in Figure 2 consisted of heating to a working temperature of 860 °C and a holding period of 9 minutes at that temperature. The process of cooling went on in a furnace at a medium cooling speed of 2 °C/s. All samples intended for the experimental analysis were prepared within a single cycle at the above-stated parameters.



*Fig. 2 Temperature Regime Record*

#### ***Metallographic Sample Preparation***

For the purposes of metallographic analysis by a light microscope, the soldered joints were cut crosswise into slices 15 mm in thickness and then sealed into a copper handle.

Using a light microscope and a CCD camera with an output to an Impor Pro2 image analyzer, the ceramic-metal interface's reaction layer was examined under both polished and corroded state conditions. The polishing of the surface was done using a chemical polishing with Struers OP-S, a commercially available suspension. The reaction layer and the solder's grain boundaries were corroded with a 3-percent solution of Nital.

#### ***Electron Microscopy and Microanalysis***

The solder-ceramic interface was analyzed using reflection electron microscopy (SEM) and transmission electron microscopy (TEM). The morphology of the transition zone and the reaction layer on corroded metallographic sections was observed using SEM TESLA BS300. The chemical microanalysis – linear profile, the surface distribution of elements, was conducted through a solder-ceramic reaction layer using the EDAX analyzer, which was a

component of the SEM JEOL JXA-840A. To supplement the study, an identification of the phases extracted from fracture surfaces by electron diffraction has been completed on TEM JEOL 200CX.

### *X-ray Diffraction Analysis*

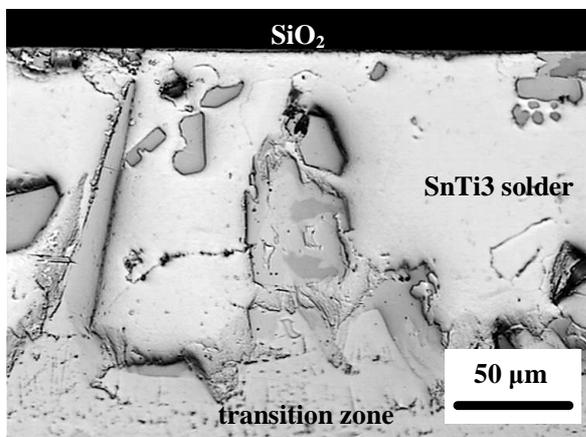
To conduct an X-ray diffraction analysis of the solder-ceramic interface, ceramic substrates of cylindrical shape with dimensions of 8.5 x 10 mm were used after their surfaces were previously wetted by molten SnTi3 active solder. After metallographic preparation, they were analyzed using an X-ray diffractometer (DRON 3M) with a goniometer operated in Bragg-Brentano geometry.

One prerequisite for a successful analysis of products in a reaction layer was polishing away a sufficient amount of the solder from the surface without further influencing the solder-substrate interface. The scanning parameters were as follows:  $\lambda_{\text{CuK}\alpha} = 0.1541 \text{ nm}$ ,  $U = 35 \text{ kV}$ ,  $I = 30 \text{ mA}$ , secondary LiF monochromator.

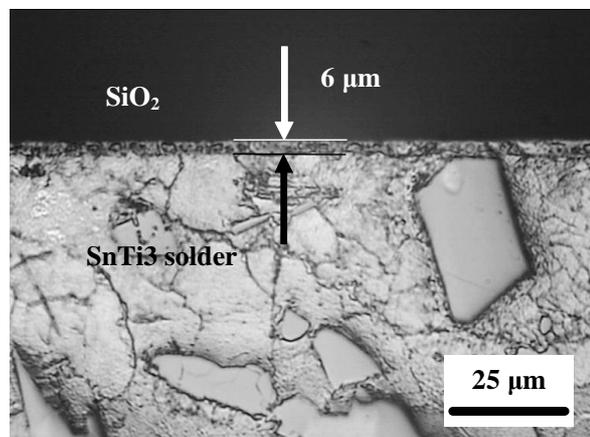
## **Experimental Results**

### *Metallographic Analysis, SEM, TEM*

Figures 3 through 6 show the interfaces of ceramic-metal soldered joints in both polished and corroded state condition. The polished interface between SiO<sub>2</sub> and solder is characteristic for its steady reaction layer; the dominant features are the intermediary phases with different morphologies (Fig. 3) that were generated in the steel-to-solder transition zone and filled the SnTi3 solder's volume. After the solder was etched, the thickness of the SiO<sub>2</sub>-solder interface's reaction layer was 6  $\mu\text{m}$  (Fig. 4).

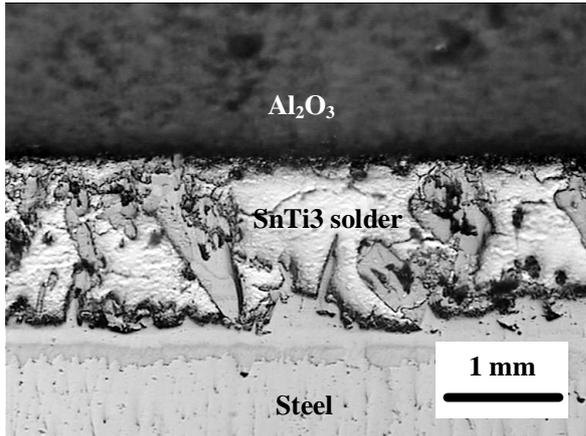


**Fig. 3** Ceramic-solder-metal composition polished interface

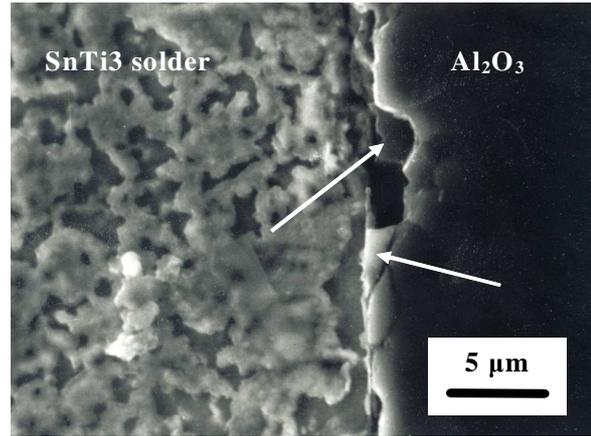


**Fig. 4** Etched SnTi3 solder with a continuous reaction layer

Figure 5 shows a polished joint between a ceramic-metal combination with a visible solder-steel transition layer and some occurrences of intermediary phases in the SnTi3 solder. The reaction layer between the solder and Al<sub>2</sub>O<sub>3</sub> was discontinuous and considerably thinner than that of the joint with SiO<sub>2</sub>. A detailed investigation into the solder-ceramic interface (SEM) showed the local concentration of the products formed by the reaction between the SnTi3 solder and Al<sub>2</sub>O<sub>3</sub> solder (in Fig. 6, these products are denoted with arrows).

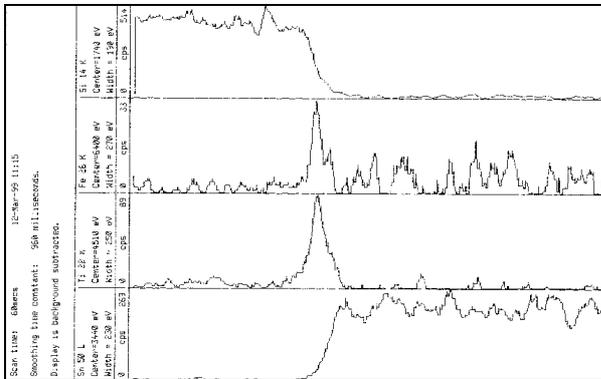


**Fig. 5** Polished ceramic solder metal composition with distinct reaction products

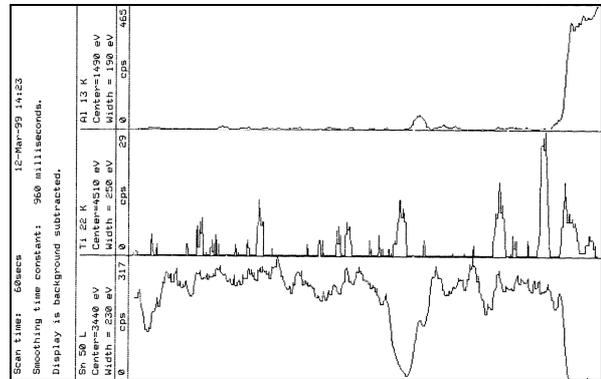


**Fig. 6** A detail of the reaction layer with the denotation of fragile phases

A linear and areal X-ray microanalysis was conducted on the  $\text{SiO}_2$ -solder interface. The results appearing in Fig. 7 show that the maximum concentrations of both Sn and the active element (Ti) are present in the  $\text{SiO}_2$ -solder interface's reaction layer. The distribution of the active element the highest concentration of which was detected in the reaction layer indicates the union of the  $\text{SiO}_2$  substrate with the active solder. Fig. 8 shows the results of an analysis made to examine the solder- $\text{Al}_2\text{O}_3$  reaction layer. The figure indicates the active element's maximum concentration at the interface between solder and  $\text{Al}_2\text{O}_3$ . As can be seen from the detailed analysis shown in Figure 6, no continuous reaction layer formation occurred at the soldering temperature of 860 °C.



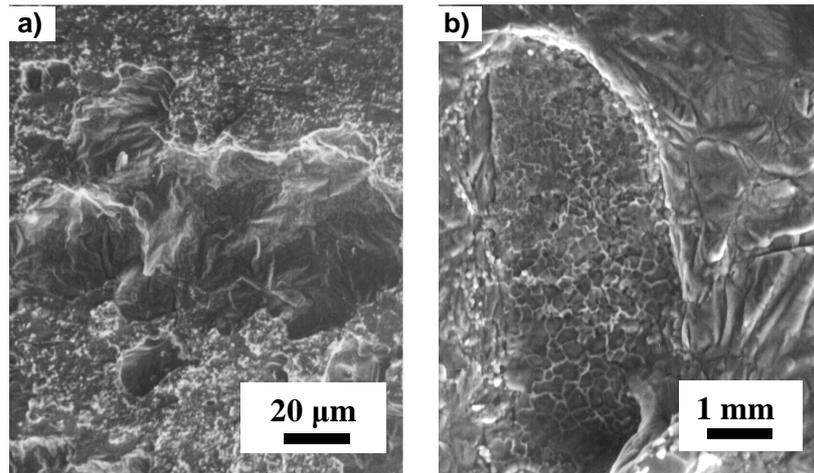
**Fig. 7** Chemical analysis through  $\text{SiO}_2$ -solder interface's reaction layer



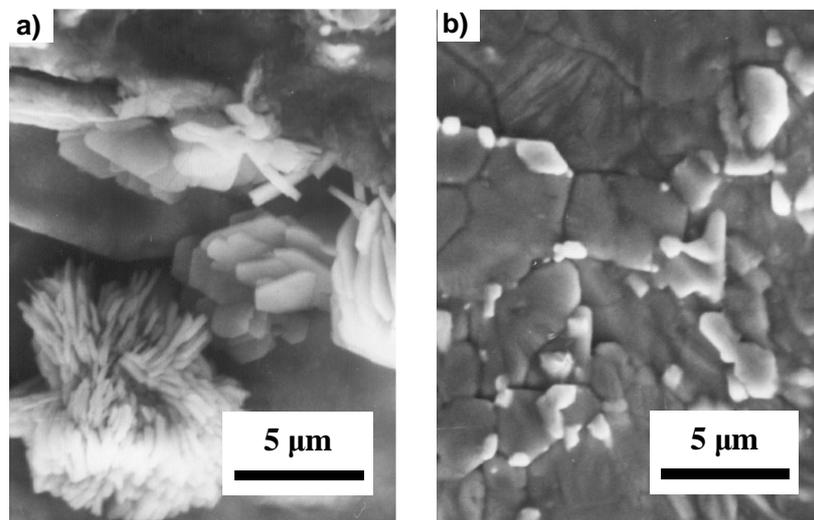
**Fig. 8** Chemical analysis through  $\text{Al}_2\text{O}_3$ -solder interface

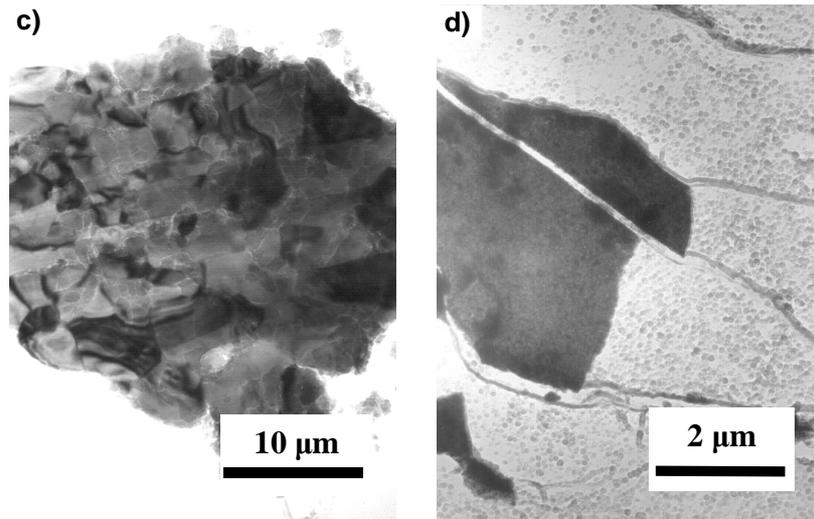
Due to shortcomings stemming from the analysis of a planar surface, the solder- $\text{Al}_2\text{O}_3$  was analyzed using fractographic investigation methods. The interface between  $\text{Al}_2\text{O}_3$  and the solder was notched, then fractured by rotary bending in a fragile condition. Figures 9a,b show a typical appearance of ruptures attained in this way. The surface of the fracture shown in Fig. 9a indicates cleavage break with a greater proportion of non-fragmented surface, which attest to the SnTi3 substrate's insufficient wetting with the solder. The proportion of the perfectly wetted area computed from the overall fragmented solder layer area on the separated portion

of the ceramic substrate only represented 20 percent. Fig. 9b shows the decohesion of a part of the Sn+Ti<sub>6</sub>Sn<sub>5</sub> eutectic in the matrix. Figure 10a shows a detailed view of the Ti<sub>6</sub>Sn<sub>5</sub> formations. Along the tin solder's grain boundaries a Ti<sub>5</sub>Sn<sub>3</sub> phase segregates. The phase identification was conducted using the method of electron diffraction after the phases had been extracted into a carbon replica. Also, foil Ti<sub>2</sub>Sn (Fig. 10c) and α-Al<sub>2</sub>O<sub>3</sub> oxidic films were identified in the same manner from the solder-Al<sub>2</sub>O<sub>3</sub> interface (Fig. 10d).



*Fig. 9a-b Morphology of fracture areas in solder- Al<sub>2</sub>O<sub>3</sub> reaction layer*





**Fig. 10 a-d** Fragmented solder- $\text{Al}_2\text{O}_3$  interface

### ***X-ray Diffraction Analysis***

A quantitative X-ray phase analyses detected modifications of Sn and Ti based phases in the interface between solder and ceramic substrate: tetragonal  $\text{Ti}_2\text{Sn}$ , hexagonal  $\text{Ti}_5\text{Sn}_3$ ,  $\text{Ti}_6\text{Sn}_5$ , and  $\text{Ti}_3\text{Sn}$ . The  $\text{Ti}_6\text{Sn}_5$  phase with a hexagonal lattice shown in Fig. 10a was part of the Sn+ $\text{Ti}_6\text{Sn}_5$  eutectic. All of the above-mentioned phases occurred in both ceramic substrates previously superficially wetted with SnTi3 solder. The solder- $\text{SiO}_2$  interface's reaction layer also contained a product of the active element's (TiO with a cubic lattice) reaction.

### **A contribution to the subject given**

The pieces of knowledge derived from the uniting of a ceramic-metal combination using the SnTi3 active solder can be summarized as follows:

- Combinations of ceramic and metallic materials can be soldered using the SnTi3 soft solder.
- The soldering temperature of 860 °C/9 min. was sufficient to fabricate the joints; in both cases, the maximum active element (Ti) concentration was detected at the solder-ceramic substrate interface.
- Using SEM, TEM and X-ray diffraction analyses, the morphology, crystalline structures and the types of the solder-ceramic reaction layer's phases were identified.
- At the solder- $\text{SiO}_2$  interface, a continuous reaction layer 6 μm in thickness was formed.
- At the solder- $\text{Al}_2\text{O}_3$  interface, no reaction layer formation occurred to the given extent, only discrete points were wetted with the active solder.
- The homogeneity of the active element's (Ti) distribution in the initial SnTi3 solder and a higher soldering temperature are the factors that determine the reactions in the  $\text{Al}_2\text{O}_3$ -solder interface.

## Conclusion

The ceramic-metal combination joints were fabricated by vacuum soldering using the soft SnTi3 active solder. The active solder was prepared from 4N purity elements with a composition of 97 wt pct Sn and 3 wt pct Ti. In molten solder, the active element (Ti) migrates towards the solder-ceramic substrate interface where, due to the effect of oxidation reaction, it forms a layer consisting of intermediary phases (i.e. forms a reaction layer). The reaction layer at the solder-ceramic substrate interface was thoroughly studied using metallographic methods of light and electron microscopy, X-ray analysis, and fractographic analysis. The transition layer between SnTi3 active solder and a metal pad (CrNi steel) was examined in another study [7].

Under the conditions of the working mode indicated in Table 1, a continuous reaction layer was formed at the solder-SiO<sub>2</sub> interface. An amorphous SiO<sub>2</sub> structure was used where no temperature-dependent changes occur. This combination's continuous reaction layer indicates perfect wetting with the SnTi3 solder.

The reaction layer at the solder-Al<sub>2</sub>O<sub>3</sub> interface was discontinuous and considerably thinner, with discrete points where occurrences of Ti<sub>5</sub>Sn<sub>3</sub> and Ti<sub>2</sub>Sn -type intermediary phases were detected. Although the distribution of the active element at the solder-Al<sub>2</sub>O<sub>3</sub> interface reached its maximum, its effect at the soldering temperature (of 860 °C) did not reach the required quality. A precise measurement of the quantity of the active element present in SnTi3 solder showed a nonhomogeneous distribution of Ti with concentrations ranging from 0.8 to 2.8 wt pct. It was proven that corundum ceramic not only requires an optimized soldering temperature, but it is also necessary that the amount of an active element in a soft Sn-based solder be increased. The above-mentioned pieces of knowledge prove that joints of diffusion quality can also be achieved at a relatively higher temperature (up to 960 °C).

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