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ULTRASONIC SOLDERING OF Cu AND Al_2O_3 CERAMICS BY USE OF Bi-La AND Bi-Ag-La SOLDERS

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Abstract. This work deals with the effect of solder alloying with a small amount of lanthanum on joint formation with metallic and ceramic substrate. The Bi-Ag – based solder with 2 wt. % lanthanum addition and Bi solder with 2 wt. % lanthanum addition were studied. Soldering was performed by a fluxless process on the air, by activation with a power ultrasound. It was found out that, during the process of ultrasonic soldering, lanthanum is distributed on the boundary, both with the copper and the ceramic substrate, which enhances the joint formation. The bond with Al2O3 ceramics is of an adhesive character, without the formation of a new contact interlayer.

Keywords: ultrasonic soldering; Bi–based solder; lanthanum; Al_2O_3 ceramic.

1. Introduction

The Bi-based solders belong to the group of solders for higher application temperatures. Soldering technology at higher application temperatures is widely spread at present and it provides irreplaceable properties to resultant products, such as excellent thermal conductivity or high reliability [2, 3]. These solders are used mainly in electronics, but also in automotive, space, aviation and power industries [4–7].

There exists exception in case of this group of solders from the ban to use lead solders until full-value substitute for Pb-Sn solders [8] will be developed. In this group of solders, exceptions are made from the ban of using the lead solders, until sufficient substitute for Pb-Sn soldiers will be developed. Several alternative alloys based on Bi, Zn and Au have been developed up to now, but none of them was capable of fully substituting the Pb5Sn a Pb10Sn solders [5].

The bismuth based solders have melting point in the required temperature range, suitable for soldering at higher working temperatures (from 250 to 400 °C). The alloy containing 2.6 wt. % Ag exerts eutectic temperature 262.5 °C [9].

The Bi-based solders offer excellent properties, such as high toughness, low elasticity modulus in shear and resistance against thermal fatigue [10]. Brittleness and lower electric conductivity, when compared to high-lead solders, belong to their disadvantages. The conductivity of Bi_{10}Ag solder is only $1.0 \cdot 10^{-6}/\Omega\,m$, that is much lower, than the conductivity of Pb5Sn ($3.5 \cdot 10^{-6}/\Omega\,m$) or SAC 307 ($8.66 \cdot 10^{-6}/\Omega\,m$) solders [11]. Therefore, this solder is alloyed with silver, from 2.5 to 11 wt. % Ag. Such solder was also used for soldering Cu and Ni, which is described in work [12]. We have also chosen to use the Bi2.5Ag and Bi11Ag solders.

Interfacial reactions between Cu substrate and Bi–Ag solder were investigated by authors [13]. Without forming intermetallic compounds (IMCs), the molten solder grooved and further penetrated along the grain boundaries (GB) of the Cu substrate. Another authors [14] studied the melting range, wetting behaviour and thermal conductivity of the Bi-Ag alloy (with Ag content between 2.6 and 12 wt. %) and compared these characteristics with Pb-based alloys.

The thermal conductivity was measured at 30 and 100 °C. The pure bismuth has the low thermal conductivity (7 W/mK at 30 °C). The addition of up to 12 wt. % Ag increases the thermal conductivity by 50 %, to 10.5 W/mK. Reactions on the boundary of Bi-solders and metallic substrates were studied in works [15–19]. Examples of another solders are in the following studies [20–28].

However, in the industrial applications, for which these solders are developed, it is also necessary to joint also non-metallic and ceramic materials. Therefore. the Bi-based solders must be alloyed with an active element, to ensure wetting of the non-metallic or ceramic substrate with the solder. An example of alloying the Bi–Ag solder is mentioned in the work [29]. Authors added 0.1 wtp of Ce into the Bi–Ag alloy. Authors changed an Ag amount in the alloy from 2.5; 5; 7.5; to 10 wt. %. Wettability of the Bi–Ag solder on the Cu substrate is fair, but it is still inferior to the Pb5Sn solder. An increase in the Ag content of solder has a positive effect on the wettability to Cu substrate. Moreover, it is clear that the lanthanides addition may promote the wetting property. The reason is related with the surface-active action of the lanthanides.

The aim of presented work was to study experimental solders type Bi11Ag2La and Bi2La, to prove the solderability of Cu and Al_2O_3 ceramics with these solders and to analyse the fabricated soldered joints.

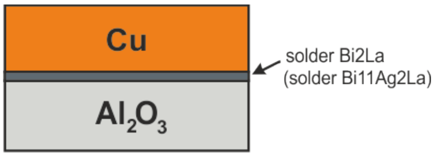

Figure 1. Soldered material combinations.

Ultrasound power	400 W
Working frequency	40 kHz
Amplitude	2 µm
Soldering temperature	290 °C
Time of ultrasonic activation	5–10 s

Table 1. Soldering parametres.

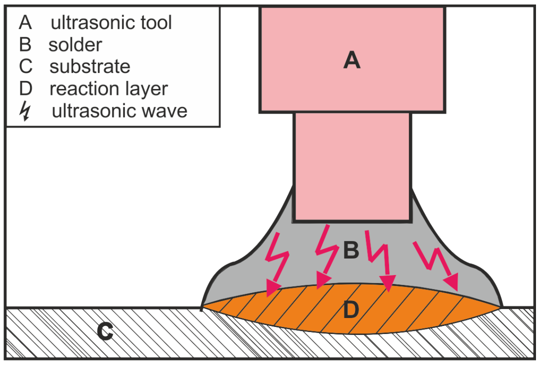

Figure 2. Ultrasonic soldering through the layer of molten solder.

2. Experimental

The Bi2La (2 wt. % La) and Bi11Ag2La (11 wt. % Ag and 2 wt. % La) solders manufactured in a cast condition in the high vacuum were used in experiments. Manufacturing procedure was as follows: the calculated charges of alloys were inserted into a graphite boat, the boat with the charge was placed into a tube of 50 mm-diameter silicon glass, the tube was then laid to vacuum resistance furnace in such a manner that it was situated in the heated zone, the tube, if needed, could be blown with an Ar gas by the use of a flange on its beginning and outlet on its end. The charge was subjected to a temperature above 900 °C, in dependence on the type of manufactured alloy.

Experimentally prepared Bi2La and Bi11Ag2La solders were used for fabrication of soldered joints. Schematic representation of joints is shown in Fig. 1. Alumina and copper substrates of 2N5, resp. 4N purity were used for joining. Substrates were in the form of rings with dimensions ∅ 15 × 2.

Soldering was performed by the use of the ultrasonic equipment type Hanuz UT2, with parameters given in table 1. Solder activation was realised via an encapsulated ultrasonic transducer consisting of a piezo-electric oscillating system and a titanium sonotrode with the end tip of diameter 3 mm. Scheme of ultrasonic soldering through the layer of molten solder is shown in Fig. 2. Soldering temperature was 20 °Cabove the liquidus temperature of the appropriate solder. Control of soldering temperature was realised via a continuous temperature measurement on the hot NiCr/NiSi plate by a thermocouple.

Soldering procedure was performed in such a manner that solder was placed on the substrate heated to a soldering temperature, and then it was heated to liquidus temperature. The molten solder was subjected to a power ultrasound for the time of 5 to 10 s without application of flux or shielding atmosphere. After ultrasound activation, the excessive layer and surface oxides were removed from the substrate surface. The copper substrate was prepared in the same way. Cu substrate was laid and centred on a ceramic substrate with the surface, on which the solder layer was deposited by ultrasound activation. In this way, the desired joint was fabricated.

Metallographic preparation of specimens from soldered joints was realised by standard metallographic procedures, used for specimen preparation. Grinding was performed by the use of SiC emery papers with 240, 320, 1200 grains/cm2 granularity. Polishing was performed with diamond suspensions with grain size 9, 6, and 3 µm. Final polishing was performed by the use of the polishing emulsion type OP-S (Struers) with 0.2 µm granularity.

Solder microstructure was studied on the light optical microscope type Neophot 32, with application of image analyser NIS-Elements, type E and by the use of the scanning electron microscopy (SEM) on JEOL 7600 F with X-ray micro-analyser type Microspec WDX-3PC for performing the qualitative and semi-quantitative chemical analysis.

DSC analysis of the Bi2La and Bi2Y solder was performed on equipment type Netzsch STA 409 C/CD in shielding Ar gas with 6N purity.

3. Experimental results

For determination of the soldering temperature and other phase transformation DSC analysis of Bi11Ag2La solder was performed. Figure 3 shows the results of the DSC analysis of the Bi11Ag2La solder at a heating rate of 1 K/min. The solder matrix, formed of a fine eutectics (Bi + 3–4 wt. % Ag), starts to melt at a temperature of 261.4 °C. Temperature of 262.8 °Ccorresponds to a temperature of an eutectic reaction in the Bi–Ag binary system. This assumption was also proved by a binary Bi–Ag diagrams of authors [**?**]. Melting of eutectics is fully completed at temperature of 263.8 °C.

From the DSC curve of the Bi2La solder at a heating rate of 1 K/min follows that the start of a melting of the Bi2La solder occurs at 270.2 °Cand the peak temperature is 271.2 °C. By the binary Bi–La diagram, the peritectic phase transformation is concerned. The peak temperature 271.5 °Ccorresponds to the melting point of the pure bismuth, whereas melting is fully completed at 271.6 °C. It can be stated that the presence of 2 wt. % La in the matrix of the Bi solder affects the melting point of the pure bismuth to a minimum extent.

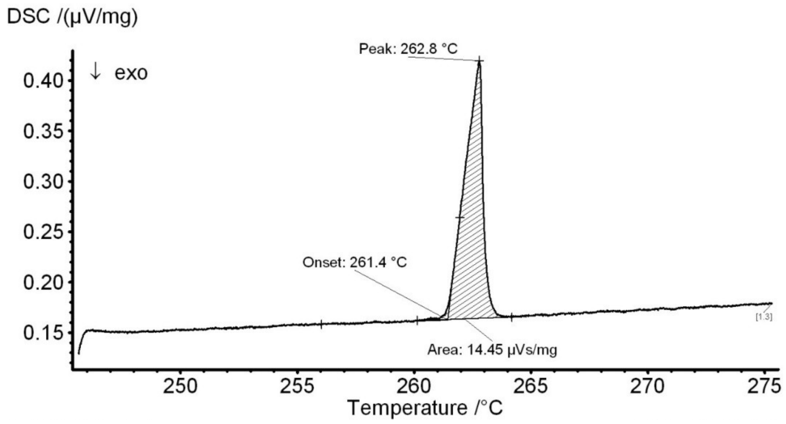

Figure 3. DSC analysis of Bi11Ag2La solder (1 K/min).

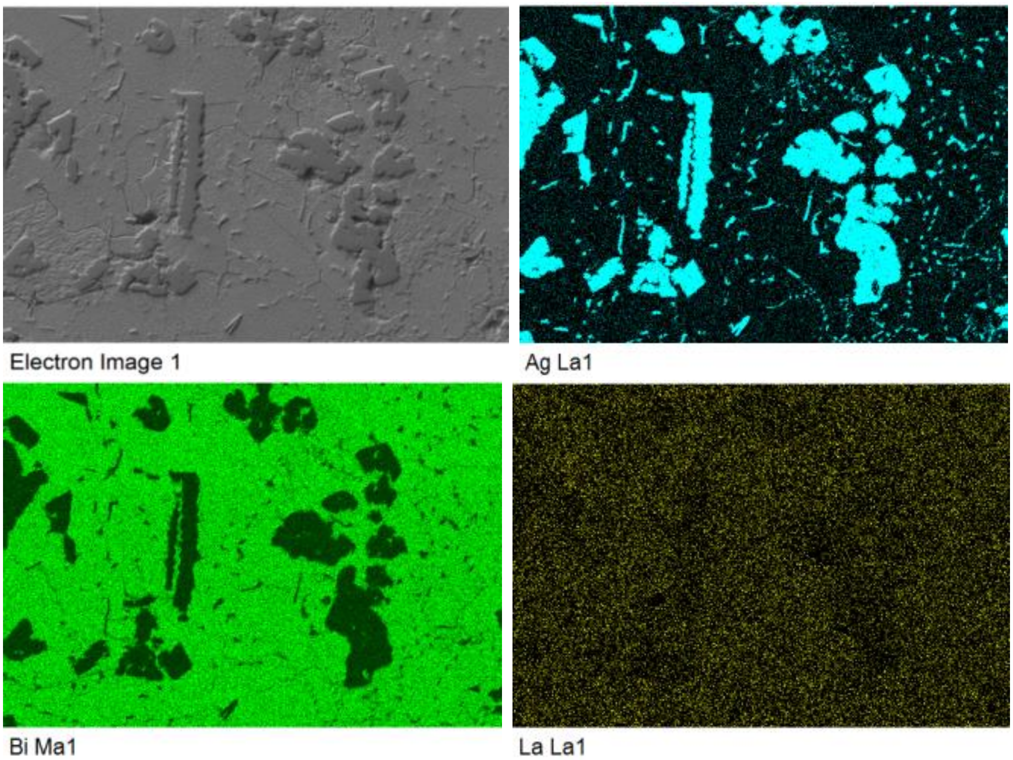

Figure 4. Planar analysis of Bi11Ag2La solder.

3.1. Microstructural analysis of Bi11Ag2La and Bi2La solders

Figure 4 shows the microstructure of the Bi11Ag2La solder. Silver crystals can be seen in the solder, since the solubility of Ag in Bi is low (up to 4.9 wt. %). Therefore, the matrix is formed of a fine eutectics (Bi + 3–4 wt. % Ag). The surroundings of Ag crystal is depleted by Ag crystals ,therefore, it is formed only of Bi, which is obvious from the planar analysis shown in Fig. 4. Lanthanum in the solder is uniformly segregated in the Bi matrix and the exceptions are only Ag phases, showing considerably less lanthanum.

Microstructural observation of the Bi2La solder has revealed that the solder consists of the Bi matrix, with uniformly distributed particles of the La phases. Smaller clusters of phases with globular character were observed in the microstructure (Fig. 5). Twins may be also seen in more detailed pictures — Fig. 5.

None La was observed in the Bi matrix of the solder (Fig. 6). Table 2 shows the documented results of the analysis of the chemical composition in the lanthanum phases (spectra 1 to 4) and in the solder matrix (spectra 5 to 9). The results of the analyses suggest that the globular phases have chemical composition, which, by binary diagram, corresponds to the composition of the LaBi2 phase.

The analysed lanthanum phases oxidize fast, owing to the oxygen presence from the air. Lanthanum generally has high affinity to oxygen. Probably, mixture of La_2O_3 and Bi_2O_3 oxides is formed. Owing to this fact, 7–8 wt. % O was identified in analyses.

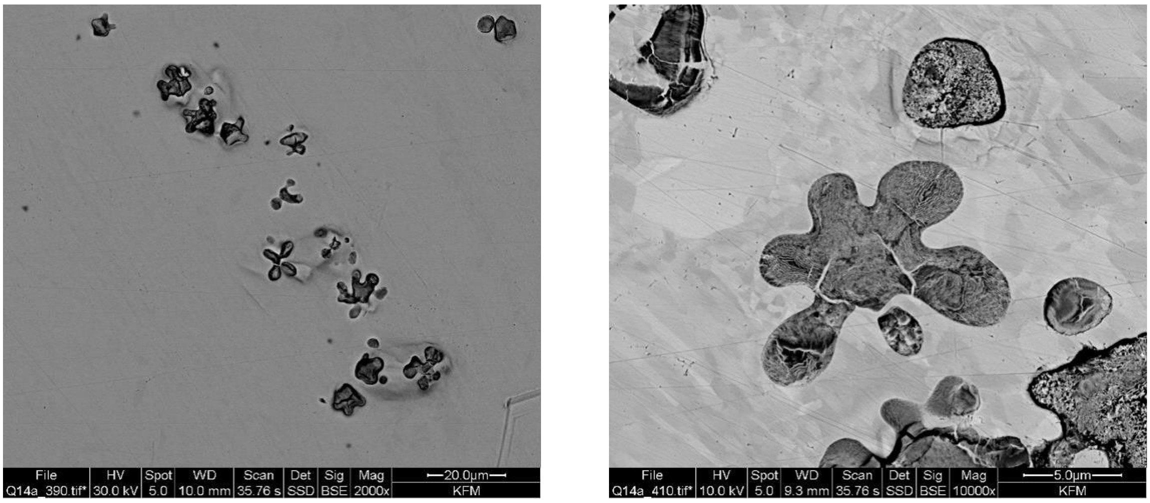

Figure 5. Microstructure of Bi2La solder with La phases and microstructure with twins.

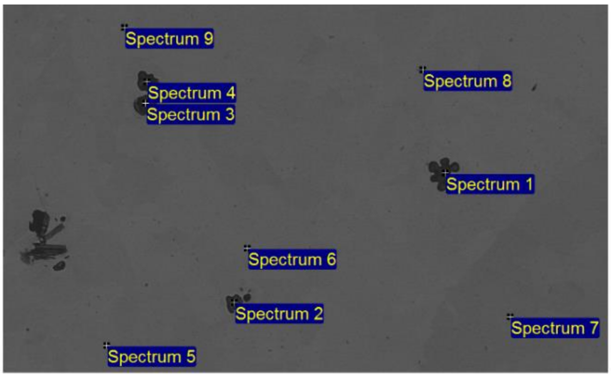

Figure 6. Analysed zones of microstructure in Bi2La solder.

Spectrum	Bi [wt. %]	La [wt. %]	O [wt. %]
1	77.27	12.26	10.47
2	66.66	22.88	10.46
3	72.08	16.93	10.99
4	82.99	10.52	6.49
5	99.05	–	0.95
6	98.74	–	1.26
7	98.81	–	1.19
8	98.87	–	1.13
9	98.97	–	1.03

Table 2. Quantitative analysis of chemical composition in selected zones of Bi2La solder.

4. Analysis of Cu/Bi2La joint

The boundary of the soldered joint between the Cu substrate and the Bi2La solder is shown in Fig. 7. Very narrow transition zone was formed on the boundary. Bismuth from the solder does not form a new intermetallic phase with Cu, nor a solid solution. From this viewpoint, the interaction between Bi and Cu is weaker. Joint formation between the copper surface and the Bi-based solder occurs due to eutectic reaction between Cu and Bi.

Lanthanum from Bi2La matrix is diffused during the UT process to boundary with Cu substrate, where it enhances the joint formation. In case of an ultrasonic soldering without the flux application, the joint is formed in a short time with the contribution of La. EDX line analysis has revealed increased concentration of La on the Cu/Bi2La boundary, which is also documented in Fig. 7.

5. Analysis of Al_2O_3/Bi11Ag2La joint

The soldered Al_2O_3/Bi11Ag2La joint is documented in Fig. 8. Increased concentration of La — Fig. 8 was observed on the joint boundary similarly as in the previous case. A new layer with increased La content, 0.5 µm in thickness, was formed. Formation of a new phase was not observed. It is supposed that an adhesive bond is formed between the solder and the ceramic substrate. La enhances the formation of the adhesive bond. Activated La element guarantees the wetting of the ceramic substrate at the activation by power ultrasound and thus contributes to the joint formation.

6. Conclusions

The aim of this work was to determine the effect of a small amount of La in the solder on the formation of the joint with the Al2O3 and Cu substrates at the application of fluxless soldering by ultrasound. The subjects of study were development solders type Bi2La and Bi11Ag2La. The following results were achieved:

(1.) The matrix of Bi11Ag2La solder is formed of bismuth, where silver crystals with a fine eutectics (Bi + 3–4 wt. % Ag) are segregated. The phases type LaBi2 occur in a globular shape in the matrix of Bi2La solder.

(2.) The DSC analysis has proved that the Bi11Ag2La solder has a melting point at 262.8 °Cof eutectics. The melting point of the Bi2La solder is at 271.2 °C,

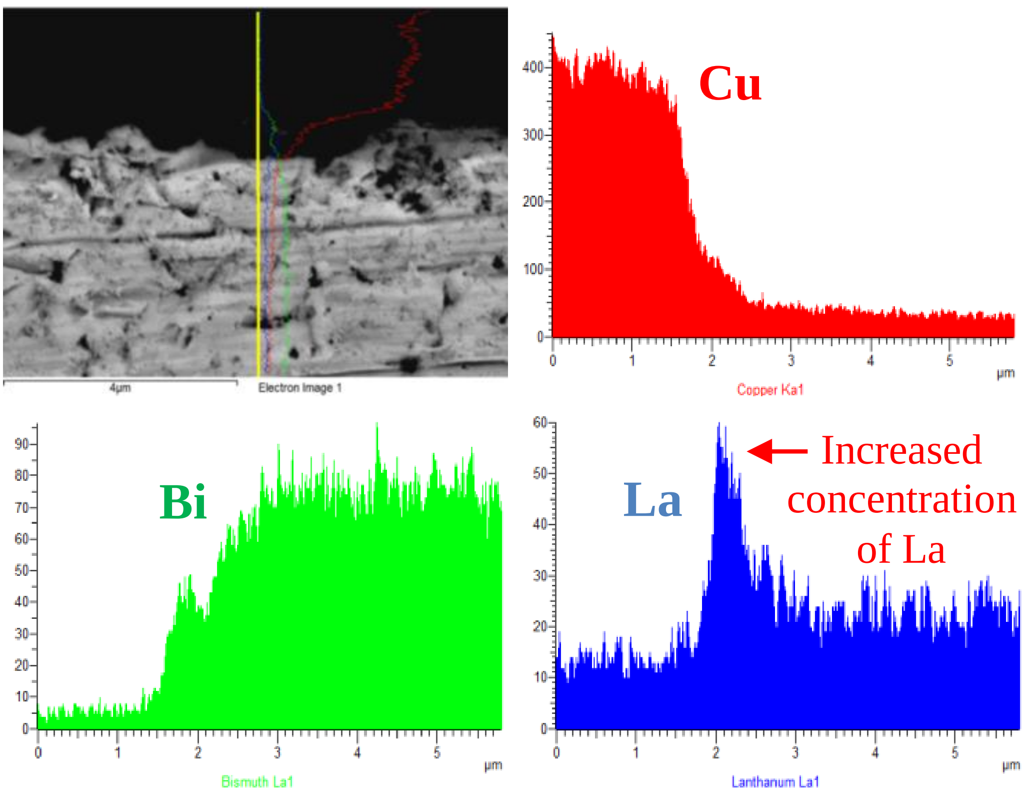

FIGURE 7. The EDX analysis of Cu/Bi2La joint boundary with concentration of Bi, La and Cu elements.

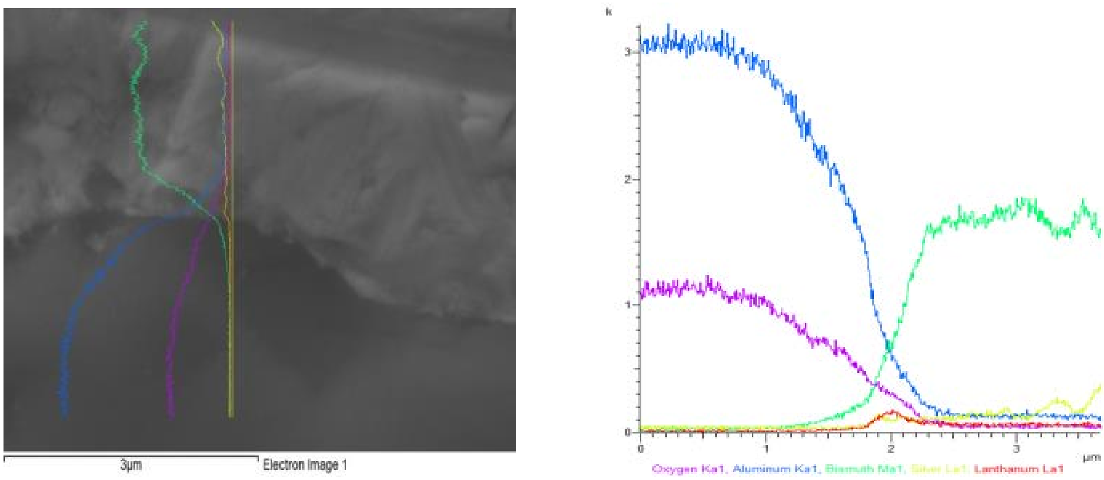

FIGURE 8. Concentration profiles of Bi, La, Ag, Al and O elements on the boundary of Al_2O_3/Bi11Ag2La joint.

which approximately corresponds to the melting point of pure bismuth. La addition affects its melting point to a minimum extent.

(3.) In case of the soldered joints with metallic and ceramic substrate, it was found out that, during ultrasonic soldering process, lanthanum is distributed to the boundary with the substrate, thus enhancing the joint formation. The bond with the Al2O3 is of an adhesive character, without formation of new phases. The bond between the copper substrate and the Bi-based solder is formed, owing to the eutectic reaction between Cu and Bi.

(4.) From the viewpoint of the mechanism of the joint formation, we suppose that the bond with metallic material is of a metallurgical-diffusion character. The bond with the ceramic materials is of an adhesive character.

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