Přiloha 2

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Interaction of Silver Nanopowder with Copper Substrate

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Abstract:

Addition of lead into tin based solders represents a serious health risk and environmental problem. Lead-free solders represent one of the ways to remove pollution of lead into environment, nevertheless, new advanced joining methods have to be considered. Aggregation effect of nanoparticles studied in this work seems to be an interesting alternative. It was found experimentally that Ag nanopowder annealed at temperatures above silver oxide decomposition forms continuous Ag layer and yields a firm junction between copper plates. Oxide layer is observed at the Cu-Ag interface. The oxide interlayer thickness reflects the temperature and annealing time. Microstructure of prepared experimental joints, composition profiles and local mechanical properties were studied on cross-sectional samples by analytical electron microscopy and depth-sensing indentation technique.

Keywords: *Silver, Copper, Sintering, DSC, Indentation.*

1. Introduction

Lead containing materials represent health risk and serious environmental problem. Electronic devices are remarkable sources of lead pollution. Since 2006, when regulations enforcing lead-free solders were implemented into the EU legislation, there is an ongoing strong drive to find the best lead-free solder alternatives. Those presently used have often reliability problems caused by worse mechanical properties, higher tendency to oxidation, higher occurrence of undesirable intermetallic phases and higher melting temperature. After some years of research in this field it turns out that there is no single replacement for the lead containing alloys, which would cover all technical applications.

An alternative to classical soldering process can be found for example in the field of nanoscience. Physical, electronic, and thermodynamic properties of metal nanopowders are significantly different from the behavior of the bulk materials. High surface/volume factor leads to advantages and also to some problems. Nanoparticles are very reactive and oxidize readily after short exposure times if unprotected. Moreover, phase diagrams of nanopowders differ substantially from those of the bulk materials [1]. The dependence of liquids temperature on the particle size is more than evident.

The phenomenon of melting point depression of the metallic nano-sized particles is

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under long time view [2-7]. It can be observed mainly in systems where metal nanoparticles (tin, gold, etc.) are enclosed inside protective shells. They can be realized by oxide layer, silica encapsulation [6], etc. The melting point of metallic nano-sized particles reveals a depression potential up to 0.6 T_m of the bulk metal in some cases (Au, 2nm) [6]. The use of environmentally friendly nano-sized metallic particles [8,9] as a solder material seems to be very promising because this green nanosolder can melt at low temperature (best at temperature close to melting temperature 183°C of Pb-Sn eutectic solder) and form a stable joint, which can be used up to bulk melting.

Unfortunately, the concomitant circumstances introduce serious problem for nanosoldering. The source can be oxidation or addition of soldering flux. They disable growth of melted metal nano-sized particles and formation of bulk and joint with the substrate. This effect does not vent itself in the case of silver, which is in the focus of the presented paper.

2. Experimental

The copper plate (purity 4N, thickness cca 0.6mm) as a substrate and silver nanopowder (Sigma-Aldrich, size <150nm) were used in our experiment. The DSC experiment on silver nanopowder was performed using Netzsch apparatus STA 409. The copper disks 5 mm in diameter were prepared from the plate, etched in 10 wt.% H_2SO_4 at 60°C and washed in 60°C ethanol to remove surface oxides. A layer of silver nanopowder (see Fig. 1.) was evenly spread over one of the disks and covered by another one. The sandwich structures were put horizontally into alumina crucible and annealed at temperatures 200, 250, 300 and 400°C for different times ranging from 0.5 to 6 hours under small vertical load (cca 10kPa) in air. Metallographic cross-sections were prepared from annealed Cu/nano-Ag/Cu sandwich samples and studied using a JEOL JSM 6460 scanning electron microscope with Oxford Instruments INCA Energy analyzer. Microhardness and other mechanical properties across the joints were measured by depth sensing indentation technique using a Fischerscope H100 tester.

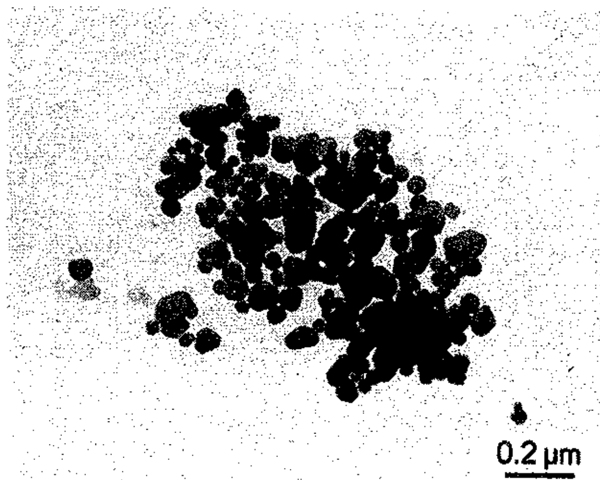

Fig. 1. The silver nanopowder (TEM micrograph)

3. Results and discussion

The silver nanoparticles were investigated by means of DSC technique in slightly oxidizing 4.7N Ar atmosphere (main impurities were nitrogen and oxygen). The gas flow rate

was 70ml/min. The results of DSC measurements are shown in Fig. 2. The shape of the first heating curve differs markedly from the second and the third run. The first run reveals low temperature exothermal effect, which splits into two stages below and above 220°C. After the first heating run the nano-silver is agglomerated and does not reveal detectable thermal effects within the subsequent runs. In all cases melting temperature of bulk silver 960°C was detected confirming agglomerated state of the samples.

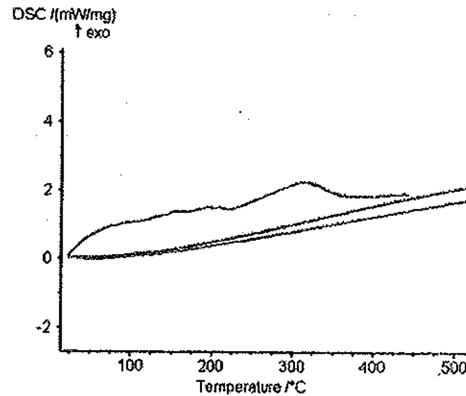

Fig. 2. Heating curves of silver nanopowder. First (green), second (blue) and third (red) heating (DSC, 10K/min)

The Cu/nano-Ag/Cu sandwich samples prepared at different temperatures and annealing times reveal good mechanical resistance to mechanical separation (approximately similar to sandwich joined with tin-lead soldered) if the annealing temperature was over 220°C. The microstructure of the cross-section perpendicular to silver interlayer is on

Fig. 3. It is evident that silver nanopowder agglomerates and a firm silver interlayer is formed between copper substrates. The nanosintering process occurs. The compactness of the silver interlayer is dependent on annealing time. The formation of the porous silver interlayer is evident at annealing conditions 300°C and 1hour.

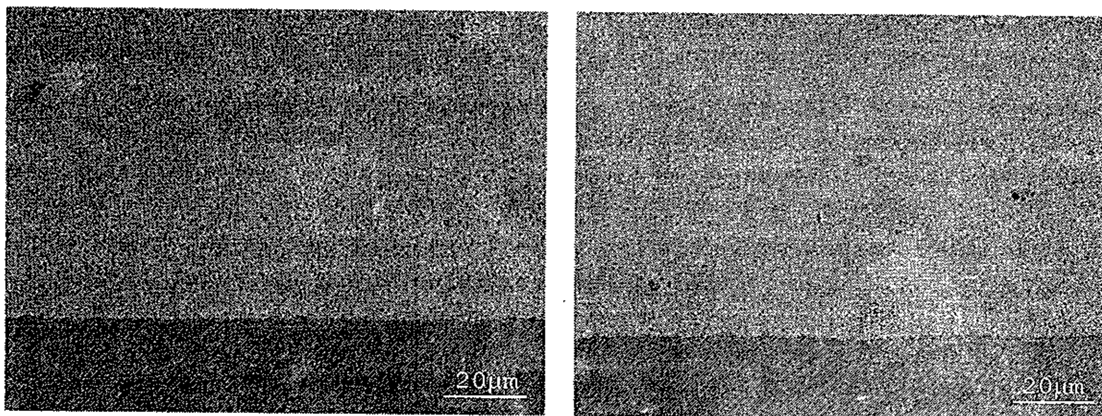

Fig. 3. The microstructure of the sintered nano-silver layer in the sample annealed at 300°C for 1 hour (left) and for 3 hours (right)

The investigation of the interface between copper substrate and nanosintered silver showed that this region reveals thin interlayer, which is shown in detail on Fig. 4. The EDX analyses across the interface show high content of oxygen, which corresponds to Cu_2O formation at the interface. The measurements of thickness of the Cu_2O interlayer in the

samples annealed at different temperature/time conditions reveal that kinetics of oxide is close to parabolic growth.

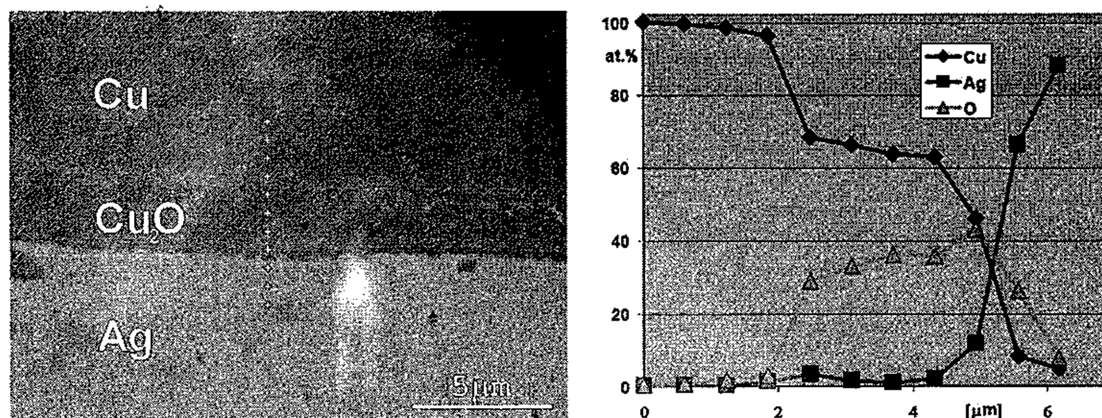

Fig. 4. A detail of the Cu | Cu_2O | Ag region of the sample annealed at 400°C for 3 hours (left) with series of point EDX analyses across the region (right)

Nanoindentation tests were carried out on cross sections of the Cu/nano-Ag/Cu sandwich samples annealed at 400°C using depth-sensing indentation method. Large number of indentation tests at different indentation loads in the range from 2 to 10 mN was done in order to map the indentation response across the Cu/nano-Ag/Cu sandwich on both studied samples. The loading and unloading time was 20s. The maximum load was kept constant for 5s in each case enabling to study the resistance of the samples against indentation creep. **Fig. 5.** shows two graphs presenting selected loading-unloading curves obtained on samples annealed at 400°C for 1 hour and 3 hours. Three groups of indentation response curves corresponding to Cu, Cu_2O and sintered nano-silver layer are clearly distinguishable at low indentation loads on both samples.

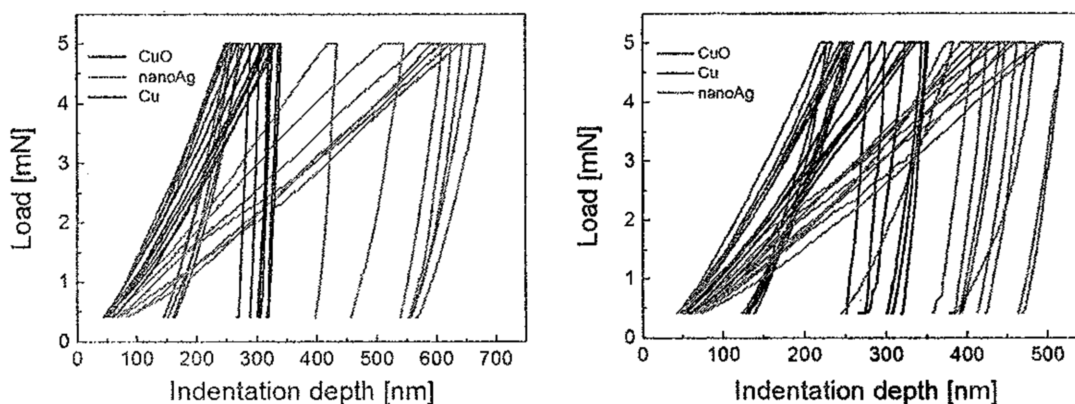

Fig. 5. The loading-unloading curves of depth-sensing indentation tests measured in various regions of the sample annealed at 400°C for 1 hour (left) and for 3 hours (right)

The bulk silver is commonly considered as noble metal but oxidation at low temperatures has to be expected from Ag-O equilibrium phase diagram. It was confirmed in this work. At temperatures below 220°C silver coats by thin oxide layer , which decomposes

to metal silver and oxygen at temperature above 220°C. The nano-silver retains the oxidation property of the silver bulk and exothermic effect of oxide formation within the first temperature run up to 220°C occurs (see Fig. 2.). In the other temperature region 220-380°°C the exothermal effect indicates superposition of thermal effect of silver oxide decomposition and agglomeration of uncovered metal silver nanoparticles.

The low temperature nano-silver sintering effect is the important phenomenon that takes place between copper plates. The nano-silver creates porous structure of silver layer (see Fig. 3.) and oxygen goes away. A part of oxygen attacks copper substrate and forms a thin Cu_2O interlayer. The growth of the Cu_2O interlayer (see Fig. 5.) continues even after the silver oxide is decomposed. It is caused by porosity of silver layer, which enables oxygen transport from air. From mechanical point of view the sandwich represents a good mechanically stable joint with low resistance (1-5Ω). The internal cracking in Cu_2O/Cu interface was observed if the cooling rate was too fast. The preparation of mechanically stable joint of two copper plates using the silver nanopowder under air atmosphere is possible but the process needs an optimization to suppress the Cu_2O interlayer formation.

Regarding indentation experiments, the indentation response of copper at maximum load of 5 mN is typical of pure metals in both cases, i.e. almost purely plastic response with negligible elastic deformation. The highest resistance against plastic deformation was obtained for Cu_2O layer. The indentation response of Cu_2O was typical of oxides: beside the irreversible (plastic) deformation there was also a significant reversible (elastic) part observable on loading-unloading dependences. On the other hand, the Cu_2O layer showed negligible indentation creep. The indentation response of nano-silver layer exhibited more plastic character with significant creep deformation at maximum load. The results of indentation tests carried out on nano-silver layer showed the highest scatter, the loading-unloading curves from different parts of the layer exhibit different character because of its inhomogeneous structure. The indentation resistance of nano-silver layer increased significantly for longer annealing time (see Fig. 5.). The indentation hardness of nano-silver increased from 525 to 570 MPa and the scatter of data slightly decreased in case of longer annealing time, i.e. the better compactness of the silver layer was reached.

4. Conclusion

Silver represents interesting model material, which can be used for study of nanosintering. The sintering temperature is 220-380°°C that is 0.42 T_m of bulk silver. The joining using the nanosintering process seems to be a good alternative to standard soldering using bulk alloys.

Joints of Cu/Ag/Cu can be prepared on air but Cu_2O oxide interlayer is formed between silver layer and copper substrate. The process needs an optimization to suppress or minimize the oxide interlayer formation.

Metal nanopowders are promising materials for the preparation of lead-free nanosolders applicable at temperatures higher than processing temperature.

Acknowledgement

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Садржај: *Додатак олова у лемове од калаја представља озбиљан проблем како здравствени, тако и проблем по околину. С обзиром да коришћење безоловних лемова представља један од начина отклањања загађења околине оловом, морају се развити нови начини лемљења. У овоме раду анализирана је једна занимљива могућност, која се базира на ефекту агрегације наночестица. Експериментално је утврђено да нанопрах сребра, загреван на температурама изнад разлагања сребро-оксида формира слој сребра који чврсто повезује две бакарне плоче. Констатовано је формирање оксидног слоја на међуслоју сребра и бакра. Дебљина оксидног међуслоја зависи од температуре и времена загревања. Микроструктура експериментално припремљених спојева, композициони профили и локална механичка својства анализирани су на попречном пресеку узорка.*

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