NEW INVESTIGATION METHODS OF INTERMETALLIC COMPOUNDS OF TIN-SILVER SOLDER ALLOYS

PhD Thesis-booklet

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Motivation

The electrical components of a circuit are fixed onto the printed circuit board (PCB) by the so called soft soldering technology. The majority of the solder joints are created with Surface Mount Technology (SMT). During the reflow soldering process the solder pads are wetted by the molten solder alloy, and Cu-Sn intermetallic compounds (IMC) are being formed with the material of the solder pad.

The mechanical properties of the solder joints are partially determined by its microstructure, especially by the thickness and structure of the Intermetallic layer (IML) formed at the solder-substrate interface. The IML evolves rapidly during the soldering process and its growth does not stop after the solidification either. [2].

![Figure 1. Optical microscopic images of the cross section of a laser reflowed sample.](image)
The intermetallic layer at the solder-copper interface and the spalled IMC fractions can be seen in the figures.

Lead-free soldering technology has been becoming more and more widespread in the past decade. The changeover from the previously used eutectic Sn-Pb solder was not trivial. The elevated technological temperatures and the presence of the additional composing elements resulted completely new phenomena. [3]-[4]. IMC fractions spalled from the intermetallic layer during the soldering process may change the microstructure of the solder joint. This is the reason why knowledge of the spalling mechanism is essential from the reliability point of view [5].

Based on the literature study of the lead-free soldering technology I concluded that there no universal observation methods exist for characterising the microstructure and the correspondent mechanical properties of one solder joint, resulted by the new phenomena.

Research Objectives

The widespread convection reflow ovens are not suitable for supporting experimental verification of the kinetic models of the formation of the microstructure. This is because the energy coupled into the solder joint can not be controlled precisely enough as the characteristic measures of a solder joint are typically one order of magnitude smaller than that of the oven. For the verification of modelling there is an urgent need of developing a selective heat transfer method, which allows us to couple the energy into the solder joint in a definite and controlled way. For this reason I developed a selective soldering method supported by numerical simulations. My aim was to model and simulate the temperature distribution and fluid motion of molten solder induced by the extreme temperature gradients of the laser process. The
primary objective of the simulation assisted laser reflow technology is to support the future experiments by generating identical and reproducible microstructures.

The most general metallographic observation is cross sectioning combined with any microscopic method, like Scanning Electron Microscopy (SEM) or Optical Microscopy (OM). The cross sectioning can reveal – besides of the overall joint geometry – the inner layer structure of the solder joint such as the distribution of the composing elements. The presence of the intermetallic layer is a reliable indicator of the properly formed solder joint. Without any IML the joint is declared not having been formed. Since the mechanical properties of the solder joint are significantly different from the properties of the composing elements the too thick IMLs might cause reliability issues [6]. Most of the quality inspection methods aim at the determination of the average thickness of the intermetallic layer, even though it is well known that morphologically completely different layers may be formed by solid state aging (densely packed, flat) and by the wetting reaction (scallop type) [6]. So it is not enough to determine the average thickness only because the mechanical properties of the solder joint are also affected by the morphology of the IML [7]. In this research field my aim is to develop a cost efficient process which is suitable for the automated determination of the structural properties and the average thickness of the intermetallic layer.

The biggest disadvantage of cross sectioning is that it can only give a narrow perspective to the microstructure of the solder joint, as it is constrained to a single sectioning plane. Therefore the true spatial orientation and distribution of the microstructure are not observable. The 3D observation of the structure inside the bulk solder alloy could only be achieved by multiple sectioning, which would be an extremely difficult and expensive process. This fact is motivating my research which is about to develop a special sample preparation method for revealing the microstructure of the solder joint in order to be able to observe it in a previously unseen way. The interpretation of the new information gained by the observation and characterisation of the exposed microstructure might be fundamental in the comparison of different solder joints. This is why my additional aim is to research a quantitative analytical method for characterization of the exposed microstructure.
Novel Scientific Results

Thesis I: I have developed a physical model for describing the laser reflow process of SAC305 solder alloy. Based on the physical model I have implemented numerical simulation for determining the temperature distribution and heat profile of the laser reflow process. The novelty of this simulation model is that also considers the mass transport inside the molten solder material induced by the temperature gradients.

- I have transmitted energy into the cylindrical symmetric experimental system with a frequency tripled Nd:YAG laser with a frequency of 355 nm. My model takes the real laser intensity profile and the temperature dependent coupling coefficient into account. The temperature distribution of the solder over time is derived from the solution of the partial differential equations of heat and convective material transfers, at a given set of boundary conditions.
- I have determined the qualitative vector field of the fluid motion of the molten solder alloy and from this I have concluded to forces that act on the elongated intermetallic crystals during the spalling phenomenon.
- I have experimentally determined the only fitting parameter of the simulation. The verification of the simulation model was also carried out in cylindrical symmetric system. Based on the verification experiments, my simulation calculates the temperature over the geometry with an error below 5°C. By applying 2D cylindrical symmetric numerical solution the necessary computational time was reduced three orders of magnitude lower than a regular 3D case.

Related publications: [L1], [R2], [R3], [R4]
Thesis II: By applying fundamental material science methods I have developed a process for automatic and objective characterization of intermetallic layers formed between tin-silver solder and copper substrates. My novel solution measures the thickness of the intermetallic layer all along its lateral dimension on the basis of optical microscopic images of cross-sectioned solder joints and creates a histogram. Resulting histograms are more meaningful sets of information than average thickness values when describing intermetallic layers and comparing them with each other.

- I have determined the optimal parameters of the special contrast enhancing technology in the case of the most commonly used material system in the electronic industry (Sn-Ag-Cu solder alloy, FR4 board copper laminate on it).
- I was observing the trenches by Atomic Force Microscope at the IML layer on the surface of the cross section mold which were formed as the consequence of the special sample preparation technique. I have discovered that the depth differences between the trenches at the copper-IMC and at the IMC-solder interfaces are identical to the sample preparation method.
- I have developed an automatic IML characterizing algorithm which is able to recognise the IML layer in the optical microscopic image of the cross section of a solder joint. The routine uses the previously proved fact of constant depth differences to measure the thickness of the IML at each pixel-column of the OM image. The IML is described by its amplitude density function.

*Related publications: [L1], [R4]*

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Thesis III: Based on electrochemical etching technique I have developed a sample preparation method which is especially selective to tin and it is suitable for revealing the fine microstructure of any tin-silver based lead free solder alloys. By taking the advantage of the step-function like nature of the reduction potential in tin-silver-copper material system I selectively etch the surface of a cross-section of a solder joint in standard three electrode setup, in 1% diluted sulphuric acid by applying -350mV voltage measured from the Hg/Hg\textsubscript{2}Cl\textsubscript{2} reference electrode. As the result of the controlled electrochemical reaction the tin is extracted from a dedicated depth of the solder, leaving the intermetallic microstructure behind intact.

- I have experimentally determined that the optimal value of the applied voltage of the electrochemical reaction in the case of tin-silver-copper material system is -350 mV measured from the Hg/Hg\textsubscript{2}Cl\textsubscript{2} reference electrode.
- I have designed two different electrochemical cell geometries and I have optimized the parameters of the cells by simulating the electrostatic distribution inside the cells.
- I have experimentally determined that the time dependence of the average etching depth of the tin-silver-copper solder is quasi linear between 30-330 s up to 30 µm depth.

Related publications: [L2], [L3], [M1], [R5], [R6], [R7]
Thesis IV: I have developed a quantitative method for the characterization of the intermetallic microstructure which was formed during reflow soldering. I measure the electrochemical impedance spectrum of the cross-sectioned polished solder sample in 0.5 M NaCl solution. In the same electrochemical cell I selectively etch the sample in 1% H$_2$SO$_4$ solution in order to reveal the microstructure of the sample. I compare the impedance spectrum of the etched sample modulated by the microstructure of the solder alloy to the spectrum obtained before etching. During the comparison I determine the parameters of the equivalent network circuit and I derive a dimensionless parameter by dividing the dominant network elements with each other. This parameter is characteristic to the microstructure of the solder joint.

- I have determined the arbitrary parameter of tin-silver solder samples quenched in different temperature cooling media. This parameter is proportional to the total surface of the microstructure of the solder joints and it showed a monotonous behaviour with the cooling rate of the samples.
- I have applied a physically independent analytical method, the small angle neutron scattering in order to verify my analytical method. The total intensity of the scattered neutrons showed us that the total surface of the intermetallic microstructure, which was acting as a scattering surface, was also monotonous with the cooling rate.

Related publications: [L2], [L3], [L4], [M1], [M2], [R6]
Exploitation of the Results

As my scientific interest could be separated into two individual fields the scientific results are utilized in two different ways. The experiences that were gained during the development of the simulation model of the laser reflow process were applied in several industrial projects. A feasibility study of selective soldering process was prepared for the Nokia plant in Komárom, Hungary. The parameters of the laser soldering were determined based on my simulation model. My controllable simulation assisted reflow process served as the reference technology in different research fields at the department several times.

The scientific results in connection with the metallographic observation methods can be grouped around my second field of interest. Great interest was following the introduction of my novel methods during several professional forums. We were invited to the Technical University of Dresden to the Institute of Electronic Packaging Technology in order to introduce the selective electrochemical method. We have been cooperating with the colleges in Dresden in many different fields ever since then.

The selective electrochemical etching method is completely integrated into the toolbar of the Failure Analysis lab at the department. The method is used for the observation of lead free solder joints. The spectacular SEM images of the microstructures revealed by this technology are incorporated into lecture notes of several subjects educated by our department.

In the framework of a scientific scholarship hosted by Robert Bosch Elektronika Hatvan Ltd. I was dealing with the reliability issues of lead free soldering technology in the automotive electronic assembling factory in Hatvan. I optimised my selective electrochemical etching process in order to be industry-compatible and I developed a new inverse electrochemical cell geometry. A custom made potentiostat circuit was also prepared which is capable of selectively etch the lead free solder alloys. The interest for quantitative analytical methods, based on the electrochemical impedance spectroscopy is continuously increasing, we are still cooperating with industrial partners in order to build an etalon database (Infineon, Robert Bosch).

One of the PhD theses of László Milán Molnár was based on characterisation of my laser reflowed and selectively etched solder joints by AFM.

The new methods of the characterisation of the solder joints were used to qualify hand soldered electronic products designed for several space related project (REXUS, BEXUS, ESEO) carried out together with European Space Agency (ESA).
Besides the above mentioned exploitation of my results the scientific merit of my newly introduced methods is relying in the possibility to reproduce previous experiments in connection with lead free solder alloys supplemented with my new methods. In this case the precisely revealed microstructure could also be observed, and the additional information of the revealed microstructure would be so detailed unlike any other before.

Non-etched solder sample  
(magn.: ~6000x )

Etched solder sample 
(magn.: ~3000x )

1. Figure Elemental composition maps of the cross-sectioned solder samples. 
   Left: a non-etched solder sample, right: an etched solder sample.

The possibility of the quantitative analysis of tin-silver based solder alloys is very valuable, as further knowledge on the correlation of the technological parameters and microstructure would be essential for the optimisation of the soldering technology. The correlation between the macroscopic properties and the character of the microstructure is important from the reliability point of view.
List of Publications

Publications Related to Thesis Points

*International, peer reviewed journal papers, written in foreign (English) language*


*Hungarian papers, written in Hungarian language*


*International, peer-reviewed conference papers, written in foreign (English) language*


**Additional Publications**

*International, peer reviewed journal papers, written in foreign (English) language*


*International, peer-reviewed conference papers, written in foreign (English) language*


Conference paper or poster, written in foreign (English) language


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References


