

Microstructure and mechanical properties of Sn-Cu alloys for shielding materials in detonating and explosive cords

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Abstract

In order to develop alloys as the substitute of Pb-based materials for shielding materials in detonating and explosive cords, the materials requirement was analyzed and Sn-Cu based alloys were selected as candidates for this purpose. Four alloys including Sn-0.3wt.%Cu, Sn-0.5wt.%Cu, Sn-0.7wt.%Cu, and Sn-1.0wt.%Cu were processed from melting, casting, rolling, and annealing. The microstructure and mechanical properties of the alloys were investigated under as-cast, as-rolled and as-annealed conditions. The results confirmed that Sn-Cu based alloys are the appropriate substitute of Pb-based alloys for the application of detonating and explosive cords. The advantages of Sn-Cu alloys include resource abundant, low materials cost, non-toxicity for health and environment, relatively high density for supplying sufficient impulse energy and momentum for penetration, acceptable mechanical properties, and easy in melting, casting, extrusion, rolling and drawings. The microstructure of hypoeutectic Sn-Cu alloys was characterized by Sn-Cu solution and Sn-Cu₆Sn₅ eutectic phase. The annealing heat treatment was not able to modify the microstructure. The Sn-Cu based alloys with 0.3 to 1.0wt.%Cu offered the yield strength from 26.1 to 50.8MPa, ultimate tensile strength from 30.1 to 51.5MPa and elongation from 87.5 to 56.0%, which were comparable with the mechanical properties of the currently used Pb-based alloys. More importantly, Sn-Cu alloys exhibited strain softening under tensile stress, which was critically beneficial to the shielding manufacture and subsequent processing after assembly with high-energy explosive materials.

Keywords:

Sn-Cu alloys; Microstructures; Mechanical properties; Casting; Rolling; Heat treatment

1. Introduction

The applications of explosion have been very popular in numbers of engineering areas. As a critical part, the detonation cord is essential to detonate charges with a controlled pattern in a very reliable rate about 9000-12000 m/s [1]. This is particularly useful for demolitions when structural elements need to be destroyed in a specific order. Although a large number of different structures have been used in industry [2], the conventional cords are mainly used for energy transfer and the cord itself does not need to provide sufficient energy for explosion. Therefore, it is not applicable for the cases where the cord is required to release impulse energies in a specific direction during explosion [3]. On the other hand, the linear shaped charges are able to provide explosion energy along a specific direction, but the size and the function of shaped charges are not suitable for thin and long tubes to form a complex profile during explosion [4]. Therefore, to combine the structural advantages in detonating cords to achieve the function of linear shaped charges, the advancement in the purpose-defined applications has enabled the development of explosive cords by altering the shielding materials in detonating cords (also called shock tube in some cases) [5, 6]. The challenges for this development are that the metallic shielding materials should meet the requirements in both manufacturing and function.

The metallic shielding materials for detonating and explosive cords were conventionally made by pure Pb and/or Pb-based alloys. These are hazard materials according to EU regulations [7,8]. Therefore, the application of substitute materials is essential for industrial manufacturing. However, it is still lack of options for the commercially available alloys. In fact, it is still unclear for the detail requirements of materials performance in detonating and explosive cords. The fundamental understanding is quite limited from the scientific point of view. As such, the present study aims to assess the criteria of materials selection and to investigate the microstructure and the mechanical properties of Sn-Cu alloys through experimental excise from casting to rolling under as-cast, as-rolled and as-annealed conditions. Discussion is focused on the microstructural evolution and the relationship between microstructure and mechanical properties.

2. Materials selection

The standard explosive linear shielding material in use for years has included a high proportion of lead (90-96wt.%) together with antimony (4-10wt.%) [9, 10]. The lead/antimony alloys are economical and provide the ease of manufacture and the reliability of performance in terms of low melt temperature, high density, efficient heat transfer of the encased explosive, and sufficient hoop strength to contain the explosive before function. The physical and mechanical properties of pure Pb and Pb-(1-12)wt.%Sb alloys are summarized in Table 1 [11,12][13, 14]. Because of the significant

difference in testing parameters and the inconsistency of mechanical properties from the different resources in Table 1 [15, 16][17, 18], the tensile properties of pure Pb and Pb-5wt.%Sb alloys were measured and the results are shown in Figure 1. The yield strength, ultimate tensile strength (UTS) and elongation is 12 MPa, 17 MPa and 76% for pure Pb, and 17 MPa, 27 MPa and 90% for the Pb-5wt.%Sb alloy, respectively. This offers good references for the development of Pb-free alloys.

To select the shielding materials for detonating and explosive cords, the materials used as liners in linear shaped charge can be a preferred option. In order to achieve the required function during explosion, a number of metals/alloys have been developed as liners of linear shaped charges [19]. The materials include Cu, Ni, Al, Ag and Au to form ductile jets, and Pb to form fluid jets. Ta, Mo and W can form coherent and ductile jets when properly designed [20, 21]. The copper based alloys such as Cu-(5, 10, 30)Zn, Cu-10Sn, Cu-(10, 30, 50, 70)Ni, Cu-72Ag, and other Cu-(28, 35, 50, 60)Ni-(0, 5, 6, 8, 12)W, Cu-80W are also reported in literatures [22, 23]. These materials provide excellent mechanical properties and can form a deep penetration in the target due to their good ductility [24]. The disadvantages of these materials are the high melt temperature and strong work-hardening performance, which increases the complexity and difficulty in manufacture with high-energy explosive materials [25].

Generally, the efficiency of explosion in the cords depends on the detonation properties of the explosive materials and the response of surrounding mass [26]. This is because the processes of fracture and fragmentation of the cord are strongly dependent on the parameters of the detonation and the dynamic response of shielding materials [27]. The detonation properties of explosive materials consist of the explosion pressure, its time history, and the total energy delivered to the shielding materials [28]. These are not in the range of the present study. However, the response of cord mass to such time varying high-amplitude stresses and the relevant strain-rate-dependent properties of shielding cord is determined by the materials properties. Based on the understanding of processing methods, the mechanical properties of Pb-based alloys and the materials for the liners of linear shaped charges, the physical and mechanical properties of shielding materials for detonating and explosive cords should satisfy following requirements:

1. Resource abundant. The elements for making alloys must be available in sufficient quantities to meet current and future needs.
2. Low cost. This is essential for industrial application and the high cost elements should be avoided.
3. Non-toxicity. The materials must meet the health and environmental requirement.

4. High density. The density is important to supply sufficient impulse, impact energy, and momentum during the flight of fractured and fragmented piece of cord materials for penetrating.
5. Acceptable mechanical properties, in particularly high ductility and soft. It is desirable that the materials will not generate strain hardening and are capable of being deformed at room temperature. The appropriate strength guarantees the cord to be fractured under low energy level.
6. Reasonably good performance in melting, casting, extrusion, rolling and drawings.

In consideration of the possible candidate materials, the alloys used in shaped charge are reviewed for Cu, Ni, Al, Ag, Au, Ta, Mo and W [29, 30]. It is found that these materials are not desirable as most of them are not able to meet the requirements mentioned above. On the other hand, it is found that a number of Sn-based alloys are used to replace Pb-based soldering materials in electronics [31, 32]. The Sn-based materials satisfy the most of the requirements specified above. However, the as-cast microstructure, mechanical properties and the wettability between joint materials are generally the main concerns for soldering materials [33, 34]. The microstructure after plastic deformation is more important in the application of detonating and explosive cords. It is still lack of the understanding of relationship among the processing method, microstructure and mechanical properties from casting to plastic deformation and the effect of annealing on the Sn-based alloys, which are important for shielding materials. Therefore, Sn-Cu based alloys were selected in the present research for the application of detonating and explosive cords.

3. Experimental

Pure Sn and Cu ingots were used as the raw materials. All the metals were supplied at a composition with commercial purity. Before melting, each element was weighted to a specified ratio with different extra amounts for burning loss compensation during melting. About 2 kg melt was prepared in a stainless steel crucible coated with Al₂O₃ coatings and the melting was conducted in an electric resistance furnace. The melt was manually poured into a metallic mold to form casting bars. All the castings were 300mm long and had a trapezoid-shaped cross section of 20×16×16 mm, as shown in Figure 2. The compositions of the alloys were analyzed by SEM/EDS analysis and the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The actual compositions of the experimental alloys are shown in Table 2.

The casting bars were rolled at room temperature using a rolling machine (Durstons FSM200 Double Sided Rolling Mill, High Wycombe, UK). The nominal size of roller is 110 mm. There are 24 square grooves on the roller surface, which results in the formation of square bars in the products. The rolling

ratios of as-cast products to final products are presented in Figure 2. The rolled bar was defined as rolling direction (RD), transverse direction (TD), and normal direction (ND), respectively. The machine was operated at a rolling speed of 5 rpm, which is corresponding to the rolling velocity of 3.1×10^{-2} m/s.

Annealing heat treatment was carried out in an electric resistance furnace with a circulating fan. The furnace was preheated to a given temperature and maintained the temperature consistently for at least 1 hour before putting the samples into the furnace chamber. The temperature inside the chamber was monitored by a separate thermocouple, which gave the temperature deviation of ± 0.5 °C during all the heat treatment experiments. The samples were taken out from the furnace for air-cooling after finishing the annealing heat treatment.

The samples for tensile properties were machined from the bars made under as-rolled and as-annealed conditions. The test part was 30 mm long and 6 mm in diameter. The tensile tests were conducted following the ASTM B557 standard using an Instron 5500 Universal Electromechanical Testing Systems equipped with Bluehill software and a ± 50 kN load cell. All the tests were performed at ambient temperature (~ 20 °C) with a strain rate of 2.0×10^{-3} s⁻¹. Each data reported was based on the properties obtained from 5 to 7 samples. Vickers hardness tests were conducted on a Wilson 432SVA digital auto turret macro Vickers Hardness Tester. Each specimen was applied to a 10 N load and a dwell time of 10 s.

The specimens for microstructural examination were cut from bars under different conditions. The microstructure was examined using a Zeiss optical microscope with quantitative metallography, and a Zeiss Supra 35VP scanning electron microscope (SEM) equipped with EDX. The grain size and volume fraction of the solid phase were measured using an AxioVision 4.3 Quantimet digital image analysis system. The quantitative EDX analysis in SEM was performed at an accelerating voltage of 20 kV. Five point analysis on selected grains were conducted for each phase to minimize the errors during the EDX quantification and the average was taken as results.

4. Results

4.1. As-cast microstructure and hardness

Figure 3 shows the size, morphology and distribution of primary β -Sn phase in the as-cast microstructure of Sn-Cu alloys with different Cu contents. It is observed that the β -Sn phase was the primary phase with dendritic morphology in Sn-Cu hypoeutectic alloys when Cu was added at 0.3 and 0.5 wt.%. With increasing the Cu contents, the primary β -Sn phases showed the changes in morphology from long and narrow dendrites at lower Cu contents to finer globular dendrites at higher

Cu contents. With the further increase of Cu to 0.7 wt.% (Figure 3c), the Sn-Cu alloy was at eutectic composition according to the equilibrium phase diagram [35]. However, on top of the conventional lamellae eutectic microstructure, it was found the existence of primary β -Sn phase in the morphology of globular rosettes with a size of 100-200 μm . When Cu concentration was further increased to 1.0 wt.% (Figure 3d), the alloys were at hypereutectic composition, resulting in not only the changes of morphology and size of the primary phase, but also the changes of the types of primary phase from β -Sn at hypoeutectic to Cu_6Sn_5 phase. However, there was no primary bulk Cu_6Sn_5 phase being observed in the matrix except the fact that the microstructure became finer than the other three hypoeutectic Sn-Cu compositions. This phenomenon was also observed by Shen et al [36], which was believed to be associated with high cooling rate and the fundamental interpretation will be given in discussion.

Figure 4 shows the backscattered SEM images for the morphology and size of intermetallics in the Sn-0.3wt.%Cu and Sn-0.7wt.%Cu alloys. The volume fraction of intermetallic phases was higher in the alloy with higher Cu contents. However, the morphology and the size of intermetallics in both Sn-Cu alloys were similar. Generally, the intermetallic phase showed a needle-like morphology with the diameter of 2 μm and the length of 10-20 μm . The eutectic spacing was measured as 3-5 μm . Figure 5 shows the XRD profiles of the as-cast Sn-Cu alloys. The eutectic intermetallics were identified as Cu_6Sn_5 . Also, the higher Cu concentration provided more intermetallics in the alloys.

Figure 6 shows the Vickers hardness of the as-cast Sn-Cu alloys with different Cu contents. The hardness was at a similar level of HV8.5 for the alloy with 0.3, 0.5 and 0.7wt.%Cu, but it was increased to HV9.6 when Cu was at 1.0wt.%. By considering the microstructure shown in Figures 3 and 4, the microstructure with more eutectic phases and finer microstructure provided higher hardness.

4.2. Effect of rolling on the microstructure and mechanical properties

Figure 7 presents the microstructural evolution of Sn-1.0wt.%Cu alloy during rolling after 1, 5 and 8 passes, in which the microstructures across the transverse direction are shown in Figure 7a1, b1 and c1, and the microstructures across the rolling direction are shown in Figure 7a2, b2 and c2. After rolling one pass (Figure 7a1&2), the primary β -Sn phase and the Sn- Cu_6Sn_5 eutectics were deformed along the rolling direction, resulting in the formation of elongated β -Sn phase. However, the outline/interfaces of the primary β -Sn phases and eutectic phases were clearly visible. After rolling five passes (Figure 7b1&2), the size of primary β -Sn dendrites was dramatically decreased and the microstructure became much finer, although the elongated grains were still visible. The Cu_6Sn_5 intermetallics were re-distributed and became less heterogeneity in the matrix. The thickness of β -Sn

grains and eutectics were reduced, but the laminar structure distribution was still clear. Further rolling eight passes (Figure 7c1&2), the severely deformed microstructure was observed and the β -Sn grains were much refined. The Cu_6Sn_5 intermetallics were mixed with the primary β -Sn phase and the laminar feature was disappeared. Figure 8 shows the detailed morphological evolution of Cu_6Sn_5 during rolling. After rolling one pass, the cracks were seen in the needle-like Cu_6Sn_5 intermetallics. However, the broken needles were still stacked together as short rods, as marked by the arrows in Figure 8a. After rolling five passes (Figure 8b), the short intermetallics rods were further broken into smaller segments and separated each other in the matrix. The size of Cu_6Sn_5 intermetallics was ranged from 1 to $6\mu\text{m}$ with an average of $3\mu\text{m}$. It was noted that the broken intermetallics were not refined after further rolling. The size appeared to be maintained stable after rolling five passes.

Figure 9 shows the Vickers hardness of Sn-1.0wt.%Cu alloy after rolling different passes. In general, the hardness was slightly increased from HV9.6 after one rolling pass to HV10.6 after 8 rolling passes. In comparison with the hardness of as-cast Sn-1.0wt.%Cu, as shown in Figure 6, the rolling was not able to significantly increase the hardness of Sn-1.0wt.%Cu alloy. However, the significant change in the microstructure of the rolled alloy might alter the mechanical properties. Therefore, the tensile properties of Sn-Cu alloys after rolling 5 passes was measured and the stress-strain curves are shown Figure 10. Clearly, higher Cu contents led to significant increases of strength and significant decreases of elongation in the Sn-Cu alloys. Figure 11 shows the detailed results. The UTS of Sn-0.3wt.%Cu alloy was 30.1MPa, which was increased to 34.0MPa and 51.5MPa when Cu was 0.5 wt.% and 1.0wt.%. Similarly, the yield strength of 26.1 MPa for Sn-0.3wt.%Cu alloy was increased to 31.9 MPa for Sn-0.5wt.%Cu alloy and 50.8MPa for Sn-1.0wt.%Cu alloy. However, the elongation was decreased from 87.5% for Sn-0.3wt.%Cu alloy to 86.4% for Sn-0.5wt.%Cu alloy and further to 56.0% for Sn-1.0wt.%Cu alloy. More interestingly, it was found that strain softening instead of strain hardening has occurred for all specimens during tensile tests. This is consistent with the results obtained by others for directionally solidified Sn-1.0wt.%Cu alloy [37, 38]. Strain softening is particularly important for the specific application as detonating cords because the further processing is required after assembly with high-energy explosive materials. The strain hardening can prevent the material deformation to the final gauge. Therefore, the strain softening is desirable characteristics for the processing of detonating and explosive cords.

Figure 12 shows the SEM fractographs of the Sn-Cu alloys after rolling five passes. Numerous dimples were observed on the fractured surfaces of Sn-0.3wt.%Cu, Sn-0.5wt.%Cu, and Sn-1.0wt.%Cu alloys, confirming the ductile fracture mechanism. The dimples in Sn-0.3wt.%Cu alloy were large and deep, showing an average dimple size: $> 28\mu\text{m}$ (Figure 12a & b). With increasing the Cu content to 0.5 wt.% (Figure 12c & d) and 1.0 wt.% (Figure 12e & f), dimples became smaller.

The average dimple size in Sn-1.0wt.%Cu alloy was at a level of 20 μ m. As shown in Figure 11, the strength was higher and the ductility was lower for the Sn-Cu alloys with higher Cu contents. Therefore, the finer dimples could enhance the tensile strength.

4.3. Effect of annealing on the microstructure and mechanical properties

Figure 13 shows the annealed microstructure of rolled Sn-1.0wt.%Cu alloy after annealing at 200°C for 8 hours. The as-annealed microstructure became finer in comparison with as-rolled microstructure as shown in Figures 7 and 8. Comparing the morphologies of as-annealed intermetallics particles with that of the as-rolled ones (Figure 13 & 8), the as-annealed intermetallics particles show much more spherical shape instead of a short rod-like morphology in the as-rolled Sn-Cu alloys. Besides, the annealing contributed to extensive uniform redistribution of the intermetallics particles in Sn matrix. Figure 14 shows the XRD profiles of the rolled Sn-1.0wt.%Cu alloy after annealing, which confirms that the intermetallics was still identified as Cu₆Sn₅. No phase transformation was found during annealing.

The effect of annealing time on the hardness is shown in Figure 15, in which the hardness was decreased with prolonged time. However, the decrease was finished within one hour of annealing. The prolonged annealing time maintained the hardness at a level of HV9.4. Figure 16 shows the tensile stress-strain curves of Sn-0.3wt.%Cu, Sn-0.5wt.%Cu, and Sn-1.0wt.%Cu alloys after annealing at 200 °C for 8 hours. The curves confirmed that strain softening maintained no change after annealing. In Figure 17, the values of UTS, yield strength and elongation of the annealed Sn-Cu alloys were displayed, showing that the UTS of Sn-0.3wt.%Cu alloy was 29.8MPa, which was increased to 32.8 and 36.0 MPa when Cu concentration was increased to 0.5wt.% and 1.0wt.%, respectively. The yield strength of Sn-0.3wt.%Cu, Sn-0.5wt.%Cu, and Sn-1.0wt.%Cu alloys were 27.1, 29.1, and 34 MPa, respectively. Inversely, the elongation was reduced with increasing the Cu contents. The elongation was 101.1% for Sn-0.3wt.%Cu alloy to 98.1% for Sn-0.5wt.%Cu alloy and 64.0% for Sn-1.0wt.%Cu alloy. Compared with the as-rolled Sn-Cu alloys, the as-annealed alloy showed a decrease in strength and an increase in elongation. Therefore, the annealing might be one of the effective approaches to increase the processing capability of Sn-Cu alloys for detonating cords.

In summary, four experimental Sn-Cu alloys with Cu contents in the range of 0.3-1.0wt.% provided good mechanical properties (UTS: 30.1-51.5MPa, yield strength: 26.1-50.8MPa, and elongation: 56.0-87.5%). Preferably, the Sn-0.3wt.%Cu alloy and Sn-0.5wt.%Cu alloy have optimum strength and ductility (UTS: <35MPa, elongation: >85%). These are at similar levels in comparison with the Pb-based alloys, which have the value of UTS in the range of 17-27 MPa and elongation in the range of 76-90% (Figure 1). Also, the work softening was found in the materials. These could be significant

benefits to the manufacture of shielding and subsequent processing after assembly with high-energy explosives. Thus, the hypoeutectic Sn-Cu alloys with Cu contents less than 0.7wt.% are appropriate materials as the substitute of Pb-based alloys for shielding materials in the application of detonating and explosive cords. In addition, the annealing was proved to be able to slightly decrease the strength and increase the ductility of Sn-Cu alloys, which could be a further guarantee in the manufacture of shielding structure.

5. Discussion

5.1 Solidification and microstructural evolution of as-cast Sn-Cu alloys

The solidification path and microstructural evolution can be understood through the equilibrium phase diagram of Sn-Cu system [39]. When the Cu contents are 0.3 wt.% and 0.5 wt.%, Sn-Cu alloys are solidified as hypoeutectic alloys, following the phase transformation: $L \rightarrow L + \text{primary } \beta\text{-Sn} \rightarrow \text{primary } \beta\text{-Sn} + \text{Eutectic (Sn+Cu}_6\text{Sn}_5)$. When Cu is 0.7 wt.%, the solidification follows the phase transformation: $L \rightarrow \text{Eutectic (Sn+Cu}_6\text{Sn}_5)$. When Cu is increased to 1.0 wt.%, the hypereutectic reaction is $L \rightarrow L + \text{primary Cu}_6\text{Sn}_5 \rightarrow \text{primary Cu}_6\text{Sn}_5 + \text{Eutectic (Sn+Cu}_6\text{Sn}_5)$. Therefore, the different solidification paths form different as-cast microstructures. The eutectic Cu_6Sn_5 is formed in all the experimental alloys. However, the different Cu contents can form different amounts of eutectics [40, 41]. In the present research, the volume fraction of Sn- Cu_6Sn_5 eutectics is proximately 31% for Sn-0.3 wt.% Cu alloy, 33% for Sn-0.5wt.%Cu, 36% for Sn-0.7wt.%Cu alloy, and 51% for Sn-1.0wt.%Cu alloy. The Cu_6Sn_5 phase is similar in morphology and size in the different experimental alloys, which implies that the cooling rate during solidification is similar according to the Jackson-Hunt models [42].

It is interesting to note that the microstructure in the eutectic Sn-0.7wt.%Cu alloy shows a large volume fraction of primary $\beta\text{-Sn}$ phase (around 64%). Generally, under equilibrium conditions, the solidification microstructure of eutectic Sn-0.7wt.%Cu alloy should mainly appear as regular Sn- Cu_6Sn_5 eutectics while the microstructure of the experimental Sn-0.7wt.%Cu alloy is characterized by mainly primary $\beta\text{-Sn}$ phase. This phenomenon was also observed in high speed solidification of Sn-Cu and other binary system [43, 44]. At a high cooling rate, ‘off-eutectic’ structure (primary dendrites and eutectics) are likely to be observed, although the alloy is at eutectic composition. This could be interpreted by a coupled zone theory [45, 46]. The coupled zone is defined as a region (in a phase diagram) of alloy compositions and interface temperatures, inside which the microstructure is wholly composed of eutectics, i.e. without primary dendrites. In the coupled zone theory, the principle of competitive growth between primary dendrites and eutectics has been widely applied to predict the expected structure (eutectic only or eutectic and a primary phase) if one knows some essential

solidification parameters, such as the growth rate, melt composition, and temperature gradient [47]. Despite the documented explanation on the transformation of microstructure from regular eutectic to primary dendrites in many other alloy systems, the underlying mechanism of the appearance of large amount of primary Sn phase in the experimental Sn-0.7wt.%Cu alloy still need further investigation with addition of detailed value of the growth rate, cooling rate and undercooling.

5.2 Strengthening in Sn-Cu alloys under casting, rolling and annealing

The results have confirmed that (1) the increased Cu contents can increase the strength, but reduce the ductility of Sn-Cu alloys, (2) the rolling can increase the hardness, but at a very limited range, and (3) the annealing reduces the strength but increases the ductility. These are associated with the strengthening mechanisms in the Sn-Cu alloys processed under different conditions.

Under equilibrium conditions, the solid solubility of Cu in Sn is very limited with the value of 0.0063 wt.% for Cu at the eutectic temperature. During casting, the increased cooling rates for non-equilibrium solidification can promote the extension of solid solubility for higher values [48]. The increased solute contents in the solid solution can increase the solution strengthening, which can increase the alloy strength. Meanwhile, the increased solute contents will move the alloy composition close to eutectic composition. As a consequence, an increase in the eutectic fraction is expected to occur in the as-cast microstructure. The strengthening from the second phase can be enhanced. Therefore, the strength of Sn-Cu alloys is increased when increasing the Cu contents.

When applying rolling on Sn-Cu alloys, the plastic deformation can refine the primary β -Sn dendrites and eutectic Sn_6Cu_5 phase (Figures 7 and 8). The refined primary β -Sn grains can increase the strength according to the Hall-Petch relationship [49]. The severe deformation can result in finer grain sizes and therefore provide more effective increase in the strength. This has been shown in the Vickers hardness (Figure. 9). However, the increased rolling number can only introduce a slight increase in hardness, which is likely to be attributed to the competition of the dislocation multiplication resulting in the hardening and the dynamic recovery contributing to the softening. Because of the temperature increase during rolling, the recovery and dynamic crystallization are likely to occur during rolling process. Therefore, the softening effects caused by recovery and dynamic crystallization might be sufficiently high to counteract the hardening process due to plastic deformation. Consequently, the hardness of the severely rolled Sn-Cu alloy is not significantly increased with the increased passes of rolling in comparison with the difference between the as-cast and the as-rolled Sn-Cu alloys.

When the annealing is applied to the rolled alloys. The relief of residual stress (or strain), and the recovery of defects and/or sub-microstructures (accumulated dislocations) becomes effective. Also, the β -Sn dendrite structure is likely to grow into larger grain structure because of the recrystallization during annealing. In addition, the Cu_6Sn_5 particles can become spheroidized, and coarsened to some extent. These could be the reasons why the strength is decreased but the elongation is increased after the Sn-Cu alloys are annealed. The change in strength and elongation is specifically dramatic in the Sn-1.0wt.%Cu alloy because the spheroidization of intermetallics is more significant in hypereutectic alloys than that in hypoeutectic alloys.

6. Conclusions

- (a) Sn-Cu based alloys are the appropriate substitute of Pb-based alloys for the application of detonating and explosive cords. The advantages of Sn-Cu alloys include resource abundant, low materials cost, non-toxicity for the health and environmental requirement, relatively high density for supplying sufficient impulse energy and momentum for penetration, acceptable mechanical properties, and easy in melting, casting, extrusion, rolling, and drawing.
- (b) Microstructures of as-cast Sn-(0.3-1.0) wt.% Cu alloys consists of Sn solutions with Cu_6Sn_5 in the matrix. The rolling does not appear to alter the phase constituent of the alloys, but significantly refined the microstructure. The annealing is unlikely to modify the phase constituent in the as-rolled Sn-Cu alloys, but it lowers the strength and boosts the ductility.
- (c) The rolled Sn-Cu alloy with 0.3 to 0.7wt.%Cu offer the yield strength from 26.1 to 50.8MPa, UTS from 30.1 to 51.5MPa and elongation from 87.5 to 56.0%, which is at a similar level of tensile properties in comparison with the previously used Pb-based alloys.
- (d) Sn-Cu alloys exhibit strain softening during tensile tests, which benefits the materials manufacture and subsequent processing in rolling and drawing after assembly with high-energy explosive materials. Strain softening is desirable for the shieling materials in detonating and explosive cords.

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References

- [1] X. Bai, J. Liu, S. Li, C. Lv, W. Guo, and T. Wu. "Effect of interaction mechanism between jet and target on penetration performance of shaped charge liner." *Materials Science and Engineering: A*, 2012, 553: 142-148.
- [2] D. Novotney. "Historical overview of explosive transfer line technology." 44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Joint Propulsion Conferences. 2008.
- [3] A. Zyskowski, I. Sochet, G. Mavrot, P. Bailly, and J. Renard. "Study of the explosion process in a small scale experiment-structural loading." *Journal of Loss Prevention in the Process Industries*, 2004, 17: 291-299.
- [4] S. Lim. "Jet velocity profile of linear shaped charges based on an arced liner collapse." *Journal of Energetic Materials*, 2013, 31(4): 239-250.
- [5] A.J. Bellamy, and S.L. Dearing. "The incompatibility of RDX and lead." *Propellants, Explosives, Pyrotechnics*, 2002, 27(6): 352-360.
- [6] H.K. Ciezki, and G. Adomeit. "Shock-tube investigation of self-ignition of n-heptane-air mixtures under engine relevant conditions." *Combustion and flame*, 1993, 93(4): 421-433.
- [7] M.R. Johnson, and M.H. Wang. "Evaluation policies and automotive recovery options according to the European Union Directive on end-of-life vehicles (ELV)." *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, 2002, 216(9): 723-739.
- [8] N. Kanari, J-L. Pineau, and S. Shallari. "End-of-life vehicle recycling in the European Union." *The journal of The Minerals, Metals & Materials Society*, 2003, 55(8): 15-19.
- [9] H. He, and S. Jia. "Direct electrodeposition of Cu-Ni-W alloys for the liners for shaped charges." *Journal of Materials Science & Technology*, 2010, 26(5):429-432.
- [10] D. Novotney, and M. Mallery. "Historical development of linear shaped charge." 43rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Joint Propulsion Conferences. 2007.
- [11] D.R. Blaskett, and D. Boxall. "Lead and its alloys." Ellis Horwood Ltd, 1990.
- [12] R. Mahmudi, R. Roumina, and B. Raeisinia. "Investigation of stress exponent in the power-law creep of Pb-Sb alloys." *Materials Science and Engineering: A*, 2004, 382(1): 15-22.
- [13] R. Mahmudi, A.R. Geranmayeh, and A. Rezaee-Bazzaz. "Impression creep behavior of cast Pb-Sb alloys." *Journal of alloys and compounds*, 2007, 427(1): 124-129.
- [14] M.M. Mostafa. "Steady state creep characteristics of the eutectic Pb-Sb alloy." *Physica B: Condensed Matter*, 2004, 349(1): 56-61.
- [15] M.K. Sahota, and J.R. Riddington. "Compressive creep properties of lead alloys." *Materials & Design*, 2000, 21(3): 159-167.

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- [16] M.F. Ashby. "Indentation creep." *Materials Science and Technology*, 1992, 8(7): 594-601.
- [17] AM Abd El-Khalek, and R.H. Nada. "Effect of structure transformation on the stress-strain characteristics of Pb-3wt% Sb and Pb-3wt% Sb-1wt% Sn alloys." *Physical B: Condensed Matter*, 2003, 328(3): 393-398.
- [18] N. Loizou, and R.B. Sims. "The yield stress of pure lead in compression." *Journal of the Mechanics and Physics of Solids*, 1953, 1(4): 234-243.
- [19] Z. Zhao, J. Liu, W. Guo, S. Li, and G. Wang. "Effect of Zn and Ni added in W-Cu alloy on penetration performance and penetration mechanism of shaped charge liner." *International Journal of Refractory Metals and Hard Materials*, 2016, 54: 90-97.
- [20] D.W. Pratt, D.S. Wesson, and J.K. Rouse. "Shaped-charge liner." U.S. Patent No. 6354219, 12 Mar. 2002.
- [21] W. Guo, S.K. Li, F.C. Wang, and M. Wang. "Dynamic recrystallization of tungsten in a shaped charge liner." *Scripta Materialia*, 2009, 60(5): 329-332.
- [22] X. Bai, J. Liu, S. Li, C. Lv, W. Guo, and T. Wu. "Effect of interaction mechanism between jet and target on penetration performance of shaped charge liner." *Materials Science and Engineering: A*, 2012, 553: 142-148.
- [23] H. He, and S. Jia. "Direct electrodeposition of Cu-Ni-W alloys for the liners for shaped charges." *Journal of Materials Science & Technology*, 2010, 26(5): 429-432.
- [24] W.H. Tian, A.L. Fan, H.Y. Gao, J. Luo, and Z. Wang. "Comparison of microstructures in electroformed copper liners of shaped charges before and after plastic deformation at different strain rates." *Materials Science and Engineering: A*, 2003, 350(1): 160-167.
- [25] S. Lee, M.H. Hong, J.W. Noh, and W.H. Baek. "Microstructural evolution of a shaped-charge liner and target materials during ballistic tests." *Metallurgical and Materials Transactions A*, 2002, 33(4): 1069-1074.
- [26] S. Lim. "Acceleration profile of a flat flyer driven by detonation isentrope." *Propellants, Explosives, Pyrotechnics*, 2013, 38(3): 410-418.
- [27] S. Lim. "Jet velocity profile of linear shaped charges based on an arced liner collapse." *Journal of Energetic Materials*, 2013, 31(4): 239-250.
- [28] F. Zhu, L. Zhao, G. Lu, and Z. Wang. "Structural response and energy absorption of sandwich panels with an aluminium foam core under blast loading." *Advances in Structural Engineering*, 2008, 11(5): 525-536.
- [29] H. Han, W. Jiang, P. Zhang, and Z. Chu. "Application of metal powders to shaped charge." *Powder Metallurgy Industry*, 2004, 3: 1-4.

-
- [30] L.E. Murr, and E.V. Esquivel. "Observations of common microstructural issues associated with dynamic deformation phenomena: twins, microbands, grain size effects, shear bands, and dynamic recrystallization." *Journal of Materials Science*, 2004, 39(4): 1153-1168.
- [31] K. Suganuma. "Advances in lead-free electronics soldering." *Current Opinion in Solid State and Materials Science*, 2001, 5(1): 55-64.
- [32] W. Feng, C. Wang, and M. Morinaga. "Electronic structure mechanism for the wettability of Sn-based solder alloys." *Journal of Electronic Materials*, 2002, 31(3): 185-190.
- [33] S.K. Kang, P. Lauro, D.Y. Shih, D.W. Henderson, and K.J. Puttlitz. "Microstructure and mechanical properties of lead-free solders and solder joints used in microelectronic applications." *IBM Journal of Research and Development*, 2005, 49(4): 607-620.
- [34] A.A. El-Daly, A. E. Hammad, A. Fawzy, and D. A. Nasrallah. "Microstructure, mechanical properties, and deformation behavior of Sn-1.0 Ag-0.5 Cu solder after Ni and Sb additions." *Materials & Design*, 2013, 43: 40-49.
- [35] J.E. Spinelli, and A. Garcia, "Microstructural development and mechanical properties of hypereutectic Sn-Cu solder alloys." *Materials Science and Engineering: A*, 2013, 568: 195-201.
- [36] J. Shen, Y.C. Liu, and H. X. Gao. "Formation of bulk Cu₆Sn₅ intermetallic compounds in Sn-Cu lead-free solders during solidification." *Journal of Materials Science*, 2007, 42(14): 5375-5380.
- [37] X. Hu, W. Chen, and B. Wu. "Microstructure and tensile properties of Sn-1Cu lead-free solder alloy produced by directional solidification." *Materials Science and Engineering: A*, 2012, 556: 816-823.
- [38] A.A. El-Daly, and A.E. Hammad. "Development of high strength Sn-0.7 Cu solders with the addition of small amount of Ag and In." *Journal of Alloys and Compounds*, 2011, 509(34): 8554-8560.
- [39] S.K. Seo, S.K. Kang, D.Y. Shih, and H.M. Lee. "The evolution of microstructure and microhardness of Sn-Ag and Sn-Cu solders during high temperature aging." *Microelectronics Reliability*, 2009, 49(3): 288-295.
- [40] T. Ventura, S.E Terzi, M. Rappaz, and A.K. Dahle. "Effects of solidification kinetics on microstructure formation in binary Sn-Cu solder alloys." *Acta Materialia*, 2011, 59(4): 1651-1658.
- [41] S.K. Seo, S.K. Kang, D.Y. Shih, and H.M. Lee. "An investigation of microstructure and microhardness of Sn-Cu and Sn-Ag solders as functions of alloy composition and cooling rate." *Journal of Electronic Materials*, 2009, 38(2): 257-265.
- [42] J.D. Hunt, and K.A. Jackson. "Binary eutectic solidification." *Transactions of the Metallurgical Society of AIME*, 1966, 236(6): 843-852.
- [43] J. Shen, Y.C. Liu, and H.X. Gao. "Formation of bulk Cu₆Sn₅ intermetallic compounds in Sn-Cu lead-free solders during solidification." *Journal of Materials Science*, 2007, 42(14): 5375-5380.

-
- [44] S.B. Luo, W.L. Wang, Z.C. Xia, and B. Wei. "Theoretical prediction and experimental observation for microstructural evolution of undercooled nickel-titanium eutectic type alloys." *Journal of Alloys and Compounds*, 2017, 692: 265-273.
- [45] W. Kurz, and D.J. Fisher. "Dendrite growth in eutectic alloys: the coupled zone." *International Metals Review*, 1979, 24: 177-204.
- [46] A. Karma, and A. Sarkissian. "Morphological instabilities of lamellar eutectics." *Metallurgical and Materials Transactions A*, 1996, 27: 636-656.
- [47] I.T.L. Moura, C.L.M. Silva, N. Cheung, P.R. Goulart, A. Garcia, and J.E. Spinelli. "Cellular to dendritic transition during transient solidification of a eutectic Sn-0.7wt%Cu solder alloy." *Materials Chemistry and Physics*, 2012, 132: 203-209.
- [48] L. Snugovsky, and P. Snugovsky, D.D. Perovic, and J.W. Rutter. "Effect of cooling rate on microstructure of Ag-Cu-Sn solder alloys." *Materials Science and Technology*, 2005, 21(1): 61-68.
- [49] P. Lehto, H. Remes, T. Saukkonen, H. Hänninen, and J. Romanoff. "Influence of grain size distribution on the Hall-Petch relationship of welded structural steel." *Materials Science and Engineering: A*, 2014, 592: 28-39.