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EFFECT OF CARBON NANOTUBES ON THE MICROHARDNESS OF LEAD FREE SOLDERS FOR NANO-ELECTRONICS APPLICATION

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ABSTRACT

In this study, varying weight percentages of multi-walled carbon nanotubes (MWCNTs) were incorporated into 95.8Sn-3.5Ag-0.7Cu solder alloy to produce lead (Pb) free composite solders. The production route was powder metallurgy following mixing, pressing and sintering. The sintered samples were then characterized for their physical, structural and mechanical properties. With the addition of increasing amount of MWCNTs, the composite solder experienced a gradual decrease in density values and an improvement in wetting property. An improvement in the mechanical properties, in terms of microhardness was also observed with the presence of increasing weight percentage of carbon nanotubes. An attempt was made, to correlate the increasing addition of MWCNTs with the physical as well as the mechanical properties obtained.

Keywords: Pb Free Solder, Composite Solder, Mwcnts, Physical Properties, Mechanical Properties.

1. INTRODUCTION

The tremendous increase in demand for consumer products with the higher speed, smaller, thinner and portable features, lead the industry to move toward higher performance devices with increased functionality and higher interconnect density at very fine pitches. Sn-Pb solder technology is used as conventional interconnect material. While implementing the conventional solder for fine pitch interconnects applications, there is certain critical issues arised due to the lower melting point, lower strength, thermo-mechanical stresses and lower fatigue life. It is imperative to develop the solder technologies to serve the purpose of fine pitch applications. Solders with enhanced mechanical, electrical and thermal requirements are needed at this stage with critical emphasis on the lower diffusivity.

The electronics industry will make substantial progress toward a full transition to Pb-free soldering technology in the near future. The current leading Pb-free solder alloys are the ternary near-eutectic Sn–Ag–Cu alloys [1]. The Sn–Zn binary eutectic system is the basis of one of the most promising group of lead-free solders with the advantages of low melting point (198°C), excellent mechanical properties and acceptable costs [2,3]. However, Sn–Zn alloys suffer from easy oxidation and relatively poor wettability [4, 5]. To improve the oxidation resistance and wetting behavior of Sn–Zn solder, the Sn–Zn–Ag alloys have been developed. Additions of Ag are also capable of increasing the ductility and improving vibrational fatigue life of Sn–Zn based solders [6, 7]. The new Sn–Zn based alloys are still under development. Considering the improvement in wetting ability by Ag doping [8], McCormack and Jin [9] also reported that small additions of Ag can improve the ductility of Sn–Zn base solders, and a larger Ag alloy content resulting in the presence of Ag–Zn precipitates is not accompanied by an increase in strength . Composite approaches have been developed in lead-free solder research in an effort to improve the service temperature capabilities and thermal stability of the solder joints. Several challenges are faced in the development of lead-free solders since they are not just drop-in substitutes for traditionally used leaded solders. These challenges may be related to the solder melt temperature, processing temperature, wettability, mechanical and thermo-mechanical fatigue (TMF) behaviors, etc. Knowledge base on leaded solders gained by experience over a long period time is not directly applicable to lead-free solders. Thus, most of the lead-free solder developments for electronic applications are aimed at arriving at suitable alloy compositions.

Carbon nanotubes (CNTs) are of special interest due to their unique electronic, metallic and structural characteristics. The nano materials are very promising for the development of novel technological applications such as batteries, tips for scanning probe microscopy, electrochemical actuators, sensors etc.

Addition of CNTs influence the microstructure of the Sn-Ag-Cu (SAC) Pb free solder alloy to a great extent. The optical and scanning electron microscopic analysis shows that the increase in weight percentage of the CNTs causes the grain size to decrease to some extent. The CNTs are stronger and stiffer and their presence act as a constraint to the movement localized plastic deformation. Again the higher difference in Co-efficient of thermal expansion (CTE) between the SAC and the CNTs resulted in an increase in the dislocation density in the matrix causing hardening of the matrix. Dislocation density increases with the increasing density of reinforcement.

2. EXPERIMENTAL PROCEDURE

The 95.8Sn-3.5Ag-0.7Cu alloy powder was weighted and taken into a porcelain crucible in which predetermined amount of carbon nanotubes (CNTs) were taken. The weight of each sample was taken to be about 1.50 gram where CNT was incorporated according to weight base with 0.01 wt.%, 0.02 wt.%, 0.05 wt.%. The mixing of alloy with CNT is very difficult and time consuming process. In the crucible the alloy powder and CNT was stirred with a stainless steel rod very carefully so as not a single particle of the alloy or the CNT was lost until there is complete mixing and no visibility of the black CNT. This takes about 2.5-3 hours. The difficulty of mixing of the CNTs can be attributed due to the following facts of the CNTs.

Firstly, the nano particles distributed at the grain boundaries of composite solders enhance the mechanical properties of the solder joint. However, the nano particles may also gather together to form brittle agglomerates in the solder matrices due to their surface energy which will degrade the strength of the composite solders. Hence they must be distributed in the solder matrix homogeneously during composite processing.

Secondly, this may sound easy but really be difficult in the actual practice of preparation of composite solders. In fact by mechanical mixing nano particles with solder powders or solder paste even when the composite mixers are stirred for a long time, agglomerates are still formed in composite solder matrix. The mixer was then pressed by hydraulic press at 5 ton. Then it took the shape of a tablet with very smooth surface. The tablets were then sintered at temperature 175°C for about 1.5 hours in inert furnace atmosphere.

The samples after sintering in the furnace in inert atmosphere were polished against cloth with γAl2O3 followed by etching with 2% Nital. Subsequently the samples were washed with clean water and cleaned the surface with acetone and then they were observed under optical microscope with digital camera (LEICA-MZFLIII) which was followed by scanning electron microscope (SEM). The backscattered electron imaging mode of the SEM was used for the microstructural study. Polishing was necessary to obtain polished, smooth and flat parallel surface before indentation testing. Thus, polished sample were placed in a Vickers shimadzu microhardness tester to measure the microhardness. At least four reading of different indentation were taken for each sample at room temperature.

3. RESULT AND DISCUSSION

The microhardness was determined using the standard loading SHIMADZU 341-64278 machine. The load used was 25gm and the loading time was 10s. The indenter was a pyramidal diamond with facing angle of 136°. The diagonals of the diamond were measured using the standard machine KYOWA, TOKYO, No: 970216, Japan. The diagonals of the diamond after measuring were taken average and with the help of the chart available in the laboratory the Vickers Hardness was measured. The Vickers Hardness data is given in fig 1.

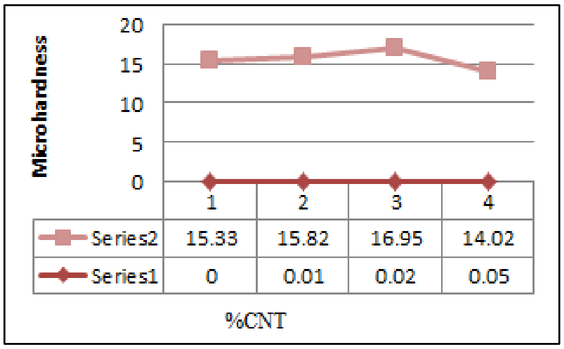

Fig 1. Microhardness vs weight percentage of CNTs

The density of the composite solder was determined by Archimedes principle [10] and distilled water was used as immersion fluid. The data obtained is listed in fig 2:

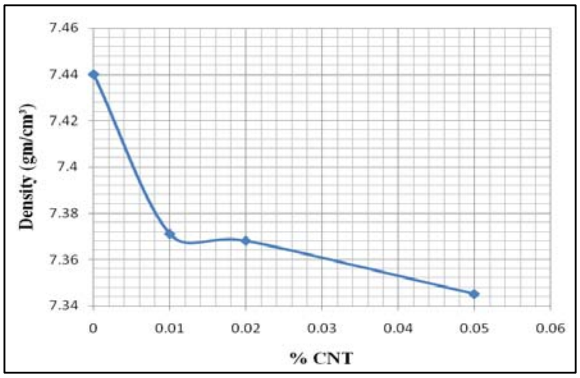

Fig 2. Density vs weight percentage of CNTs

The above data shows that the addition of increasing percentage of CNTs results in decreasing the density of the solder alloy. This could be primarily due to the much lower density of CNTs (upperbound density = 2.6 g/cm3) [10] as compared to that of SnAgCu solder (density = 7.44 g/cm3).

The microstructures of the CNT doped SAC alloy were also examined with Scanning Electron Microscope in the BSE and SE mode. The structures obtained are shown below. The first figure shows the as cast sintered structure. It shows the matrix consists with the Sn in which some intermetallic are distributed more or less uniformly. The amount of the intermetallic is not higher in number. The grain size is also large. The structure with 0.01% CNT shows the refined grains compared to the non-doped structure. Here the number of intermetallic is higher. Successively the increasing amounts of CNTs represent their grain refining effect and the higher degree of intermetallic formation.

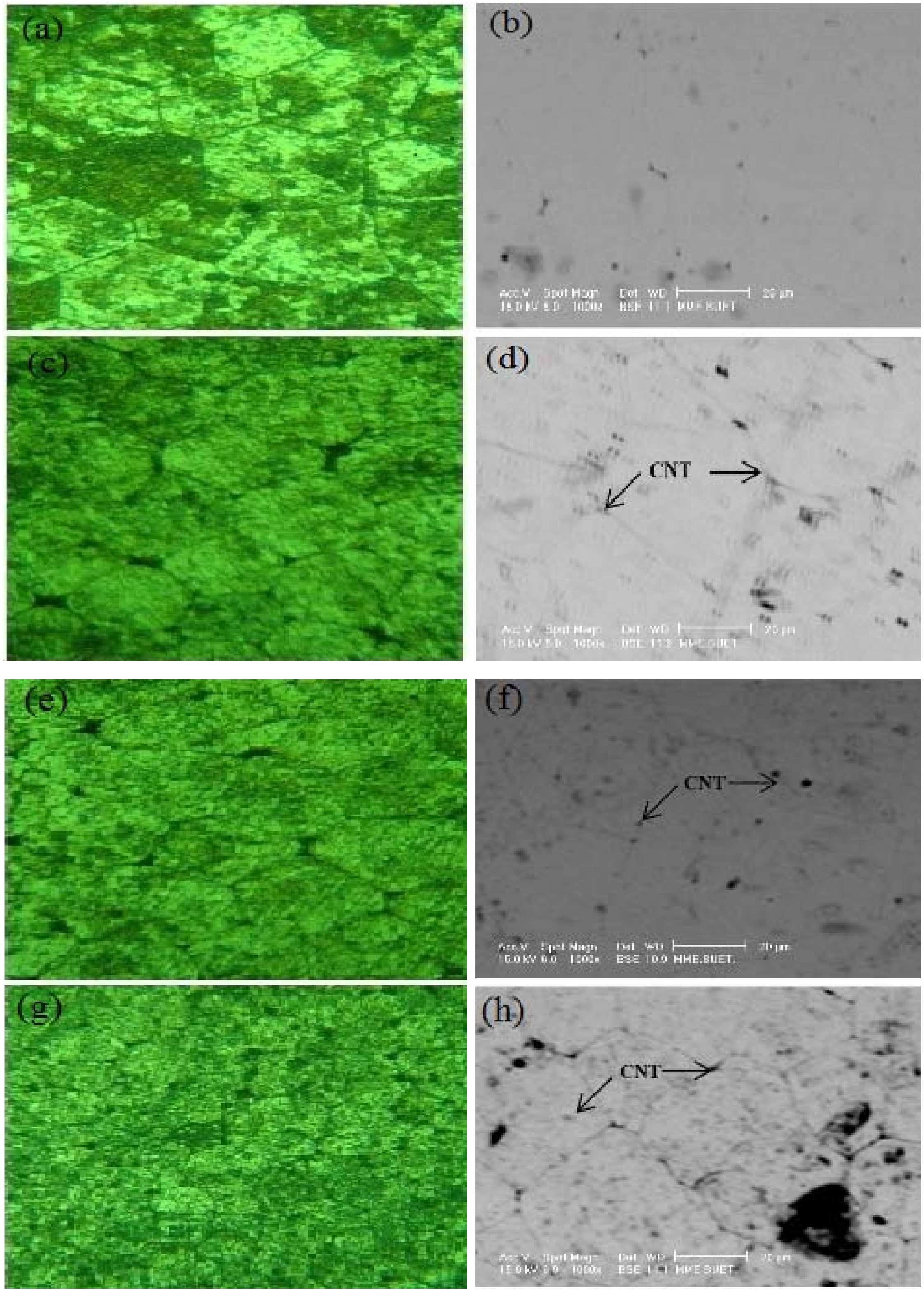

Fig 3. Micrograph of alloys; (a) 95.8Sn-3.5Ag-0.7Cu (optical) (b) 95.8Sn-3.5Ag-0.7Cu (SEM)
(c) 95.8Sn-3.5Ag-0.7Cu-0.01CNT (optical) (d) 95.8Sn-3.5Ag-0.7Cu-0.01CNT (SEM)
(e) 95.8Sn-3.5Ag-0.7Cu-0.02CNT (optical) (f) 95.8Sn-3.5Ag-0.7Cu-0.02CNT (SEM)
(g) 95.8Sn-3.5Ag-0.7Cu-0.05CNT (optical) (h) 95.8Sn-3.5Ag-0.7Cu-0.05CNT (SEM)
under compacted condition

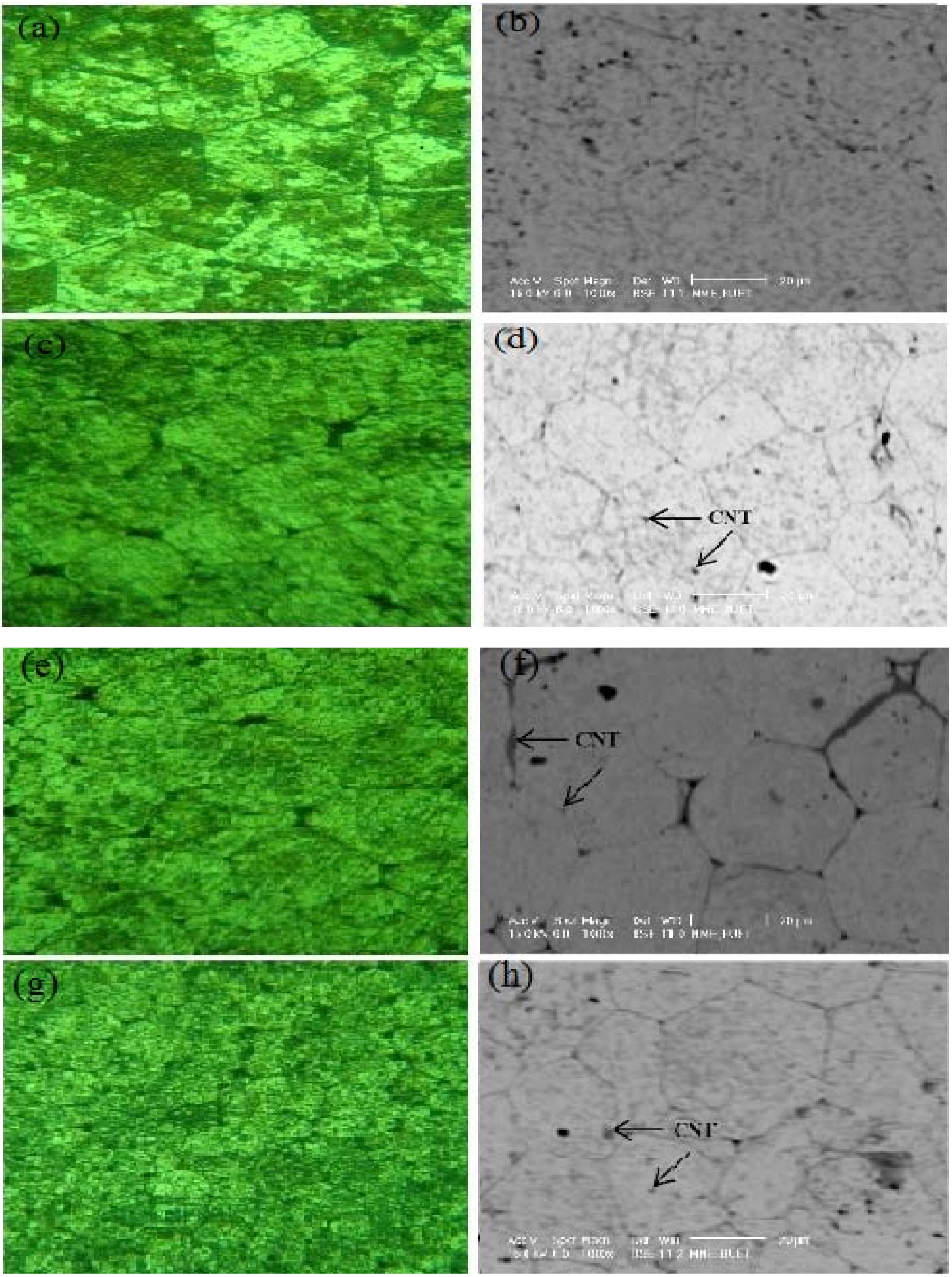

Fig 4. Micrograph of alloys; (a) 95.8Sn-3.5Ag-0.7Cu (optical) (b) 95.8Sn-3.5Ag-0.7Cu (SEM)
(c) 95.8Sn-3.5Ag-0.7Cu-0.01CNT (optical) (d) 95.8Sn-3.5Ag-0.7Cu-0.01CNT (SEM)
(e) 95.8Sn-3.5Ag-0.7Cu-0.02CNT (optical) (f) 95.8Sn-3.5Ag-0.7Cu-0.02CNT (SEM)
(g) 95.8Sn-3.5Ag-0.7Cu-0.05CNT (optical) (h) 95.8Sn-3.5Ag-0.7Cu-0.05CNT (SEM)
under sintered polished and etched condition

The energy dispersive X-ray was done in order to determine the phases present in the composite solder and their percentages. The graphs showed that there were four distinct elements named Sn, Ag, Cu, and C. In the as cast structure there were some C available which may come during blending or pressing operations. Moreover in the solder alloy contained 0.05%CNT showed less C content which may be due to agglomeration of the C nano particles. But the results obtained were consistent with the addition percentage of the CNTs into the solder matrix.

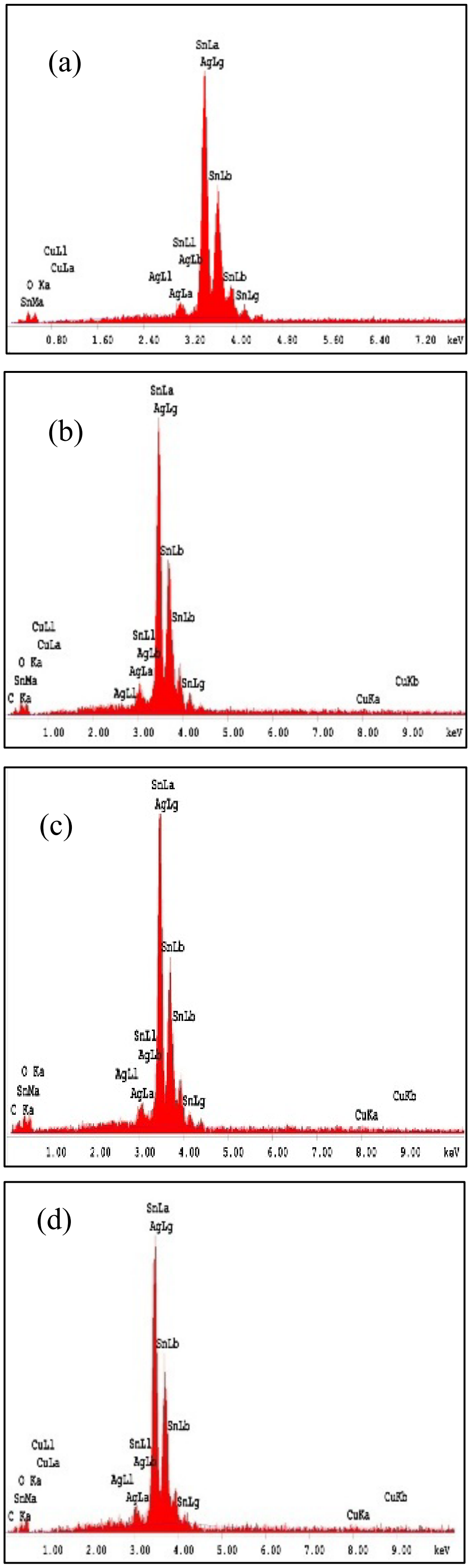

Fig 5. EDX graph of (a) 95.8Sn-3.5Ag-0.7Cu
(b) 95.8Sn-3.5Ag-0.7Cu-0.01CNT
(c) 95.8Sn-3.5Ag-0.7Cu-0.02CNT
(d) 95.8Sn-3.5Ag-0.7Cu-0.05CNT

4. CONCLUSION

- SnAgCu solder composites, reinforced with 0 wt. %, 0.01 wt. %, 0.02 wt. %, 0.05 wt. % of MWCNTs were successfully synthesized via the power metallurgy technique.
- Mechanical characterization results revealed that the presence of increasing weight percentage of CNTs in solder matrix led to overall improvement in microhardness.
- A threshold addition of reinforcements was observed to aid in optimizing the properties of the composite solder.

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