Reduction process of Cu/Sn nanocomposite by Plasma Furnace

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Abstract: Pre-milled copper and tin powder was subjected to heat treatment to investigate the effect of polyethylene glycol surfactant powder on it. The existing thermographic shows that the delta value of the copper-tin phase powder formation reaction is much higher than other chemical reactions, and this increase in energy is related to the new phase formation. Results of the DTA heat test in the direction of temperatures 300, 600, and 1000 °C were selected for this heat treatment and after that non-destructive and mechanical tests were performed on it, the phases Copper and tin are formed with great intensity and the particle size is reduced to 5 µm. On the other hand, the hardness of the resulting powder is greatly increased and about 220 HV0.1, all of which are due to the effects of adding a surfactant to copper and tin powder and ceramic phase made in this alloy.

Keywords: Cu/Sn, mechanical thermal, surfactant, polyethylene glycol, Nanocomposite.

Highlights:

- Mechanical alloying can achieve a very good quality alloy with the lowest cost and highest efficiency.
- Polyethylene glycol is used as a highly functional surfactant, which is mixed to prevent the powders from agglomeration.
- New phases of copper and tin had been formed with the surfactant, and the peaks were very high, indicating a large amount of these phases.
- Powder particle size shows that the average size was about 5 μm.
- The resulting hardness is greatly increased from 170 to 220 HV5.

1. Introduction

Today, almost everyone is aware of the properties of copper and tin and knows that these two precious metals are used in our daily lives. Mori *et al.* Found that when materials are reduced to finer nanometer-sized particles, they can have special mechanical and physical properties [1].

However, the production process of these powders sometimes faces many problems that prevent a desired and effective alloy. In the case of copper powder and tin powder during mechanical alloying, the main problem is the excessive adhesion of these two powders to each other, which makes the mechanical alloying process difficult.

Rosen and Kunjappu, in their book "*Surfactants and interfacial phenomena*", published in 2012, used substances called surfactants to explain the solution to this problem [3]. Surfactants are substances that, when used in very small amounts, significantly reduce the surface tension of water [1]. Brenntag mentioned in his paper that, surfactants help distribute one phase into another [5]. This definition is not limited to solid-liquid suspensions and may include liquid-liquid systems. When these materials are used to stabilize solid particles in a liquid, they are called dispersants. The molecules that make up surfactants tend to accumulate in the interface. This is because their structure consists of two parts, one part of which is soluble in the solvent and the other part of which is insoluble. These molecules are preferentially oriented in such a way that the soluble part binds to the liquid and the insoluble part binds to the solid surface [2]. Surfactants are usually organic compounds that have hydrophobic groups that act as tail and hydrophilic groups that act as heads, so they usually dissolve sparingly in water and organic solvents.

Rezayat *et al.* in 2020, performed mechanical alloying of copper oxide powder and tin oxide powder in which carbon was used as a separator or surfactant, but the results of the effect of carbon in this alloy from a mechanical and hardness point of view have not been stated [6].

Polyethylene glycol has always been welcomed in industry and medicine due to its chemical nature [7]. By adding this material to copper and tin oxide powder and combining the two and performing mechanical alloying steps, unique properties can be expected from this alloy. The formation of new phases in this alloy has occurred by the addition of polyethylene glycol and its effect is directly evident in the mechanical properties [9]. Among the industries, oxides are always mentioned as disposable materials, but by using the plasma tube furnace and performing the process of heat treatment of oxide reduction, very practical materials with high and desirable mechanical properties can be obtained from the same materials.

Tanzi [10] was found the desired temperatures for the desired heat treatment to reduce oxide work, which can be made a little easier with new methods and the use of various tests, one of which is differential thermal analysis with high-temperature accuracy demonstrates the optimal performance of heat treatment with a tube furnace [11].

The purpose of this project in the first stage is to produce alloy powder by a simple and accessible method and then to optimize this method of mechanical alloy production. In the next step, investigate the effect of adding a surfactant to the alloy powder produced in this process, which can improve the mechanical properties of the alloy.

2. Materials and Methods

Copper oxide powder, tin oxide with an average particle size of 50 μm, and pre-milled graphite powder with sheet-shaped particles with a particle size of fewer than 50 μm were used. As shown in figure 1, polyethylene was added to these raw materials as a surfactant and all materials entering the mill chamber and the final product was prepared for various tests. To perform this process, the desired metal powder or alloy must be poured into containers filled with hard bullets. As a result of the collision of the pellets and the chamber with the powder particles, the grain size of the material gradually decreases and finally reaches the nanometer size. Because a lot of energy is applied to the powder particles during the alloying process and mechanical activation, and in general, due to the severe plastic deformation of the powder particles during mechanical alloying, the crystals are severely crushed and finally the powder particles continue to grind. The by-grains are converted to 1 nm compared to nano-crystalline powders prepared by conventional methods, when the powder particles are compressed by hot methods, the final structure of the particle-containing nanometer grains is almost free of misplacement. In other words, nano-crystalline regions in powders prepared by the mechanical alloying method are separated by high-density displacements, and the final properties of nanopowders prepared by mechanical alloying are different from nanopowders obtained by conventional methods. In this case, approximately 50% of the atoms are in the grain boundaries, which causes many changes in mechanical and physical properties. This process is typically done to prevent environmental pollution in a neutral atmosphere and is used to make solid metal and ceramic powders. Cold welding and failure are two major phenomena in mechanical alloying. The alloying process continues only until the welding rate reaches equilibrium with failure [6].

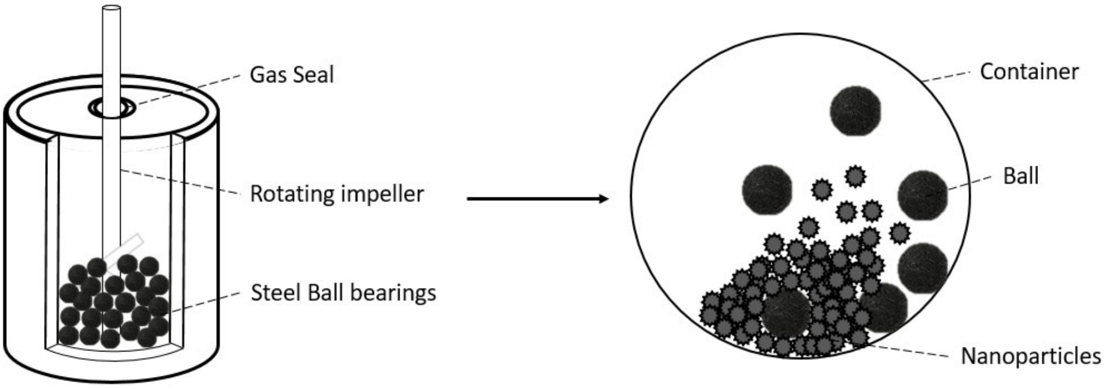

Figure 1. Schematic of Ball milling chamber with elements.

Surfactants reduce the surface tension of water and particle by adsorption of the air-water interface. They also reduce the interface tension of the water-oil interface by adsorption of the liquid-liquid interface. A large number of surfactant molecules can bind together in solution to form masses [12], [13] [14]. They call it micelle, the concentration at which these micelles begin to form is called the critical concentration of micelles. When the micelles begin to form, their tails form a nucleus like a drop of oil and their ionic head forms an outer shell that improves optimal contact with water [15]. In figure 2, the chemical structure of polyethylene glycol is shown as a compound of ether with various industrial and medical uses with the chemical formula $C_2nH_4n + 2On + 1$ [16].

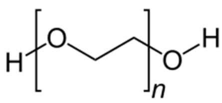

Figure 2. Chemical structure of Poly Ethylene Glycol as a surfactant.

When polyethylene glycol is added to copper and tin oxides, the following compounds and chemical equations are obtained for the products [3].

$$CH_2 = CH_2 + 3O_2 + Sn + Cu \rightarrow CuSn + 2CO_2 + 2H_2O \quad (2\text{-}1)$$

$$K_C = \frac{[CuSn][CO_2]^2[H_2O]^2}{[CH_2{=}CH_2][O_2]^3[Sn][Cu]} \quad (2\text{-}2)$$

$$\text{Rate} = -\frac{\Delta[CH_2{=}CH_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = -\frac{\Delta[Sn]}{\Delta t} = -\frac{\Delta[Cu]}{\Delta t} = \frac{\Delta[CuSn]}{\Delta t} = \frac{1}{2}\frac{\Delta[CO_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} \quad (2\text{-}3)$$

$SnO_2+CuO+1.5C \rightarrow Sn\text{-}Cu+1.5CO_2$ ΔG_{298} =54.1 kJ/mol., ΔH_{298}=144.6 kJ/mol. (2-4)

$SnO_2+C \rightarrow Sn+CO_2$ ΔG_{298} =12.1 kJ/mol., ΔH_{298}=184 kJ/mol. (2-5)

$2CuO+C \rightarrow 2Cu+CO_2$ ΔG_{298} =-67.8 kJ/mol., ΔH_{298}=-394.5 kJ/mol. (2-6)

In figure 3, all the above equations are drawn and it shows that (SnCu) has a big ΔG and a lot of energy for creating new phases.

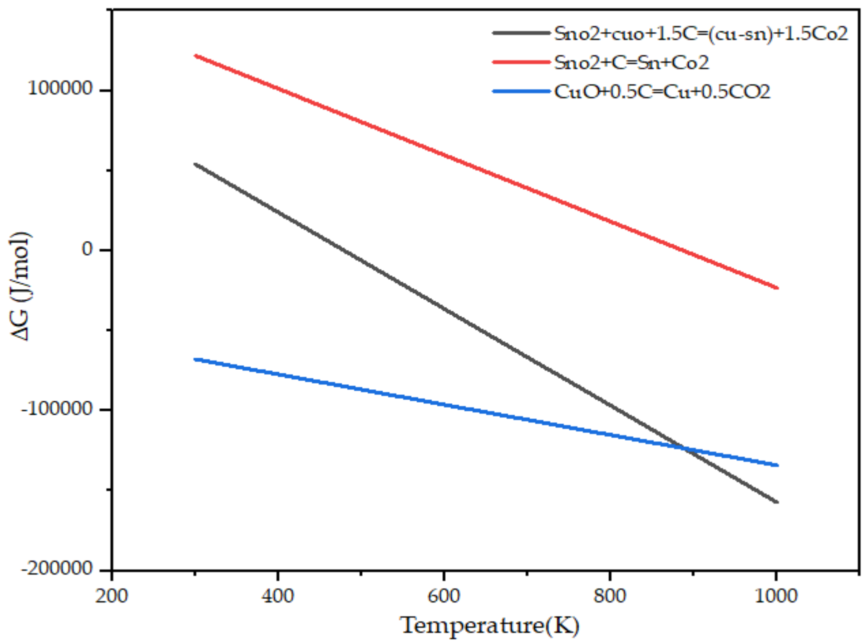

Figure 3. Thermograph of Sn and Cu balanced equations.

All the contents inside the mechanical mill chamber undergo different interactions when mixed. According to figure 4, it can be seen that part B first breaks the phases and transverse failure occurs in the case of brittle particles, and in part C cold welding occurs between the particles, which these interactions cause new ductile phases and becomes very resistant to mechanical tests.

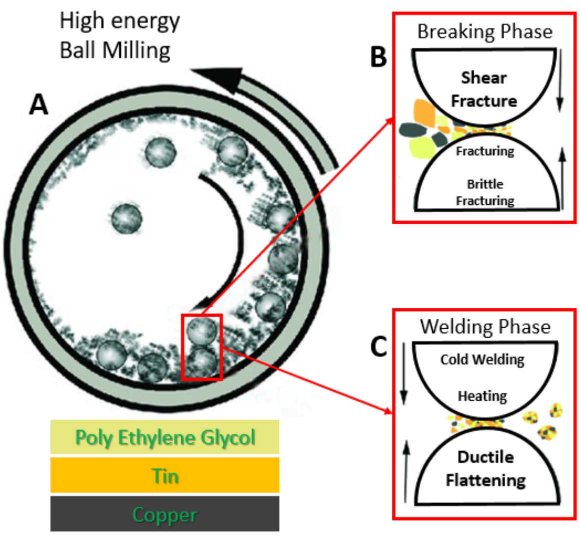

Figure 4. Schematic of process and reactions with surfactant in the ball milling chamber.

After grinding the powders, heat treatment was performed in a tubular plasma furnace, which reduced the metal alloy powder. The fine particles of poly Ethylene glycol surfactants reacted well with copper and tin oxide powders, and the final powder had very good mechanical properties. According to the obtained heat and chemical reactions, heat treatment was performed with a tube furnace at temperatures of 300, 600, and 1000 °C all samples for 1 hour. All tests were performed on a sample of heat treatment at 1000 °C and the results were fully has been expressed.

In figure 5 schematic of the plasma, tube furnace showed, there is a lot of reasons for using this furnace but one of the big reason is avoiding pollutions and oxidation because this powder alloy is very sensitive to combination with air and by using this furnace in the final product there are no impurity particles.

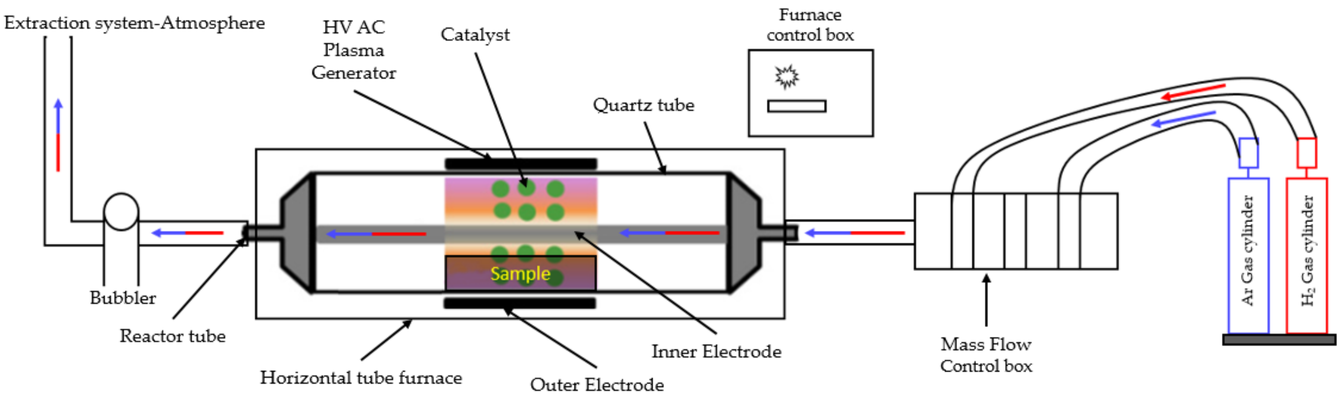

Figure 5. Schematic of Plasma tube furnace.

In this furnace, a catalyst is used which is a fresh model of Hydrodesulphurization (HDS) type, and this catalyst contains the elements like cobalt, nickel, and molybdenum. The process used argon gas as a vacuum condition and for this powder temperature raised until 1500 °C, the point it was to prevent re-oxidation of the regenerated products, not to use very high plasma temperatures.

3. Results and discussion

1.1. *X-Ray Diffraction (XRD)*

The X-ray diffraction patterns of the samples were obtained by HUBER, equipped with a $Cu_{K\alpha}$ beam manufacturer with a voltage of 40 kV. In this system, the scattering angle and the speed of the detector count are controlled by the computer, and thus the width and intensity of the peaks can be easily calculated. According to the XRD diagram, figure 6, in the case of the copper and tin sample in figure 7, there was a copper and tin phase at 45 degrees, which was lost after the heat and mechanical operations, and partly due to the effects of polyethylene glycol. At 27 degrees, the peak has shifted, which also happened at 34 degrees, indicating the creation of a new hard phase. Finally, at 35.6 and 38.85, we have very large dupes, and at 48.9, this peak is repeated, which is all the result of a combination of copper and tin with the surfactant of polyethylene glycol.

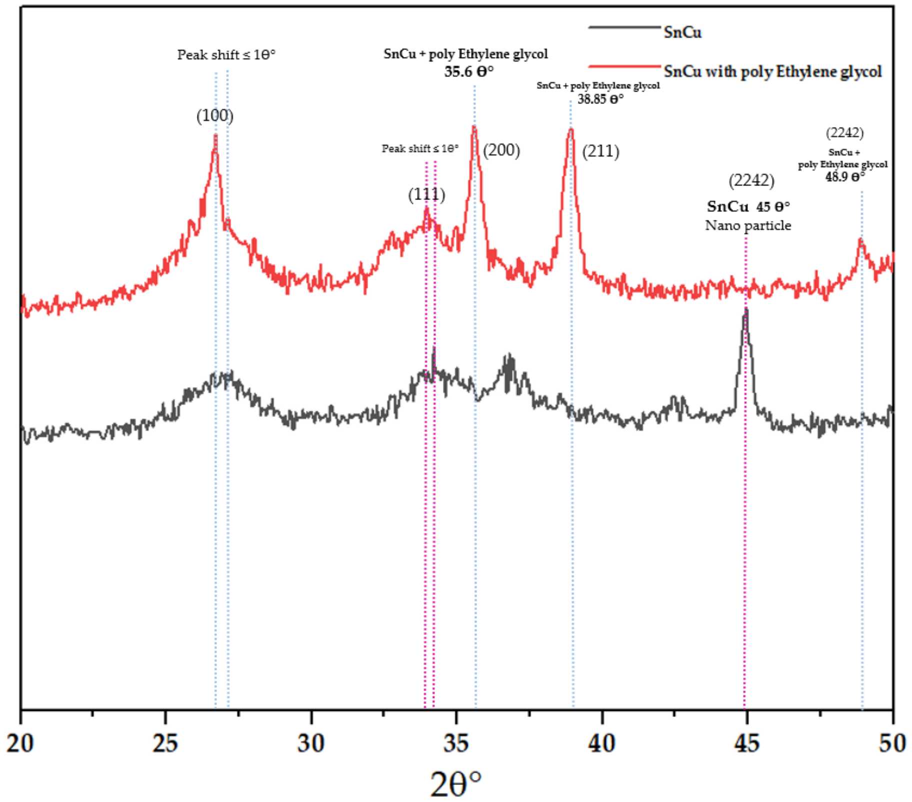

Figure 6. XRD diagram of SnCu and SnCu with polyethylene glycol.

1.2. Differential Thermal Analysis (DTA)

Thermogravimetry/Differential Thermal Analyzer STA7200RV by Hitachi was used for the DTA test, a weight of 7.485 grams of copper and tin powder with polyethylene glycol was selected for heat testing and the results are shown in figure 7 in this diagram. It is quite clear that both the TG and DTA diagrams have occurred together in the parts marked on the diagram, and this change in the peaks indicates the creation of a new phase, the copper and tin phase, concerning the temperatures obtained from this test, which are approximately 300, 600 and 1000 °C, were performed by heat treatment of the tube furnace on the powder.

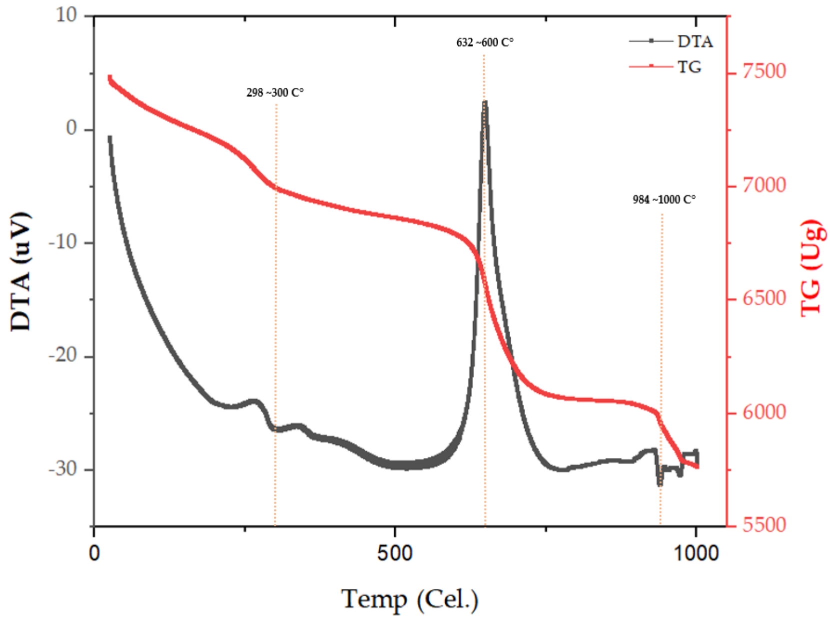

Figure 7. DTA and TG diagram of SnCu with polyethylene glycol till 1000 °C.

According to the diagram, it can be seen that the gram weight has decreased from 7.485 grams to about 5.755 grams, and the powder in this process has lost some water between the particles and moisture, and these phase changes are also due to these interactions.

1.3. Grain Size of the final product

The particle distribution of copper oxide and tin oxide powders as well as copper and tin as metallic is shown in figure 8. The predominant size distribution of the powder in this material is in the range of 1-15 μm and the average particle size is 5 μm.

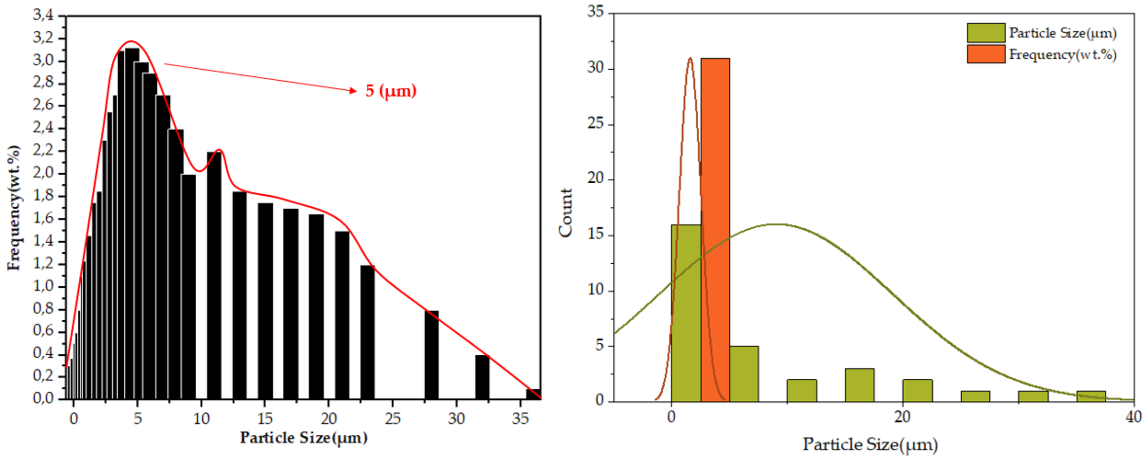

Figure 8. Grain size histogram with Gauss line guide as average particle size.

Figure 9 shows the contribution of a particle in the area of 5 μm^2 and this image generated with ImageJ software, as it clearly showed in this area most of the particles have overlapping, that it means the particle size could be changing to a range of 1 to 5 μm, and deviation standard of particles is about 5 μm, that is completely mentioned in figure 8 and figure 10.

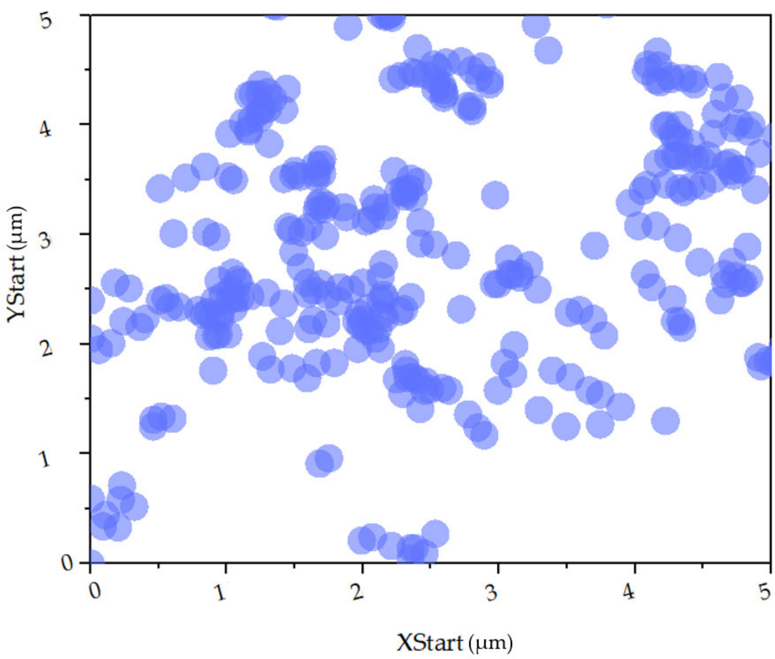

Figure 9. Contribution of Cu, Sn, and surfactant particles in 5 µm² area.

1.4. Scanning Electron Microscopy (SEM)

Electron microscope images of the sample and the final powder produced clearly show the adhesion between the powder particles. Figure 10 is taken at magnification 30kX and the particles are well defined and then transferred to magnification 60kX and magnification 100kX to better understand how the particles fit together and their adhesion and dimensions and shapes. The EBS diagram is also drawn for better analysis of the reactions that occur between the elements, which shows the resulting elements and the surface of the powder sample.

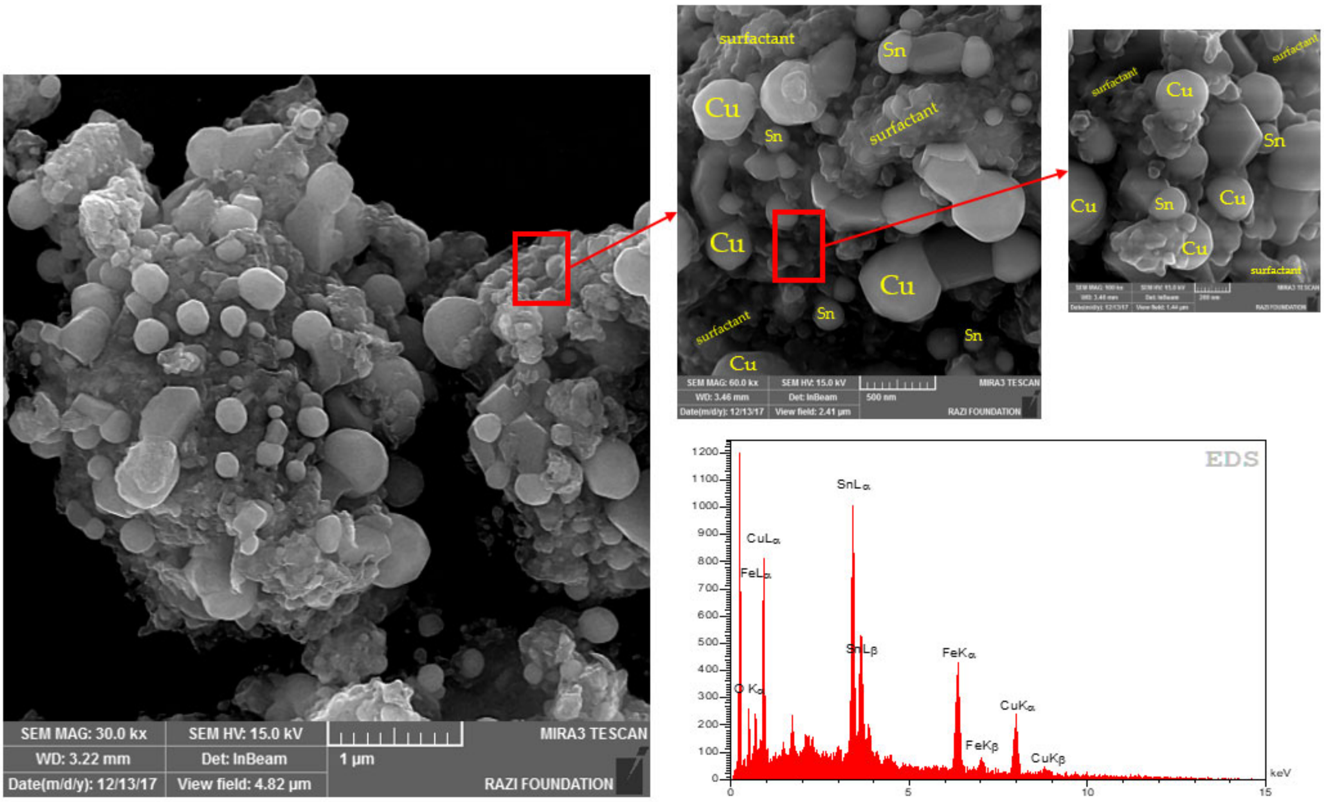

Figure 10. SEM image of final product SnCu with polyethylene glycol and EDS diagram.

1.5. Micro Hardness

In the First step, the sample after heat treatment by 1000 °C was selected for this test, because all properties and all phases exist in that sample. mechanical samples of Cu, Sn, SnCu, and, SnCu with polyethylene glycol as a surfactant were produced in the form of tablets using the cold press to be sent for rigorous mechanical testing. These samples were pressed according to figure 11, the results of which can be examined and show that the sample showed a higher density with surfactant.

After compression test and production of hardness test specimens, this hardness test is performed that the exact hardness values are given for all specimens and confirms the high hardness results of copper and tin specimens with surfactant.

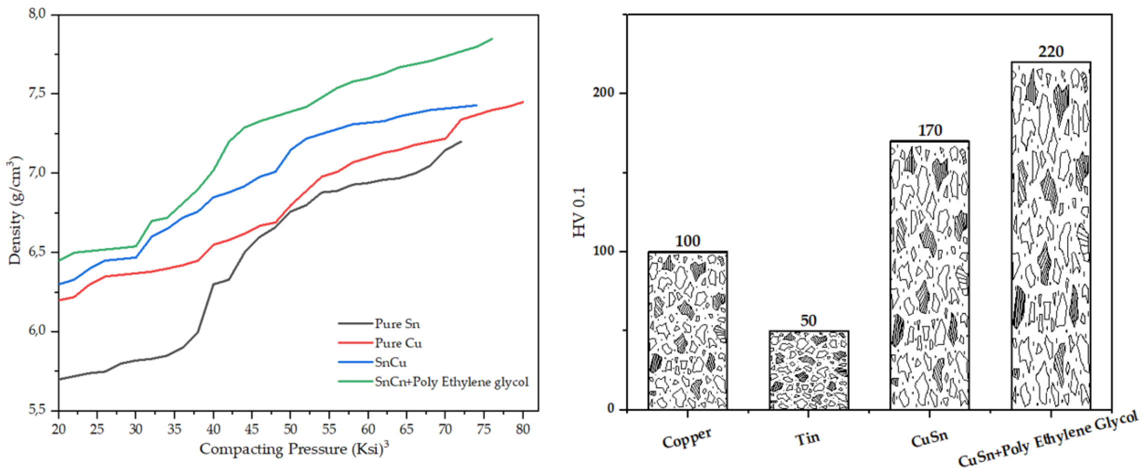

Figure 11. Compacting diagram and hardness of Cu, Sn, SnCu, SnCu with polyethylene glycol.

5. Conclusions

Mechanical alloying, as mentioned in most articles, is one of the easiest and best methods for alloying, which can achieve a very good quality alloy with the lowest cost and highest efficiency.

The powder obtained in this method can be created from various dimensions, the least of which can be nanometer dimensions. During mechanical milling, fine and coarse particles are successively broken and welded together, resulting in the production of nanocrystalline powder. But in the meantime, the particles are very sticky and the result is that they become agglomerated, which is undesirable, which is why a substance called surfactant is used. Polyethylene glycol is used as a highly functional surfactant, which is mixed as a powder with copper oxide and tin oxide powder to prevent the powders from sticking together.

This powder shows different mechanical properties at different temperatures, and some of its properties were shown by performing various experiments on it. X-ray diagram showed that new phases of copper and tin had been formed with the surfactant, and the peaks were very high, indicating a large amount of these phases. To perform the heat treatment of this powder reduction, it was necessary to carefully study the DTA and TG diagrams. This diagram showed new changes in the diagram at 300, 600, and 1000 °C with a decreasing trend in the diagram. It means creating a new phase of copper and tin.

Measurement of powder particle size shows that the average size was about 5 μm, which can also be seen in the SEM images. In microscopic images, the shape of the powder particles and how they are placed can be seen, and they also show diagrams of the available elements.

The hardness of the resulting powder was determined and the results show that with the addition of surfactant and the creation of a ceramic-like phase, the hardness is greatly increased.

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