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## The Effect of Chemical Composition on Grain Size and Formability of the Free-Lead Cu-30Zn Alloy: A Short Review

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# The Effect of Chemical Composition on Grain Size and Formability of the Free-Lead Cu-30Zn Alloy: A Short Review

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**Abstract.** The increasing demand for free-lead Cu30Zn alloy for all industrial applications has prompted to develop the grain size and formability. One of the major challenges facing the researcher and industry is decreasing the formability and machinability which requires continuous improvements in design and fabrication techniques. The current trend for free-lead Cu30Zn alloy in these categories is reviewed. Results show that developments in free-lead Cu30Zn alloy are affected by a lot of factors such as chemical composition, microstructure, grain size, strain and hardness. A highly developed system with characteristics of compromised decision making became more favorable and initiated an interesting intervention since the casting, cold working, and heat treatment is controlled.

## 1. Introduction

Demand for copper and brass, especially Cu30Zn alloys (also called brass cartridges) continues to increase in the applications of the military, automotive and building industries; it requires an increase in mechanical and technological properties with the addition of suitable alloying elements [1]. Despite increasing demand, finished or semi-finished products often experience rejection due to various defects and imperfections of Cu30Zn alloy products that arise during various stages of manufacturing [2]. Product defects also occur due to the standard requirements of the metallurgical properties (such as grain size) unaccepted, mechanics (such as yield strength, tensile strength, hardness, and impact) and technology (such as formability, and machinability) standards to improve the properties of brass materials must be done first by repairing the main alloying elements and additional alloying elements. Previously in brass, especially in additional alloying elements: lead (Pb) and Bismuth (Bi); but today, the world community has issued strictly restrictions to overcome the harmful effects of lead and provide a driving force for the development of free lead brass alloys [3].

Attempts to find the free-lead brass alloys both looking for other chemical elements as a substitute for lead and reducing lead content below the safe threshold, in the past two decades, have been conducted by researchers. H. W. Mielke [4] said that the major problems in the context of large and small communities, smelters and lead industries. Unlike lead which is prohibited for use, bismuth (Bi) is only



recommended not to use as the main alloying element for brass and substitutes for lead in soldering and coatings, because Bi has a detrimental effect on the life cycle of other metals, the environment and human health, limited supply in the world. It can only be fulfilled by product of lead and tungsten processing, and technical superiority is lower than lead [5].

Unlike Al and Mg alloys, refining grains with the addition of other elements in Cu alloys is still in consideration. A. Cziegler, O. Geraseva, and P. Schumacher [6] studied the potential for grain refining with the addition of alloying elements, Mg, S, P, Te, Ti, Zr, Ni, Cr, and Bi to the Cu system. The experimental results turned out that the grain size decreased with increasing alloy concentrations observed independently of the potential growth limitation of alloy elements. Furthermore, excessive grain coarsening with increasing solute content can occur due to the removal of nucleation particles.

Cartridge brass alloy is gaining huge industrial significance because of their outstanding combination of mechanical, metallurgical and formability properties over the copper based alloys [7]. These properties obtained through addition of alloy elements, cold working and heat treatment. Alloying elements are selected based on their effects and suitability. Therefore, to understand the effect of the chemical composition on grain size, machinability and formability of the free lead Cu30Zn alloy that other researchers have studied, it is necessary to be reviewed.

## 2. Alloying Elements of Free Lead Cu30Zn Alloy

Prohibition of lead (Pb) content in various manufacturing products such as Cu30Zn alloys is due to these heavy metals are toxic, harmful to humans and the environment such as anemia [8], neurotics disorder, pregnancy disorder and social effects [9]. Depending on the country and its applications, Europe sets a maximum lead content of 0.1% [10]; California, United States limits the lead content (Pb) to 0.25% [11]; and even many people want zero-lead in the world. The chemical composition of conventional CuZn30 alloys is usually produced for bullet casings, plumbing, tubing, etc. It needs to be given additional alloying elements including Sn, Pb, Si, Mn and Fe which are kept below 0.05% by weight, to provide the highest ductility possible for the best deep draw ability [12]. However, unleaded brass can reduce significant machinability, because good machinability brass usually contains 1.5 - 3% Pb [13]. Having excellent machinability, corrosion resistance and other specifications, lead brass alloys can cause several types of defects that occur during the production process, especially casting, heat extrusion, cold drawing and hot forging if there are not exact of alloy designs and technology parameters [14], and in-service applications [15].

Indeed, researchers have tried to find other chemical elements as a substitute for Pb element in brass alloys. Tin (Sn) has been studied by K. Narayana and N. S. Naveen [16] and M. A. Mustafa et.al [17] as a substitute for the Pb element that at the addition of 3.3% Sn can present a eutectoid phase with a  $\gamma$ -Sn distribution in a fine microstructure and tin brass alloy improves the machinability better than lead brass, and tin brass alloy having an elastic modulus of 1.6 times lead brass. Z. Rajabi and H. Doostmohammadi [18] researched a lead-free brass alloy using some variations in lead (Sn) content instead of lead (Pb) and microstructure behavior, hardness and machining ability of Cu-30% Zn alloy compared to Cu-30% Zn - x% Sn (x = 1.2, 3.2, 5.4, 8, 11.4, 13.9, 17.4). Based on their research, it shows that the addition of Sn to a single  $\alpha$ -phase brass causes the formation of duplex brass ( $\alpha + \beta'$ ) and then the formation of brass ( $\beta' + \chi$ ) with increased hardness and machinability properties.

A. Adegbenjo et.al [19] studied the effect of Manganese (Mn) as additive instead of Pb and combined with a low annealing temperature on the tensile properties of Cu30Zn containing Nickel (Ni) and Iron (Fe) as impurities. A. Adegbenjo et.al [20] also conducted the experiment on silicon (Si) as instead of Pb. From their studies, it was found that the same results as cartridge brasses that were alloying and annealing and increased yield and tensile strengths. However, tensile properties were improved and controlled within acceptable limits at stress relieve annealing temperatures. F. A. Ovat, L. O. Asuquo, and F. I. Abam [21] investigated the effects of aluminum (Al) and manganese (Mn) in different proportions on mechanical properties of brasses. They concluded that the optimal mechanical properties of brass such as tensile, hardness and impact properties using aluminum and manganese as alloying

elements whose percentage increase should be in the range of 1-5%. Therefore, a more reliable result of brass can be achieved when the proportion of aluminum and manganese is in the range of 2% -5%.

Imagine that to find another chemical element which is ideal as a substitute for Pb still needs more time, to modify the chemical composition of low lead Cu-Zn alloys. According to STN EN 42 3210, the standard specifications of brass cartridges with chemical composition consist of 69.5-72%wtCu, 0.05% (max) Fe, 0.03% (max) Sn, 0.03% (max) Al, 0.2% (max) Ni, 0.02% (max) As, 0.05% (max) Pb, 0.01% (max) Si, 0.04% (max) Mn, 0.05% (max) P, 0.01% (max) Sb, 0.04% (max) Bi, and the rest Zn. Based on the standard specifications of the brass cartridge mentioned above, a number of researchers like I. Basori, H. I. Pratiwi, and B. T. Sofyan [22] studied the effect of adding Mn content on Cu-Zn alloys and determined the content of 0.005% Pb, 0.005% Si and 0.002% Al with various variations of other elements. A. Arisgraha, I. Angela, N. A. Arandana, and B. T. Sofyan [23] studied the effect of adding Aluminum (Al) content on Cu-Zn alloys and determining the content of 0.006 – 0.009%Pb, 0,015%Fe, 0.002%S, 0.002% (max) P, and 0.001%(max) Mg; where their result is an increase in hardness and strength but decreases elongation and form-ability. Furthermore, M. S. Ghazani, et.al [24] investigated the effect of Bismuth (Bi), by maintaining the content of 0.005% Pb, 0.005% Si and 0.002% Al, to the deformation and texture of the Cu<sub>29</sub>Zn alloy; but Bi often promotes casting segregation and poor elastic property [25]. Thus, efforts to find chemical elements instead of lead are still focused on lead, aluminum, magnesium, manganese, bismuth, arsenic, iron and nickel but all these elements have not been satisfactorily associated with the desired mechanical, and technological properties.

### 3. Grain Size of Free Lead Cu<sub>30</sub>Zn Alloy

The optimum metallurgical and physical properties of metal is obtained by using a heat treatment process. The effect of precipitation heat treatment temperature on metallurgical microstructure, thermal properties, and micro hardness of alpha brass was studied I. Rojas-rod ríguez et al. [26]. The samples were heated for 2 hours at 300°C, 400°C, 500°C, 600°C, and 700°C. The results showed that the crystallite decreased as the temperature of the precipitation heat treatment increased. Metallurgical microstructure and micro hardness are correlated with the temperature of the precipitation heat treatment which determines the effect on metallurgical and mechanical properties, as well as the effects on the thermal properties of alpha brass.

The Grain size depends on twinning deformation in face-centered-cubic metals. X. L. Ma, et.al [27] found that alloying changes the relationship between energy stacking-fault and twin-fault and therefore affects the optimal grain size for twinning deformation. This observation must apply to other alloy systems. A. K. Verma, et.al [28] examined the grain size of Cu-30Zn (wt%) alloys widely used for cartridge cases. The average grain size increases as rolling increases in rolling direction. The grain size distribution shows a higher frequency for larger grain sizes with rolling deformation.

The Grain size and structure are generally used as machinability indicators [13]. The Grain size of microstructure phase of unleaded Cu<sub>30</sub>Zn alloys due to alloying, cold work, and heat treatment processes greatly affect their mechanical, machinability and formability properties. Metallographic evaluation was focused on the change of the shape and grains size after the individual technological procedures [29].

The effect of grain size on the density of twin deformations in the material must be well understood. Y. Li et al [30] have chosen Cu-30% Zn alloys as a model material to study this phenomenon; and their results show that the twin and matrix widths decrease with decreasing the grain size but increase the twin density, and reaches the maximum value in critical grain size. The optimal grain size for the highest twin density is largely independent of the treatment process, and under the critical grain size, the twin density decreases when decreases further grain sizes.

M. S. Ghazani, et.al [24] researched the addition of Bismuth (Bi) to Cu-29Zn alloys. It showed that addition of Bi prompted Bi-rich dispersed phase which segregated inside the grain and along the grain boundary in globular forms. Bi is completely insoluble in brass and thus tends to segregate to the solid-

liquid interface during solidification and form isolated particles inside the grain and along the grain boundaries.

There is a synergistic effect of strain and temperature on the density of annealing twins. M. Tajally, E. Emadoddin, and E. A. Shahi [31] shown that annealing of brass alloy resulting in the formation of annealing twins which at higher annealing temperature were reduced by increasing grain size. Best deep draw ability would be achieved by annealing at moderate temperature 400–450°C which microstructure consists of fine grain and twin bands.

Cartridge brass undergoes significant changes in mechanical properties as a result of cold work. These changes are effectively reversed in the annealing process returning the metal to its pre-cooled-worked state. J. Klein and J. E. Indacochea [32] studied and its results indicate that mechanical changes from cold work are more prominent during the first stages of cold work. The time to reach recrystallization is reduced in response to increases in annealing temperature as well as increasing cold deformation. The recrystallization temperature is reduced when time of anneal is increased or degree of cold work is increased. Therefore, recrystallization is driven by strain imposed on the metal during cold working and is a thermally activated process. The energy configuration in the grain boundary is lower than the recrystallization grain [32] [31]. Grain growth in material is affected by temperature, specimen size and material texture.

For better understanding, R. Ohlsson [33], studied and the results showed some small differences in hardness and microstructure but they both show the same tendencies and there are no clear differences between the two brass cases and their manufacturing and annealing processes. Although only grain size does not provide a complete understanding of violence and violence cannot be determined only by grain size, but based on the grain size can predict some mechanical and technological properties such as tensile, hardness, impact energy, machinability, and formability.

#### **4. Machinability of Free Lead Cu30 Zn Alloy**

Metal hardness must correlate to size and in the field as a machinability indicator [13]. Although unleaded Cu30Zn alloys are more widely applied in the metal forming and cutting industry which usually involves the process of blanking, piercing, and parting, but it is not impossible to do the machining process; so, it needs to be glimpsed about the machinability properties. In according S. Genculu [34], there are four factors affecting machinability along with four common methods used to judge machinability consist of tool life, tool force and power consumption, surface finishing, and chip formation. According to C. Nobel, F. Klocke, D. Lung, and S. Wol [35] have conducted fundamental investigations on machinability of lead-free brass alloys, it turns out that microstructure and silicon as alloying elements influence good chip breaking, high cutting forces, tool temperature and low tool wear during the turning process.

When viewed from the effect of the alloying elements on the machinability properties of the Cu30Zn alloy which can be briefly discussed below [34]. Aluminum is very easy to machine but has poor surface finishing; Beryllium is machine-able, but because the fine particles produced during machining are toxic; Cobalt is abrasive and highly work hardening; Brasses are easy to machine, in particular with the addition of lead (leaded free-machining brass), but the toxicity of lead and associated environmental concerns have to be dealt with however; Magnesium is very easy to machine, with good surface finish and prolonged tool life but its high rate of oxidation (pyrophoric) and the danger of fire; Molybdenum is ductile but work hardening, so that it has to avoid producing poor surface finish sharp tools; Nickel is work hardening, abrasive, and strong at high temperatures but its machinability must be improved with annealing; Tantalum is very work hardening, ductile, and soft, but it produces a poor surface finish, and tool wear is high; Titanium is very poor thermal conductivity (the lowest of all metals) but poor surface finishing, highly reactive and can be difficult to machine; Tungsten is brittle, strong, and very abrasive, but low machinability at room temperatures; and Zirconium has excellent machinability but requires a fluid coolant type because of the danger of fire and explosion.

K. Hajizadeh, et al [36] studied the effect of Lankford parameter and anisotropy of mechanical properties on formability of cold-rolled and annealed cartridge brass sheets at different temperatures (300-600 °C) and the results were related to texture components which analyzed by EBSD technique. The cold rolled texture components mainly Cube {100} <001> component changes to Copper {112} <111> component with increasing the annealing temperature up to 500 °C. An offset in average R value has resulted in improvement of deep draw ability. Maximum flow stress anisotropy was found at 400 °C because of the presence of enormous twins and grain boundaries that lead to improving persisting dislocation structures and accumulation of dislocations.

A. I. Toulfatzis, et al.[3]studied the machining performance on fracture behaviors indicated that the lead-free brass alloy possessed a good combination of tensile strength and fracture toughness, similar to the conventional leaded brass. In according to Z. Rajabi and H. Doostmohammadi [18], the addition of Sn to lead-free Cu-30% Zn alloy results in a decrease in the equivalent machining force ( $F_m$ ), surface roughness and also the promotion of chip breaking due to  $\beta$  phase formation which is an increase in machinability.

## 5. Formability of Free Lead Cu30Zn Alloy

The metal forming process has the most advanced technology in mechanical engineering because it allows producing a large number of products in a short time with adequate utilization of materials [29]. The heat and cold forming processes will run well if the materials have good formability. To determine changes in deformation in semi-product materials for individual withdrawal steps and it mainly relates to dimensional and areas changes with the largest plastic deformation and the decrease in the cup wall thickness. Therefore, Forming Limit Diagram (FLD) is constructed to express the safe and failed zones on a metal that will be applied to the forming process. The FLD of brass sheets can be determined theoretically based on the mechanical properties which obtained in tensile testing and equibiaxial testing to explain geometric inhomogeneity of material.

F. Stachowicz [37] found that the larger the grain size the material possesses, the lesser sheet forming can be achieved due to more intensive surface roughness growth and internal voids growth, especially in the range of biaxial stretching. Furthermore, F. Stachowics [37] expressed that the beneficial effect of the increasing strain-hardening exponent with the grain size increasing is decreased by the growth of material inhomogeneity. The growth of surface roughness seems to be a more important factor that affected the level of the FLC than the inhomogeneity component caused by void growth, especially in the case of fine-grained materials

The effect of the formability of the sheet metal is made using different material and anisotropy, the strength of the material, the indicated strain limit ratio, the material properties, and the sensitivity of the material reviewed Sivam, et al. [38]. They found that the high r-value, which is effective in improving cup formability, and thanks to this, its limit-drawing ratio is higher for material formability. The strain at maximum stress and ultimate strain of the sheets increases as sheet thickness increases after which the strain values remain almost the same or slightly decrease. The minimum bending radius linearly increases as the sheet thickness increases[38].

The forming process is also often associated with flow stress, flow forming, and the final finishing of a workpiece using traditional machines. Thus, D. Marini, J. Corney, and J. Corney [39] proposed a methodology for assessing the feasibility of flow forming process is very important to allow evaluation of how easy, or difficult, it is to produce a component with this cold forming technology.

By considering the crystal lattice constants and material crystallographic orientation parameters in the calculation procedure, F. V Grechnikov, et al. [40] [39] analyzed the effect of crystallographic texture on the formability properties in typical sheet metal forming processes: stretch forming, hole expansion, drawing and bending. They define that the best formability (maximum cupping depth, flanging ratio, drawing depth, minimum bending radius) are provided by the orientation of the rotating cube; the worst - with Goss orientation. Some texture components provide better formability than

isotropic cases (rotating cubes), some texture components provide worse formability (cube, goss) or close to isotropy (copper, brass or S-orientation).

## 6. Conclusion

The research and development of free-lead brass on grain size, machinability and formability are becoming a trend, some technical problems still appear which deserve further investigation. Alloying elements are selected based on their effect and suitability of physical, metallurgical, mechanical and technological properties. Based on some of the literature was referenced, it appears that the chemical elements as candidate substitutes for lead (Pb) from free lead Cu<sub>30</sub>Zn alloys are still limited to Al, Si, Mn, Sn, Fe, Bi, and Mg. Even sometimes these elements are combined with setting the casting, cold rolling and annealing methods to get the same tensile, hardness, machinability and formability properties with the properties of conventional Cu<sub>30</sub>Zn alloys. But the results of those works still do not seem to be technically satisfying because they have not succeeded in optimizing the chemical composition with cast ability, machinability and formability. Therefore, it is stated that it needs to consider the selection of alloying element for better understanding of materials application.

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