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# Vpliv deleža silicija na mikrostrukturo in mehanske lastnosti mednih livnih zlitin brez svinca

# The effect of silicon content on microstructure and mechanical properties of lead-free brass casting alloys

**Izvleček**

Preiskovali smo vpliv dodatkov silicija (Si) na mehanske lastnosti mednih zlitin brez svinca. Delež silicija v mednih zlitinah je bil 2–4 mas. %. Rezultati kažejo, da so dodatki silicija občutno povečali, tako največjo natezno trdnost kot raztezek. Preiskava mikrostrukture je pokazala, da se je pri dodajanju silicija medni zlitini brez svinca udrobnilo zrno in faza α + β.

**Abstract**

In this study, effect of silicon (Si) additions on mechanical properties of lead-free brass alloys was investigated. Content of silicon in the brass alloys varied between 2 to 4 (% mass fraction). Results showed that additions of silicon increased both ultimate tensile strenght and elangation considerably. The microstructure results show that when Si is added into the lead-free brass alloy, the grain is refined, α + β phase is refined.

## 1 Uvod

Med je zlitina, ki jo sestavljata predvsem baker in cink. V zadnjih letih je med postala ena največ uporabljanih konstrukcijskih zlitin zaradi svoje dobre obdelovalnosti, dobre korozijske odpornosti in okrasnega videza. Duktilne medne zlitine se uporabljajo predvsem za sanitarne armature, ki se izdelujejo z litjem in iztiskanjem. Za povečanje duktilnosti in tečenja pri velikih hitrostih deformacije se je duktilnim mednim zlitinam dodajal svinec [1,2].

Zaradi široke uporabe medi pri strojni obdelavi so njeno mikrostrukturo preiskovali v številnih študijah [3-5]. Svinec se je dodajal medi kot neke vrste mazivo pri strojni obdelavi, ker je izboljševal obdelovalnost

## 1 Introduction

Brass is an alloy consisting primarily of copper and zinc. In recent years, brass has become one of the most used structural alloys due to its high machinability, high corrosion resistance and decorative aspects. Particularly in the production of materials for sanitary installations (casting and extrusion), ductile brass alloys need to be used. In order to obtain more ductile and better flow properties at high deformation rates during the production of ductile brass alloys, the addition of lead is carried out [1,2].

Due to the wide range of machinable brass applications, the microstructure of this alloy has been investigated in a number mednih zlitin [6,7]. Topnost svinca v medi je zelo omejena. Svinec se porazdeli po medi v obliki delcev v mikrostrukturi. Danes se svinec smatra kot strupen element za človeško telo in ga je zato treba nadomestiti z drugimi zlitinskimi elementi [8]. Pri zadnjem razvoju obdelovalnih medi sta se uporabila Bi in Si kot alternativi za svinec v obdelovalnih medeh [3-5]. Majhni dodatki Bi spremenijo mikrostrukturo v Widmanstättnovo [9]. Vendar učinek Si na mikrostrukturo medi ni dobro poznan. Glede na nove raziskave bo treba razviti in izdelati medi brez svinca, ki se bodo v prihodnje široko uporabljale. Zato smo v tej študiji preiskovali učinke silicija v medeh brez svinca. Ta študija je del projekta za razvoj medi brez svinca.

## 2 Materiali in metode

### 2.1 Materiali

Za izdelavo medi smo dobili Cu, Zn, Pb in bloke kovinskega silicija s čistostjo 99,99 % od podjetja Ertas Metal Co., Turčija. Kemično sestavo zlitin prikazuje razpredelnica 1.

### 2.2 Metoda

Indukcijska peč in livni lonec za taljenje in ulivanje medi sta prikazana na sliki 1. Talilna peč s kapaciteto 2 kg taline medi je bila izzidana s šamoto, njen zunanji premer

of studies [3-5]. Lead is added to brass to play the role of a lubricant in the machining process, promoting the machinability of brass alloys [6,7]. Lead has very limited solubility in brass and is distributed as particles in the microstructure. Today lead is considered to be a toxic element for the human body and so should be replaced by other alloying elements [8]. In recent developments of machinable brasses, Bi and Si have been used as alternatives to lead in free-cutting brass [3,5]. The addition of small amounts of Bi made the microstructure of Widmanstätten structures [9]. However, the effect of Si on the microstructure of brass is not well known.

In accordance with new research studies, there will be need for production and development of lead-free brass alloys, which are expected to become widespread in the near future. Therefore, in this study, the effects of the addition of silicon in lead-free brass alloys were investigated. The present study is a part of a project to develop a lead-free brass alloy.

## 2 Materials and Method

### 2.1 Materials

Cu, Zn, Pb and metallic silicon ingots with a minimum purity of 99.9% were provided by Ertas Metal Co., Turkey for the production of brass alloys. The chemical compositions of the studied alloys are shown in Table 1.

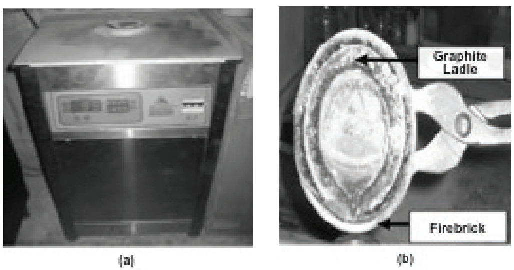
**Razpredelnica 1.** Kemijska sestava različnih medi

**Table 1.** Chemical compositions of brass alloys

| Med / Alaşım | Cu | Zn | Pb | Sn | Fe | Si |
|---|---|---|---|---|---|---|
| CuZn39Pb3 | 58,35 | 38,20 | 2,89 | 0,17 | 0,25 | 0,0055 |
| CuZn22Si2 | 75,59 | 21,13 | 0,01 | 0,01 | 0,08 | 2,13 |
| CuZn21Si3 | 75,21 | 21,83 | 0,02 | 0,02 | 0,08 | 2,80 |
| CuZn20Si4 | 76,17 | 19,79 | 0,001 | 0,007 | 0,07 | 3,92 |

je bil 150 mm. V peči je bil grafitni talilnik z notranjim premerom 110 mm. Najprej smo stalili ingote bakra, ker ima najvišje tališče med uporabljanimi kovinami. Potem smo v talilnik dodali še ostala dva elementa in talino zmešali z grafitno palico, da smo dobili homogeno mešanico.

Temperaturo kovinske taline v talilniku smo merili s termoelementom. Livna temperatura 950 $^{o}$C je bila nastavljena na kontrolnem inštrumentu. Po končanem taljenju smo talilnik vzeli iz peči in staljeno kovino ulili v pripravljene kokile. Kemično sestavo ulitkov smo ugotavljali s spektrometrom Spectrolab v laboratoriju za materiale podjetja Ertas Metal Co. Zlitine so bile ulite v jeklene kokile, da bi preiskali njihovo mikrostrukturo in napravili mehanske preskuse. Trdnostne lastnosti zlitin z različnimi deleži silicija smo ugotavljali z merjenjem natezne trdnosti, napetosti tečenja, raztezka v %, trdote ter analizirali njihovo mikrostrukturo.




**Slika 1.** Talilna enota a) talilna peč, b) talilnik

**Figure 1.** Melting process unit a) Melting furnace, b) Casting ladle

## 3 Mehanski preskusi

Preskušance za natezne preskuse smo ulili v jeklene kokile. Natezne preskuse smo naredili v laboratoriju za materiale Univerze Karabuk s 5 t nateznim strojem Shimadzu pri hitrosti vpenjalne glave nateznega stroja 0,5 mm/min in pri sobni temperaturi v skladu

## 2.2 Method

Induction furnace and casting ladle as shown in Fig. 1, were used for melting and casting of brass alloys. Melting furnace was made of firebrick with a capacity of 2 kg melt brass alloy and an outer diameter of 150 mm. A graphite ladle with an inner diameter of 110 mm was placed in metal ladle. Melting process was begun with melting the copper ingots since it has the highest melting temperature among the used metals. After that, other alloying elements were put into ladle and the melt was stirred by the use of graphite bar to obtain a homogen mixture.

The temperature of metal melt in the ladle was measured by thermocouple and a casting temperature of 950 ºC was set on the control unit. After the melting process was completed, the ladle was taken out and the liquid metal was cast in prepared moulds. The chemical analysis of the metal castings were made by Spectrolab spectrometer in Ertas Metal Co. Materials Laboratory. The alloys were cast in steel moulds in order to perform microstructural investigations and mechanical tests. Strength properties of the alloys with varying amounts of silicon were investigated by tensile, yield, elongation, hardness measurements and microstructural investigations.

## 3 Mechanical Test

Tensile specimens were produced by casting the liquid metal in the prepared steel moulds. Tensile tests were performed in Karabuk University Materials Laboratory by 5 tons capacity Shimadzu Tensile Test Machine in accordance with ASTM E8M-99 standard with a crosshead speed of 0.5 mm/min at room temperature. Hardness test specimens were cut from the tensile test specimens with a dimension of $\varnothing$35x10 and s standardom ASTM E8M-99. Vzorce dimenzij ∅35x10 mm za merjenje trdote smo izrezali iz nateznih preskušancev in jih spolirali z 3µm diamantno pasto. Uporabili smo merilnik trdote po Brinellu firme Eslinger Leckar z vtiskovalno kroglico premera 2,5 mm, obremenitev je bila 62,5 N. Trdoto smo merili na petih različnih mestih, ki smo jih predhodno določili. Nato smo izračunali povprečne vrednosti.

## 4 Mikrostruktura

Vzorce za mikrostrukturne preiskave smo brusili z brusnimi papirji 100, 220, 340, 600, 800, 1000 in 1200 in nato polirali najprej s suspenzijo 80 µm $Al_2O_3$. Ko smo jih oprali z vodo in alkoholom, smo jih ponovno polirali, tokrat z 3 µm diamantno pasto. Železov(III) klorid smo uporabili za jedkanje površine obrusov. Mikrostrukturne posnetke smo naredili s svetlobnim mikroskopom Nikon Epiphot 200.

## 5 Rezultati in razprava

### 5.1 Mikrostruktura

Slika 2 kaže spremembe v mikrostrukturah zlitin Cu-Zn z dodatki Si. Jasno se vidi, da dodatek Si vpliva na porazdelitev intermetalne faze β na kristalnih mejah. Mikrostruktura medi z 20 mas. % cinka je sestavljena iz dveh trdnih raztopin: končne trdne raztopine Cu in Zn, bogate z bakrom, ki se imenuje α, in vmesne trdne raztopine β. Na slikah 2 a-d je faza α svetlejša in faza β temnejša. Taka mikrostruktura nastane predvsem pri začetnem strjevanju faze β, ki mu sledi nukleacija in rast faze α v osnovi iz faze β. Nadaljnje znižanje temperature povzroči pretvorbo neurejene faze β v urejeno faze β.

polished with 3µm diamond paste. Hardness tests were carried out by Esslingen Leckar Brinell Hardness Test Machine with a ball indenter diameter of 2.5mm and an applied load of 62.5N. During hardness testing, five different points on the specimens were specified and the measurements were made on these points. After all, average values were calculated and reported.

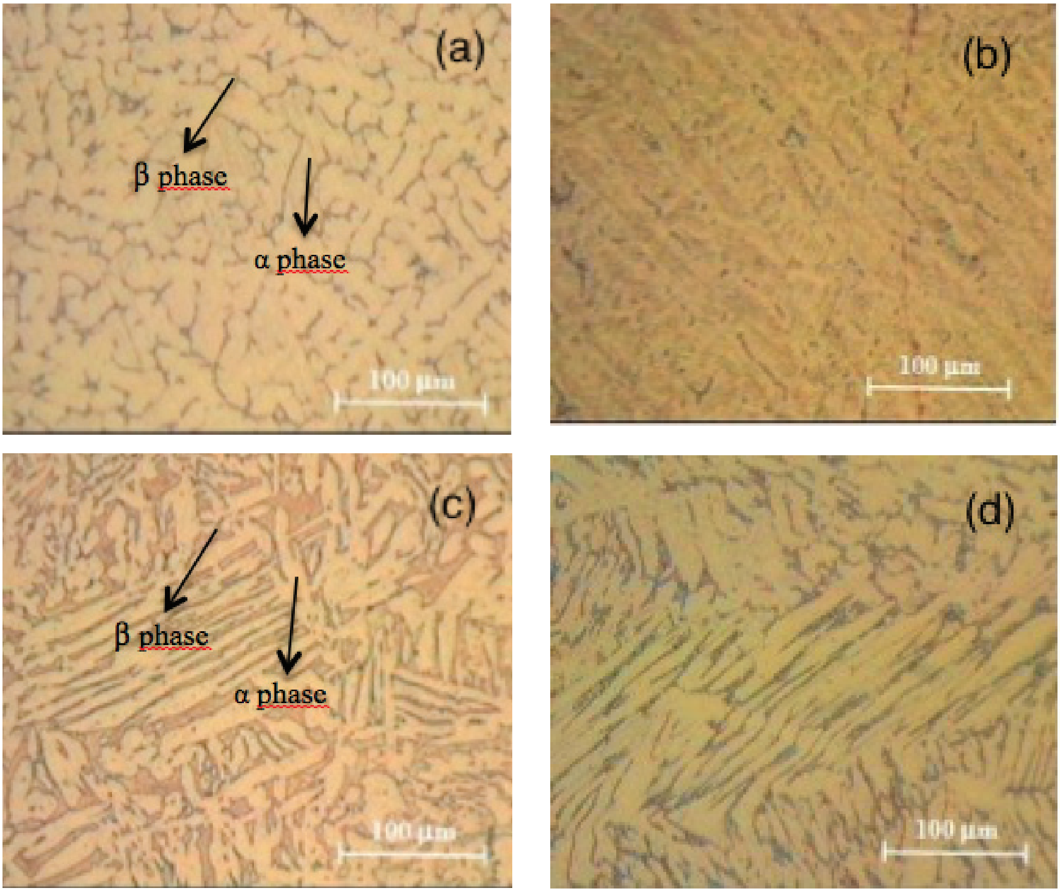
## 4 Microstructure

Specimens were grinded with 100, 220, 400, 600, 800, 1000 and 1200 grit emery papers then followed by first polishing with 80 µm $Al_2O_3$ suspension. After the first polishing, the specimens were washed in water and alcohol and they are taken to the second polishing made on 3µm diamond paste for microstructural investigations. %3 iron (III) chloride was used as etchant solution by applying to the surfaces of the specimens. Microstructure images were taken by Nikon Epiphot 200 Optical Light Microscopy.

## 5 Results and Discussion

### 5.1 Microstructure

Fig.2 shows the changes in microstructures of Cu-Zn alloy with Si. It can be clearly seen that the addition of Si in Cu-Zn affects the distribution of β intermetallic phase on grain boundaries. The microstructure of brass alloy with 20 Zn (mass fraction) % consists of two solid solutions: α terminal solid solution of Cu and Zn rich in copper called α and an intermediate solid solution β. The α phase is the lighter phase and the β phase is the darker phase shown in Fig.2 a-d. This structure was mainly formed from the initial solidification of β followed by nucleation and growth of α from the β matrix. Further reduction in temperature transformed disordered β to the ordered β phase.




**Slika 2.** Mikrostrukture zlitin Cu-Zn z različnimi dodatki Si **a)** CuZn39Pb3, **b)** CuZn22Si2, **c)** Cu Zn21Si3, **d)** CuZn20Si4

**Figure 2.** Microstructures of Cu-Zn alloys with varying amounts of Si **a)** CuZn39Pb3, **b)** CuZn22Si2, **c)** Cu Zn21Si3, **d)** CuZn20Si4

Dodatek 2 mas. % Si zlitini Cu76Zn24 je povečal delež faze β in udrobnil fazo α (slika 2b). Večji dodatek Si (4 mas. % Si) osnovni zlitini je povečal prostorninski delež faze β in osnova iz faze β je na kristalnih mejah in v notranjosti zrn vsebovala fazo α (slika 2d). Povedano z drugimi besedami, med ohlajanjem se je faza β pretvarjala v fazo α in Si je pomaknil črto topnosti Zn v faznem diagramu Cu-Zn k nižjim vrednostim Zn. Rezultati te študije kažejo, da so se le

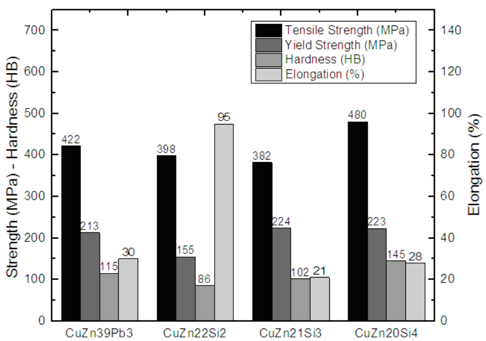
The addition of 2% Si to sample (Cu76Zn24) led to an increment of the β phase and made the α phase finer (Fig. 2b). By adding more Si (4 %) to the base alloy the volume fraction of the β phase increased and the β matrix included the α phase at the grain boundaries, as well as inside the grains (Fig. 2d). In other words, during cooling β phase was transformed into α phase and also Si shifted the solubility line of Zn to lower contents of Zn in the Cu–

majhne količine Si raztopile v fazah α in β ter da niso nastale nove trdne raztopine. Vendar je imel Si pomemben vpliv na deleže faz, delež faze β se je povečal in faze α zmanjšal. Zmanjšanje velikosti zrn v bakrovih zlitinah so pred tem opazili že pri dodatkih Fe [10]. V naši raziskavi je Si predstavljal udrobnilno sredstvo. Učinek topljencev kot udrobnilnega sredstva se kaže v spodbujanju heterogene nukleacije in/ali zmanjševanju hitrosti rasti obstoječih zrn. Iz naše raziskave sklepamo, da se gonilna sila strjevanja zmanjšuje z večanjem deleža topljenca [11]. Manjša gonilna sila strjevanja pospešuje hitrost nukleacije.

### 5.2 Natezni in trdotni preskusi

Trdoto vzorcev smo merili po Brinellu in ugotovili, da Si povečuje trdoto zlitine Cu76Zn24. Spreminjanje trdote z deležem dodanega Si prikazuje slika 3. Kot smo povedali že zgoraj, delež Si vpliva na nastanek in rast faze β. Ta faza ima večjo trdoto od faze α in zdi se, da je to eden od vzrokov za povečanje trdote vzorcev, legiranih s Si.

Slika 3 kaže tudi, da natezna trdnost pri pretrgu doseže najvišjo vrednost pri deležu Si 4 mas. %. Nadalje lahko sklepamo, da se




Zn phase diagram. Based on the results of this study, only small amounts of Si were dissolved in α and β phases and they did not form a new solid solution phase. However, Si played an important role in the fraction of phases where it increased β and decreased the fraction of α. The reduction of grain size in copper alloys was previously observed by the addition of Fe [10]. In this study, Si as a solute played role of a grain refinement agent. Effectiveness of solutes as refining agents is because of promoting heterogeneous nucleation and/or reducing the growth rate of the existing grains. In a recent study it is concluded that the solidification driving force decreases with increasing solute content [11]. The lower solidification driving force promotes nucleation rate.

### 5.2 Tensile and Hardness Tests

The hardness of samples was measured by the Brinell method and it was found that Si increased the hardness of Cu76Zn24 alloy. The extent of variation of hardness due to Si concentration is shown in Fig. 3. As discussed earlier, increase in Si content resulted in formation and growth of the β phase. This phase has greater hardness than the α phase and this seems to be one of the reasons for increments of hardness in the silicon alloyed samples.

Fig. 3 also show that the UTS reaches the peak value as Si content is 4 %.

**Slika 3.** Natezna trdnost pri pretrgu, trdota, raztezek in napetost tečenja mednih zlitin Cu76Zn24 pri različnih dodatkih Si

**Figure 3.** Ultimate tensile strength (UTS), Hardness (HB), Elongation (EL) and yield strength (YS) of Cu76Zn24 brass alloy as a function of Si content

kaže tendenca večanja napetosti tečenja z naraščajočim deležem dodanega Si, čeprav je skoraj enaka pri zlitinah, ki vsebujejo 3 in 4 mas. % Si. Povečanje trdote, natezne trdnosti pri pretrgu in napetosti tečenja se lahko pripiše udrobnjenju mikrostrukture. Odnos med velikostjo zrn in napetostjo tečenja lahko zapišemo s Hall-Petchevim izrazom:

$$\sigma_s = \sigma_o + kD^{-1/2}$$

kjer je $\sigma_s$ napetost tečenja, $\sigma_o$ in *k* sta konstanti, *D* pa je velikost zrn. Enačba pove, da se napetost tečenja povečuje z zmanjševanjem zrn.

## 6 Sklepi

Vpliv dodajanja Si zlitini Cu76Zn24 se kaže:

1. dodatek Si spreminja deleže faz v zlitini in povečuje fazo β,
2. dodatek Si zmanjšuje velikost zrn in povečuje delež faze β, kar skupaj povečuje trdoto zlitine,
3. zaradi povečanja faze β kot tudi trdote lahko napovemo izboljšano obdelovalnost razvite zlitine v primerjavi z osnovno zlitino Cu76Zn24.

Furthermore, it can be inferred that there is a tendency for YS to increase with increasing amount of Si although it is almost the same for the alloys containing 3 % and 4 %. The increase in HB, UTS and YS was attributed to decrease in grain size of the microstructure. The relationship between grain size and YS can be expressed according to Hall-Petch formulation as follows:

$$\sigma_s = \sigma_o + kD^{-1/2}$$

where $\sigma_s$ is the YS, $\sigma_o$ and *k* are constant, and *D* is the grain size. It is known from Eq.(1) that the YS increases with decreasing grain size.

## 6 Conclusion

The addition of Si to Cu76Zn24 alloy results in the following:

1. Si content changes the phase fractions of Cu76Zn24 and increases the β phase.
2. The addition of Si decreases the grain size and increases the fraction of the β phase, which overall leads to an increase in the hardness of the alloy.
3. Due to increasing the β phase as well as hardness, the developed alloy is predicted to have improved machinability properties in comparison to Cu76Zn24 alloy.

## 7 Viri

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