

Sn-Pb and lead free solders containing active carbon particles

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Abstract. Upon the legislations issued by the governmental agencies, many companies are in effort of using lead free solders for their electronic products. Many researchers have also focused on lead free solders and determined their physical properties to the merit of their desired strength and conductivity which turns out to be a potentially advantageous after all. The addition of nano particles into the solder alloys has been attempted to investigate the property change caused by such addition from which a main outcome was a limited improved mechanical and physical properties such as lowering the melting temperature. In this study, the addition of nano active carbon particles to Pb-Sn and Pb-free solder alloys were made and characterization studies were conducted to determine their basic properties such as electrical conductivity, microstructural study and also phase transformations. The results indicate that the addition of active carbon particles brings about a change in thermal properties more markedly than other properties with respect to the amount of addition.

1. Introduction

The activated carbon is produced from organic material such as food extracts, for places where high surface area for filtration of contaminants from air and water. Activated carbon is extremely porous substance and hence can be used for adsorption of relatively low-molecular-weight organic compounds such as phenols [1-2].

The environmental concern over the toxicity of Pb has led the companies to abide by strict regulations of government agencies and the research on lead-based solders is promoted through regulations [3]. Various research agencies and companies have produced enormous data on binary alloys as candidates for replacement of the traditional Sn-Pb solder alloy. Properties such as wettability, electrical and thermal conductivities and the amount of alloying additions, mechanical properties such as ductility, creep resistance, thermal fatigue and also manufacturability are desirable main characteristics for mainstream solder alloys. Solders alloys of Sn-Ag and Sn-Cu binary system and ternary additions are favourable for their good mechanical behaviour [4-5]. The typical hypoeutectic Sn-X alloys have usually Sn-rich dendritic matrix and a eutectic mixture of a Sn-rich phase and intermetallic phases such as Cu_6Sn_5 and Ag_3Sn [5-6]. Sn-Cu alloys as an alternative to Sn-Pb alloys are cheaper to produce with conventional methods and have a eutectic reaction at 227°C situated between intermetallic Cu_6Sn_5 phase and the Sn-rich phase and the addition of some alloying elements, such as Ni, Ag and Zn have been the subject of study for the improvement of their certain properties [6-8]. These intermetallic phases accelerate the corrosive deterioration due to galvanic corrosion mechanisms. The dissolution of tin is main breakdown mechanism for the failure [9]. There are very few studies regarding the addition of carbon derivatives into solders which may potentially prevent such failure and improve the properties [10-12]. The addition of carbon black was found to



improve the mechanical properties of Sn-3.5Ag alloy due to uniform distribution of the Ag_3Sn particle and help inhibit the growth of Ag_3Sn IMC layer by the adsorption of carbon black particles at the phase boundary in the IMC layer[10]. There was no change associated with melting temperature. The addition of carbon nanotubes, however, caused a change in melting temperatures and improved the mechanical properties and did not cause a substantial change in electrical resistance, too[12].

In this study, the additions of nanosized active carbon (AC) particles in the lead containing (Sn40Pb60) and lead free solder alloys (SnCu3 and SnCu0.3) have been made and characterization of alloys was conducted to determine their basic properties.

2. Experimental procedure

The activated carbon was produced from orange peel in a high temperature reactor made of stainless steel which can be pressurized upto 15 Bar and can be operated at 300°C. The food extracts such as orange peel, hazelnut shells have been used to produce active carbon powders. The reactor has a steam disposal mechanism to let the unwanted gasses and water vapour come out of the reactor. The heating process was conducted for 2 hrs at a maximum pressure of approximately 5 bar. The extract was then dried over a night at a temperature of 90°C in N_2 containing autoclave. Following the manufacturing of activated carbon, BET (Micromeritics Gemini 2360) was used to measure the surface area and average size of powders and it was shown that the average particle size was approximately 146 ± 58 nm. Following the manufacturing of activated carbon, BET (Micromeritics Gemini 2360) was used to measure the surface area and average size of powders and it was shown that the average particle size was approximately 146 ± 58 nm.

Three types of solders have been used for the experiments: Sn40Pb60 (LK1X), SnCu3 (3% Cu) (LK2X), SnCu0.3 (0.3% Cu) (LK3X). The mixing process of active carbon into solders was made by remelting and casting of solders containing no addition (LKXA series), approx. 0.14 (LKXB series) and 0.3 wt% (LKXC series) of active carbon additions. At a temperature of 270°C, the casting was made into Al crucible which was heated to 45°C, then; the specimens were subjected to standard metallographic examination. SEM with EDX attachment was employed for microscopic investigation to reveal the elemental change within the matrix. No etching was carried out but BSE (Back Scattered Electron) mode was used for imaging during SEM analysis.



Figure 1. Remelting pot for casting of solder without and with active carbon additions



Figure 2. Resistance measurement jig for solder alloys

Hardness measurements were made using Shimadzu microhardness tester HMV01 with a load of 100 g using Vickers tip. The measurement was repeated more than five times and results were given in average of total measurements.

Electrical conductivity measurements were conducted by using GW Instek GOM 802 milliohmeter with a precision of 1 micro ohm. An apparatus was built, as seen in Figure 2, with a constant load of approximately 1.3 Kg applied by a spring. The measurements were made at room temperature using pure copper pins between which the inter distance length from pin to pin was 11.5 mm.

Melting point of alloys was measured using a electrically isolated thermocouple sensor with a diameter of 1mm by dipping the thermocouple into the melt. Data logger DI145 of DATAQ was used to capture the change in temperature during cooling after casting.

3. Results and discussion

3.1. Hardness and Electrical conductivity

In table 1, hardness of each solder alloy were measured and the results showed that there is slight increase in hardness with respect to addition of carbon particles, which is possibly result of matrix hardening effect from particles as well as the cooling rate associated with casting process. Since there is no difference in casting method, it is difficult to determine the reason for hardening based on casting effect. However, it is possible that the use of Al pipe to direct the melt to the mould may have helped to the introduction of Alumina into the alloys, contributing to the hardness of the matrix. The hardness values are usually similar to each other with very little difference but this not true for the series of LK2X which contain 3% Cu.

Table 1. Hardness values of solders in HV_{0.1} (± 2.2)

LK 1A	LK 1B	LK 1C	LK 2A	LK 2B	LK 2C	LK 3A	LK 3B	LK 3C
12.5	13.1	14.4	11.2	11.7	12.8	9.3	10.8	11.3

The experimental results of electrical conductivity measurements are presented in table 2. The results revealed that the electrical conductivity of the bulk composite solders were comparable to that of the unreinforced Sn-Cu solder and were also better than that of conventional Sn40Pb60 solder. In fact, in all series the addition of AC (Active Carbon) resulted in changes in the measurement values especially in Sn40Pb60 series which caused serious changes hardness and resistivity/conductivity values. The disturbance of normal motions of electrons is primarily attributed to lattice scattering and impurity scattering which reduces the mean free path of electron motion within the matrix phase. A reduction in electron mobility and hence an increase in the resistivity value are inevitable for composite solders[12]. The total volume fraction of the electron scattering will result in an increase in the materials resistivity value, however, the electron contribution from other sources will result in a positive change in resistivity.

Table 2. Electrical conductivity coefficient of solder alloys ($\mu\text{ohm.m}$)

LK 1A	LK 1B	LK 1C	LK 2A	LK 2B	LK 2C	LK 3A	LK 3B	LK 3C
0.179	0.165	0.136	0.122	0.110	0.116	0.118	0.113	0.101

Table 3 shows the approximate melting temperatures of each solder studied, measured during cooling with dipped thermocouple. In general, the melting temperatures of solders without AC additions are similar to their original manufacturer's data, however, the additions of AC has caused slight changes in the melting point. The mechanism for such improvement may be due to the presence of AC particles by inhibiting the formation of inter-metallic compounds, which is not studied in this work. It

is also possible that inhibition the IMC formation may be due to a layer of AC at the interface of Sn rich and other phases acting as a diffusion barrier.

Table 3. Approximate transformation temperatures of solders studied

LK 1A	LK 1B	LK 1C	LK 2A	LK 2B	LK 2C	LK 3A	LK 3B	LK 3C
186.6	185.8	186.2	226.3	225.2	224.4	228.6	228.3	227.8

3.2 Microscopy

3.2.1. Leaded solders

Electron microscopy results were obtained from specimens with and without additions of nanoactive carbon particles are given in Figures 3-5 below. The results indicate that, in Sn/Pb standard alloy, particles are embedded in the softer phase of Pb, which is in light grey colour in Figure 3. All alloys in this series possess a matrix microstructure of primary Sn dendrites with inter-dendritically formed Sn-Pb eutectic, which is partly deteriorated during casting processing. The processing route to cast may influence the shape and size of the primary Sn phase within the microstructure. This has been well documented by Fan (9) and Ji and Fan (13). Since there is no additional thermal or mechanical processing on liquid/solid phase during or after the casting, which may affect grain sizes detrimentally (14), the grain sizes appear to be similar in all specimens. This is also dependent on the heat removal process at the interface of alloy and Al mold which was heated upto 35 degrees centigrade prior to casting to prevent excessive fast cooling. Sn phase separation is ensured through this process but two phase interdendritic phase was not observed possibly due to unetched surface.

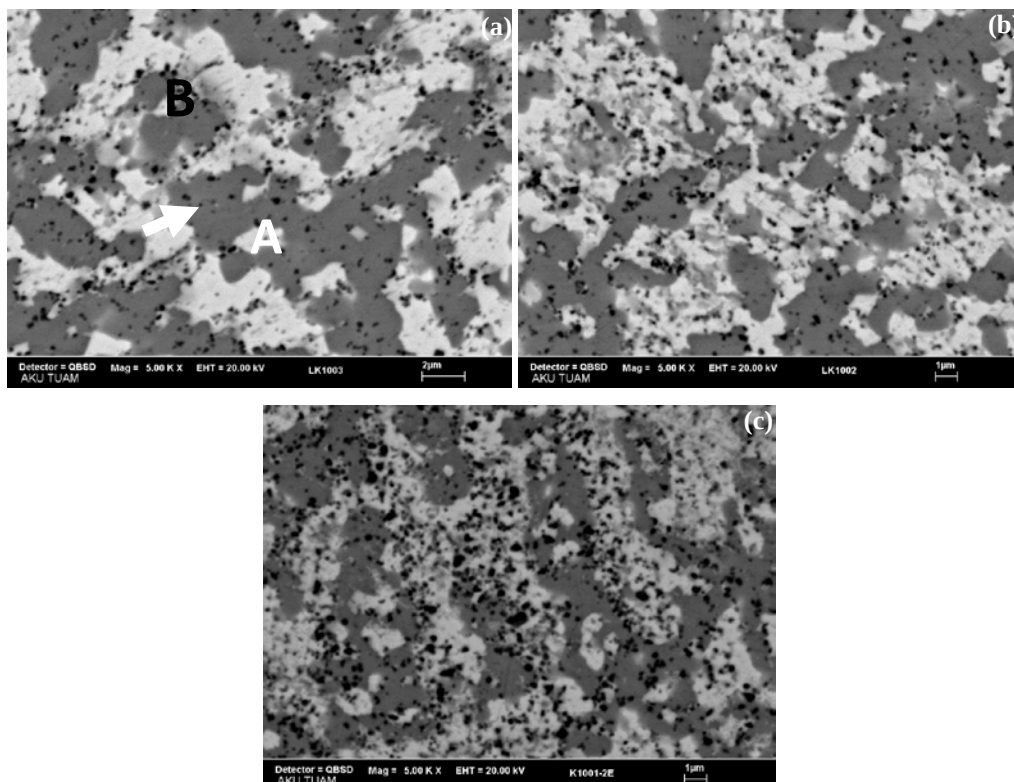


Figure 3. a) Sn/Pb alloy without addition (LK 1A), b and c) Active carbon additions were made to Sn/Pb solder alloys at the amounts of 0.14 (LK 1B) and 0.30 wt% (LK 1C), respectively. (A indicates Pb rich and B indicates Tin rich phase. The arrow in Figure 3a and Figure 3c indicate particles and the dendrite arm, respectively.)

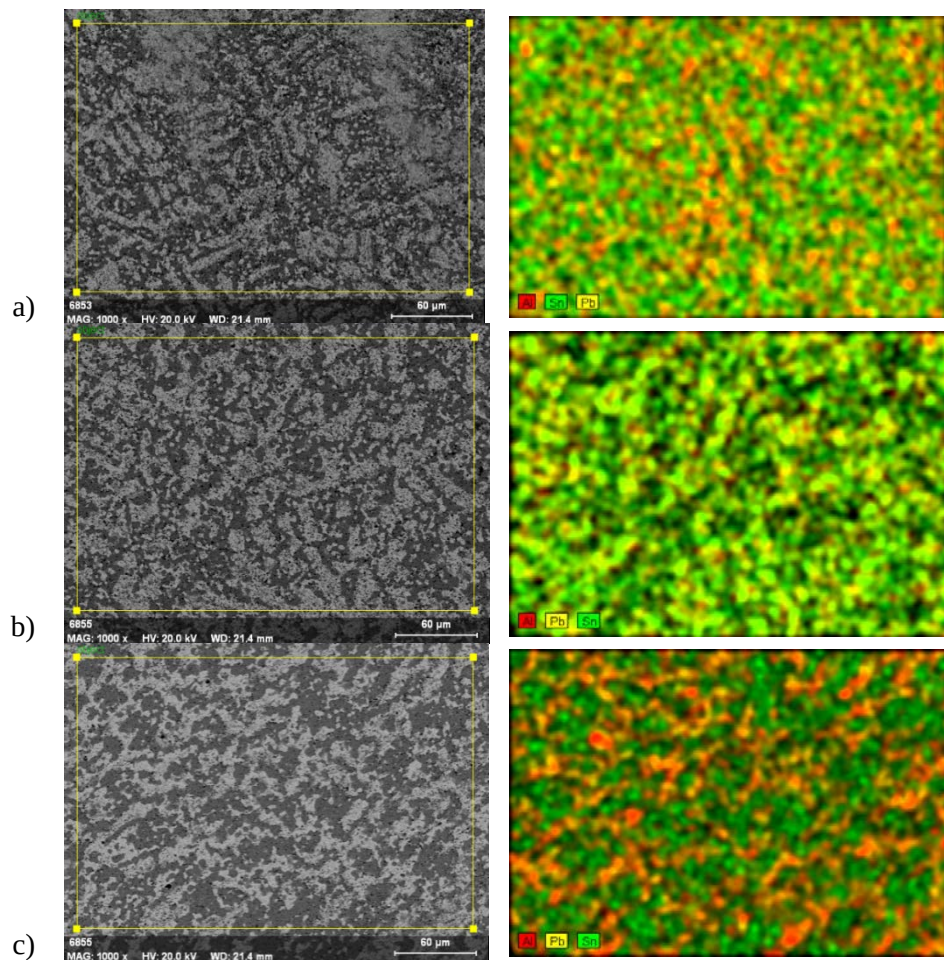


Figure 4. Effects of active carbon additions on the microstructural development of Sn/Pb alloys; a) no addition, b) 0.14 wt% and c) 0.3wt% AC additions with EDX mapping

SEM images in Figure 4 show that, as the amount of active carbon increases, the phase separation becomes more distinctively different by the selective separation of Tin into Tin rich regions, leaving dendrites morphologically deformed and poor in Tin. At high concentration of AC, it is more obvious to discern that the phase separation and the breakdown of dendrites may be associated with high surface area of AC particles which increases the surface energy of second phase regions in liquid state with instability of interface to dissociate in ample time.

3.2.2. Lead free solders

The unetched EBSD image of SnCu3 (Figure 5) and SnCu0.3 (Figure 6) alloy microstructures are shown with respect to the amounts of additions. A relatively well distributed carbon particles are random. The mixing of carbon particles are relatively successful, however, the coagulation of these particles are possible as seen in Figures 5 and 6. SEM image in EBSD mode does not show significant compositional difference due possibly to single phase of Sn matrix, although, hypothetical Sn-Cu alloy has a eutectic point. The inhibition of second phase may well be due to the presence of AC in Figure 5b and Figures 6b and c. Figure 5a and Figure 6 a do not contain any AC, which indicates that the amount of Cu is so small that it is not detectable by EDX sensor. Considering the pattern of particles, it can be said that particles follow the solidification fronts of grains and trapped in the grain boundaries as in Figure 5a. As the amount of AC increased, it has become more complex and indiscernable.

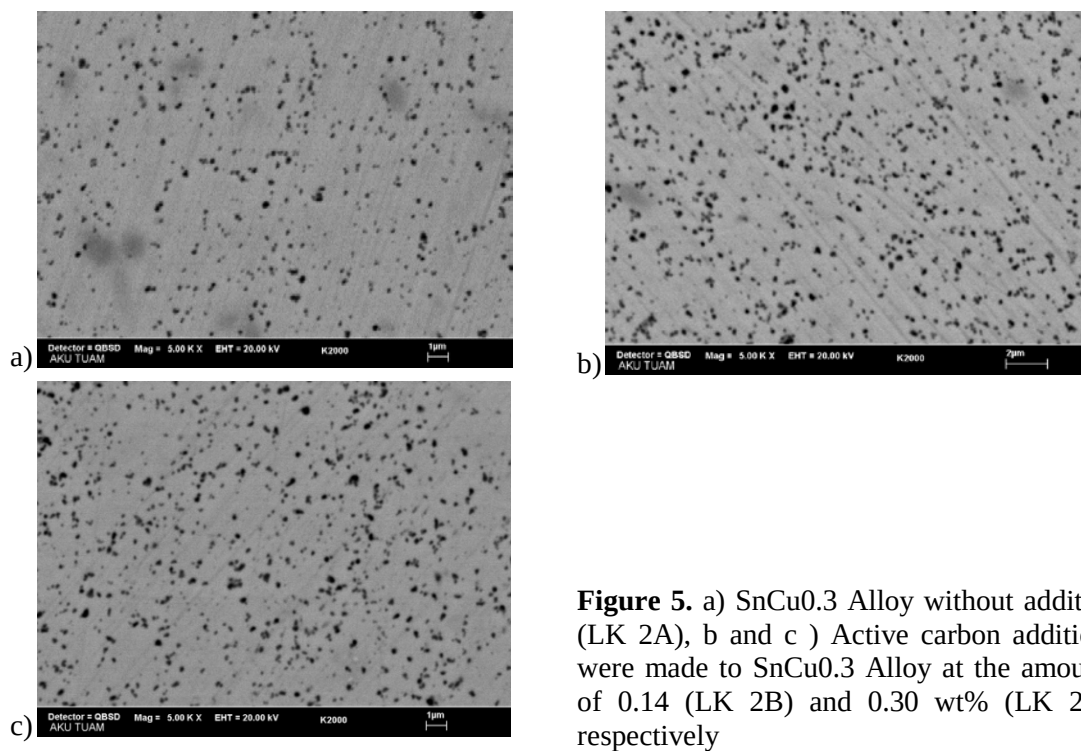


Figure 5. a) SnCu0.3 Alloy without addition (LK 2A), b and c) Active carbon additions were made to SnCu0.3 Alloy at the amounts of 0.14 (LK 2B) and 0.30 wt% (LK 2C), respectively

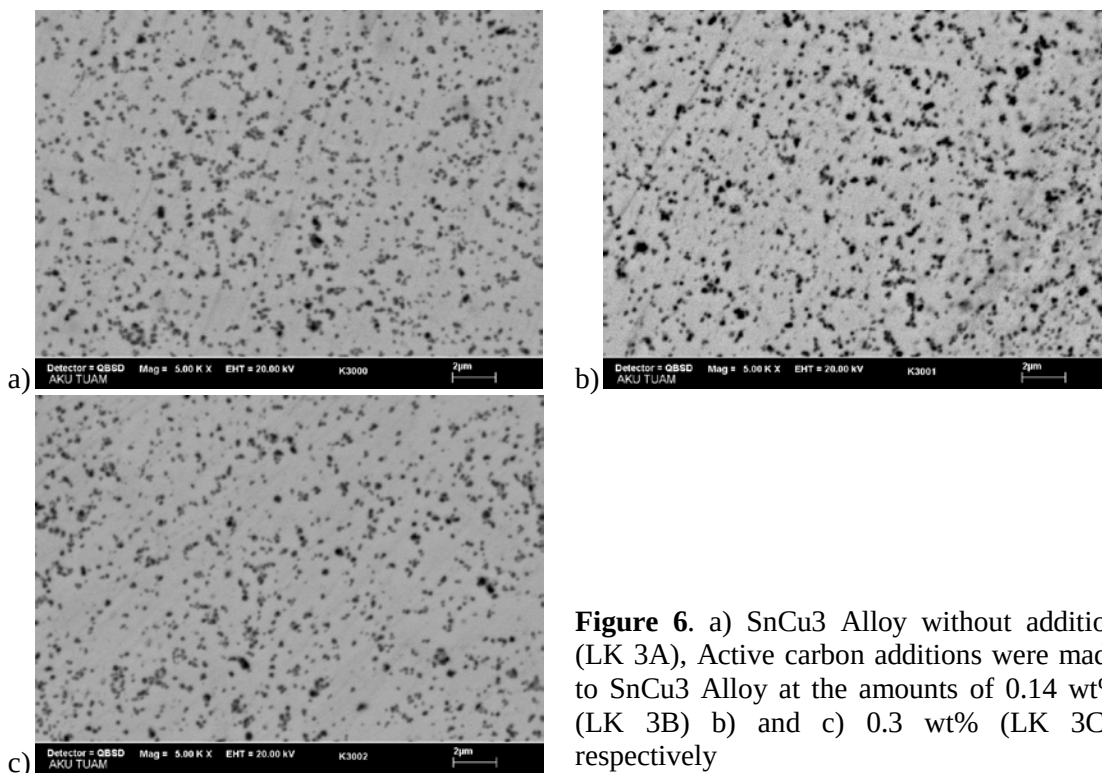


Figure 6. a) SnCu3 Alloy without addition (LK 3A), Active carbon additions were made to SnCu3 Alloy at the amounts of 0.14 wt% (LK 3B) b) and c) 0.3 wt% (LK 3C), respectively

4. Conclusions

Leaded solders were micro structurally affected by active carbon additions which possibly promoted phase separation at microscopic level. A possible mechanism for the phase separation may be due to the difference in surface energy effect of active carbon particles on the phases, resulting in the increase of their surface energies. Unleaded solders did not show any differentiation in their microscopic properties because of their single phase matrix and the additions did not cause any phase separation. However, the resistivity values may be positively affected by the addition of active carbon particles.

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