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THE SOLDERABILITY OF CERAMIC MATERIALS WITH ACTIVE SOLDERS UNDER HIGH-INTENSITY ULTRASONIC CONDITIONS

SPÁJKOVATEĽNOSŤ KERAMICKÝCH MATERIÁLOV AKTÍVNYMI SPÁJKAMI PRI APLIKÁCIÍ VÝKONOVÉHO ULTRAZVUKU

Abstract

Joints of combined metallic or non-metallic materials prepared by lead-free tin solder. The analysis of phase interface of joints using fractographic techniques, new phase identification by X-ray analysis and electron microscopy analysis. Effect of new phase on the mechanical properties of solder joint and the possibility of reaction layer study by in-depth etching technique.

Abstrakt

Spoje kombinovaných kovových a nekovových materiálov vytvorených prostredníctvom bezolovnatej cínovej spájky. Analýza fázového rozhrania spojov fraktografickými technikami, identifikácia nových fáz prostredníctvom röntgenovej analýzy a analýzy pomocou elektrónovej mikroskopie. Účinok nových fáz na mechanické vlastnosti spájkovaného spoja a možnosť skúmania reakčnej vrstvy technikou hlbokého leptania.

1 INTRODUCTION

Lately, combined engineering materials have been used in a wide range of technical applications. One undisputable advantage is that their extraordinary properties can be used in a controlled or targeted manner for demanding technical applications. Ceramic and metal combined in the form of a soldered joint are one of such combinations. From the perspective of soldered joints production, the critical factor is the selection of a suitable type of solder. As far as soft solders are concerned, the current legislation prohibits the use of well-proven solders containing lead, thus the research tries to find a suitable replacement for toxic lead previously used in some solders by other elements (such as In, Bi, and Ag) that are expected to generate better results in terms of reaction properties in the production of a joint [1]. From the physical point of view, the wettability of the substrate with solder is first condition for producing a high quality joint – such as the wettability of a ceramic material without additional metallization of the ceramic substrate with a Mo-Mn layer is difficult to be achieved with commonly used solders. That is why it is required that solder contain one or more elements characterized by a higher affinity to the element contained in the chemical composition of the substrate's material. Such an active element's role in a soldering alloy is to ensure the satisfactory wetting of a substrate by way of reactive decomposition of the substrate's surface layer. Such soldering alloys may then be used for the production of joints with various substrates, be it ceramic or metallic ones. However, the soldering of ceramic materials using metals is far from being simple [5].

With the development and introducing of the so called alternative (as they are commonly understood nowadays) soldering alloys, it is becoming ever more necessary to find suitable technologi-

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cal procedures and the most advantageous methods of soldering. One of the methods that may potentially win through in a broader context, along with the coming of new alternative alloys, is ultrasonic soldering. Although the history of ultrasonic soldering technology dates back many years, its attributes and a sort of “exotic" nature made it remain ranked among special soldering methods. It is the lead-free alloys and the successful verification of ultrasound’s suitability as tool for the production of high-quality soldered joints that leads to the situation where unquestionable advantages of this technology will be exploited even better. The progressiveness of this technology lies in the elimination of the need to use an addition agent. Compared to other technologies where the role of an addition agent is to clean the material being soldered and protect it from the possible generation of impurities, in this technology the function of an addition agent is replaced with the erosion induced by ultrasonic cavitation. For that reason, also the necessity no longer exists to laboriously remove an addition agent’s corrosive residues that might induce qualitative degradation of a joint’s mechanical properties.

In this paper, we summarize the results obtained by soldering various technical substrates combinations with soft lead-free Sn-based soldering alloys using the energy of ultrasonic vibration.

2 EXPERIMENTAL MATERIALS AND PREPARATION OF JOINTS

The soldered joints production process in a high power ultrasonic field consists of several phases. One important stage in the production of a joint is the preheating of the soldered substrates to soldering temperature (slightly above T_{sol} of the solder used). Here, the preheating has several roles in the process of forming a soldered joint: It serves to melt down the deposited solder, because the role of ultrasound is not to melt the solder down but ensure that the substrate surface is adequately wetted. The most suitable method of layer-to-layer (deposit) soldering using an ultrasound head is the method of heating using a hot plate. Resistance heating does not involve the risk of contaminating both solder and substrates, the heating is uniform and the device is compact. The device is equipped with a switch by which the heating time for substrates can be set while, at the same time, the substrate preheating temperature is controlled through an external device (a thermocouple and a thermometer). Figure 1 shows a principle scheme of the device for deposit soldering in an ultrasonic field.

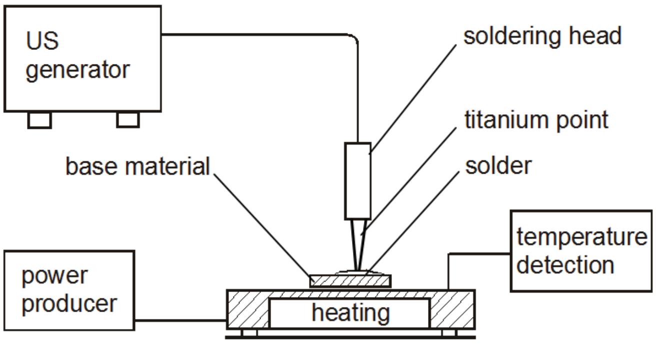


Fig. 1 Diagram of equipment for soldering by ultrasound

Joints produced using such a method thus consist of areas induced by ultrasound where substrates are wetted with solder; these areas are of adhesive or (according to the elements used in the solder (substrate)) diffusive nature (Fig. 2). Soft tin solders alloyed with In, Ag and Ti were used for the experiment. Solders were deposited onto various substrate combinations through ultrasonic activation while metallic substrates consisted of the following materials: Al-alloy, technically pure copper, and CrNi austenitic steel 18/10. To represent non-metallic substrates, the following materials were selected for the study: corundum ceramic (Al_2O_3), semiconductor materials such as germanium (Ge) and silicon (Si) (4N impurities) and, eventually, rough gems (industrial stones: ruby, sapphire). For combinations of ceramic and metallic materials, alloy solder was used in the form of SnAg6Ti4 fine wire with a maximum content of 4.5 wt. pct of Ti alloyed with a small amount of cerium and gallium (up to 0.2 wt pct). This soldering alloy was deposited at a temperature from 250 to 270 °C. As for the other soldering alloy – SnInAgTi – and a combination of metals and industrial stones, the temperature at which deposit soldering was performed was above the melting temperature of pure tin, i.e. between 240 and 250 °C.

The heating to the soldering temperature was carried out using the technique of hot plate. Soldering was then performed at the temperature of the surrounding atmosphere. Ultrasonic equipment made by HANUZ with an output of 300 W was used for this purpose.

Deposit soldering on the substrates' surface using the energy of ultrasonic vibration was only performed at the preset soldering temperature. The length of the period during which the effect of ultrasonic oscillations at a frequency of 40 kHz was applied was of the order of magnitude of a few seconds. Depending on the type of a joint, the holding period at the soldering temperature was from 2 to 10 minutes.

Joints between combined materials produced using this method were subsequently cut with a diamond saw into a series of samples, then subjected to experimental study.

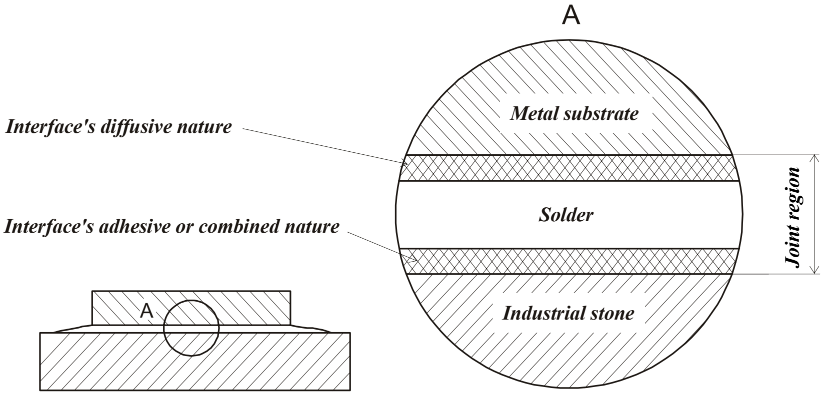


Fig. 2 Distribution and nature of regions in a joint

3 RESULTS ATTAINED AND DISCUSSION OF THEM

Figure 3 shows the interface of a joint that has been produced at a low soldering temperature using the layer-to-layer soldering process in an ultrasonic field. For joints produced using the SnAg6Ti4 solder, a continuous reaction layer is typically achieved at the Al_2O_3-solder interface. Tin-based solder in its initial form contains two phases: Ti_6Sn_5 where titanium is bound and, eventually, Ag3Sn. The energy of ultrasonic oscillations caused the disintegration of the ceramic's complex surface layer where the intermetallic phase is enriched with titanium – Ti_6Sn_5. Depending on the type of a joint, the thickness of a reaction layer may fluctuate from 2 to 17 µm. Where a longer holding period is applied (10 minutes) at a soldering temperature of 270 °C, the newly-formed phases are produced within the range of metallic substrates' solubility (Fig. 3). Their morphology may be either oval or acicular while, at the same time, formations of Ag_3Al rich in silver (identified in Fig. 5) emerge through reaction between aluminum and silver in the solubility range of silumin (see Fig. 4). In the solubility range of copper, a continuous layer of a new Cu_3Sn phase is formed at first onto which (directed into the solder's volume with a higher concentration of Sn) Cu_6Sn_5 is added – see detail in Figure 6. A detailed analysis of copper's range of solubility was conducted by way of etching away the solder's tin matrix to a depth of several µm.

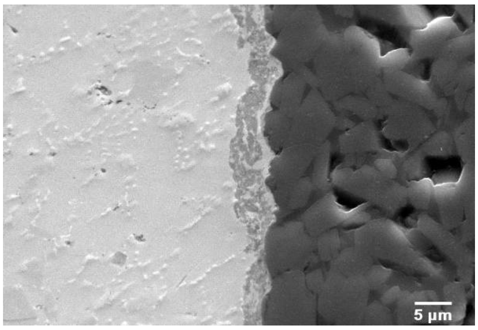


Fig. 3 Reaction layer between solder and ceramic substrate

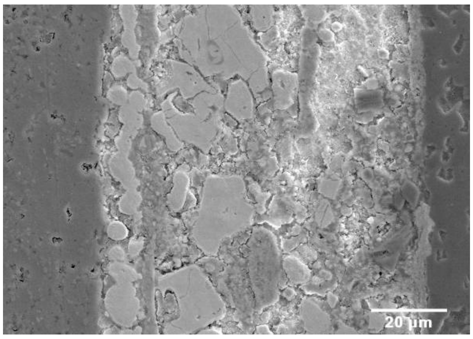


Fig. 4 Solubility range and reaction layer in a joint between silumin and ceramic

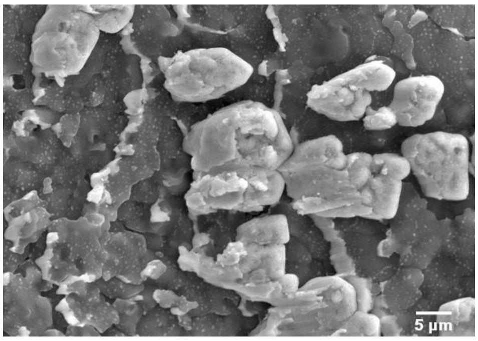


Fig. 5 Fragmented Ag_3Al particles in the interface of silumin's reaction layer

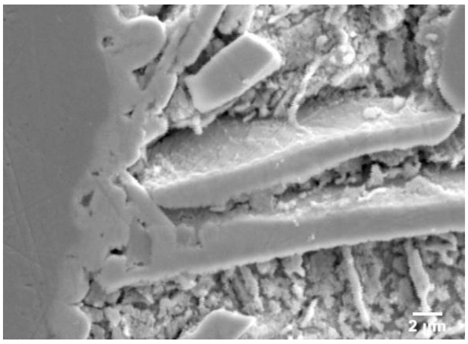


Fig. 6 Acicular forms in the Cu substrate's reaction layer

The effect of these particles upon mechanical properties of a joint was studied through shear strength testing. The separated halves of testing samples were subjected to a fractographic analysis using a scanning electron microscope. The results achieved in this manner confirm the suitability of the deposit soldering technology for the production of combined joints with required mechanical properties; the evaluation criterion is the shear strength value that well corresponded to the values shown in the manufacturer's material certificate, i.e. between 17 and 30 MPa. The reaction of active titanium in the interface between a semiconductor substrate and solder was also expected in combined joints of semiconductor materials such as germanium and silicon and a metallic substrate. For joints involving copper, an acicular phase of Cu_6Sn_5 (Fig. 7) was surprisingly identified in the Ge substrate interface; this phase, due to the effect of ultrasonic oscillations, got into the liquid solder from a disintegrated layer of the copper substrate. A prerequisite for this phase's heterogeneous nucleation was the reaction between titanium and the surface oxides occurring during the deposit soldering process (activated by ultrasound), which resulted in the formation of a TiO_2 phase. The presence of oxides during the formation of a reaction layer is beneficial for the heterogeneous nucleation of existing solder phases or it triggers the formation of new phases – like in the case of the silicon substrate shown in Figure 8 where Ag_3Sn and $AgTi_3$ were identified.

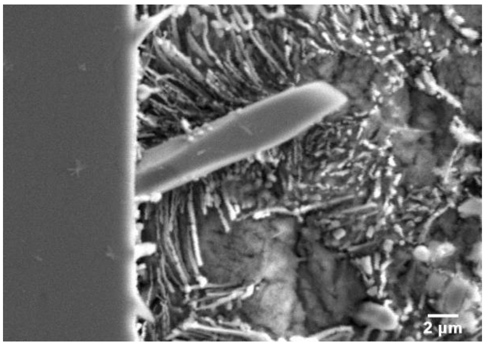


Fig. 7 Ge-Cu joint interface

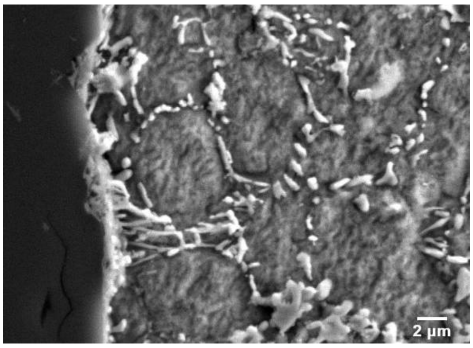


Fig. 8 Si-Cu joint interface

The formation of reaction layers was also expected in the soldering of industrial stones with metals using the SnInAgTi alternative soldering alloy. Based on examining metal substrates' interfaces, at least partial diffusive nature of these interfaces was detected in all cases examined. Reactions of substrates' elements with the tin component of the solder prevailed, while their diffusion products were being formed. A narrow gap with solder matrix (rich in tin a indium) highly etched away can be seen on a side of the industrial stone shown in Figure 9, which indicates that these joints' interfaces have rather an adhesive nature. An analysis of the joint interface at the Cu side (Fig. 10). confirmed the presence of Cu_3Sn-type phases and Cu_6Sn_5-type phases.

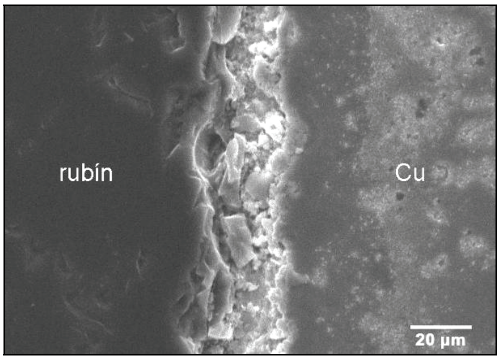
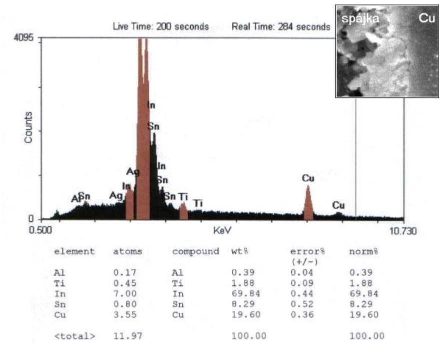


Fig. 9 A view of the copper-ruby interface



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element   atoms    compound  wt%     error%   norm%
                                     (+/-)
Al        0.17     Al        0.39    0.04     0.39
Ti        0.45     Ti        1.88    0.09     1.88
In        7.00     In        69.84   0.44     69.84
Sn        0.80     Sn        8.29    0.52     8.29
Cu        3.55     Cu        19.60   0.36     19.60

<total>   11.97              100.00           100.00
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Fig. 10 Chemical analysis of the interface

4 CONCLUSIONS

During the application of ultrasonic vibration, the SnAg6Ti4 solder wetted the following non metallic materials: Al_2O_3 ceramic, non metallic Si and Ge materials; and the following metallic materials: AlSi5, Cu and CrNi steel. Depending on the type of soldered material, various reaction products are formed during the interaction between solder and the material being soldered. When the Al_2O_3 ceramic is used, the formation of the TiO_2 oxide prevails; for aluminum, an Ag_3Al phase arises, and the following phases are formed at the interface during the soldering of copper: Cu_3Sn and Cu_6Sn_5. It can be stated that when the SnAg6Ti4 solder is applied, different mechanisms of formation of a joint apply depending on the nature of soldered material, and the joints are of diffusive nature.

When the tested SnInAgTi solder was applied, it was found that this solder is also capable of wetting the following experimental materials: industrial stones (ruby, sapphire) and metallic materials (AlSi5, Cu and CrNi steel), while different mechanisms of joint formation were identified in the soldering of ceramic materials. The effect of indium was greater than that of titanium at the interaction of ruby and sapphire with the SnInAgTi solder, but no distinct diffusion area was formed. It is supposed that indium has a high affinity to oxygen and that, during the soldering process, it combines with air oxygen with simultaneous formation of complex indium oxides that subsequently enter into reaction with the surface of a ceramic substrate. When metallic materials are soldered, the mechanism is similar to that observed with the SnAg6Ti4 solder; reaction with indium only applied in the case of copper.

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