



# Fabrication and properties of lead-free machinable brass with Ti additive by powder metallurgy

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## ABSTRACT

The aim of this paper was to investigate the properties of Cu<sub>40</sub>Zn<sub>2.2</sub>Bi + Ti for the development of a new lead-free, high-strength and machinable brass by powder metallurgy. The effect of Ti addition on the mechanical properties and machinability of BS40-2.2Bi (Cu<sub>40</sub>Zn<sub>2.2</sub>Bi) brass was studied with respect to different contents of Ti addition. BS40 (Cu<sub>40</sub>Zn) and BS40-2.2Bi brass powders were prepared by water atomization process, and the β phase was retained in the raw powders predominately. The BS40-2.2Bi powder and Ti powder were elementally mixed to prepare BS40-2.2Bi + xTi (x = 0.3, 0.5 and 1.0 wt.%) premixed powders. The alloy powders and premixed powders were solidified at 1053 K for 600 s by spark plasma sintering (SPS) and extruded subsequently. It was observed that intermetallic compounds (IMCs) such as Ti<sub>2</sub>Bi were formed via the reaction between additive Ti and Bi alloying elements, and improved the ductility of BS40-2.2Bi significantly. The yield strength (YS) and ultimate tensile strength (UTS) were increased by increasing the contents of Ti addition, however, the elongation showed a decrease trend and the machinability became worse. The optimal content of Ti addition was 0.3 wt.%, which served excellent mechanical properties and machinability comparing with BS40-2.2Bi. For example, it had a YS of 235 MPa, a UTS of 459 MPa and an elongation of 39%, which showed 4.9%, 4.1% and 18% higher than that of extruded BS40-2.2Bi brass, respectively.

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## 1. Introduction

Brasses are widely used in many applications, such as lead frames, connectors and other electronic components, pipes, valves, and fittings in a potable water system and so on, because of their excellent electrical and thermal conductivities, outstanding corrosion resistance, good formability, and suitable strength and fatigue resistance. Lead is added in brasses to improve their pressure tightness and machinability, with the high scrap value of turnings and no need for expensive electroplating. The total cost of leaded brass products can be significantly lower than that of steel parts [1–3]. In recent years, considering the adverse health effects of lead, the stricter regulations for allowable lead content levels in products provide the impetus for the development of lead-free brass. Meanwhile, the development of the electronics industry has led to a number of new applications for copper alloys including lead frames, connectors and other electronic components. These applications require alloys with unique combinations of strength and conductivity coupled with environment amiability [4].

Bismuth can be expected to play the role of substitute lead in the alloy but without the adverse health effects, which is next to lead in

the periodic table and with similar properties. However, it has been reported that the tensile ductility is reduced when brass contains Bi element [5]. It is well known that bismuth segregates in copper, as a single atomic layer at the grain boundaries. The grain boundary embrittlement of copper by bismuth is a classical embrittling and segregating system and has been extensively studied for many years [6]. However, the role of bismuth segregation in more complex copper alloys, such as the lead-free brasses has not been as widely investigated. In such copper-based alloys, it maybe that the bismuth, in addition to forming particles throughout the alloy, segregates to the grain boundaries, this would provide an explanation for the reduced tensile ductility when compared to the conventional brasses. On the other hand, the presence of additional alloying elements may alert the segregation behavior of the bismuth from that in pure copper.

The binary phase diagrams of copper alloys [7] indicate that Cr, Fe, Ti, Zr, V, Co, Mg, Sn, etc. could be served as candidate alloying elements for precipitation strengthening, to develop high-strength and high-conductivity copper alloys. This was because the solid solubility of these alloying elements in copper would decrease sharply with the decreasing temperature. Cu–Ti binary alloys have a precipitation strengthening effect by the spinodal decomposition mechanism [8,9] involving composition modulations and long range ordering in the initial stages of ageing. According to Kumar et al. [10], the phase diagram shows five intermediate phases in the Cu–Ti system, i.e., Cu<sub>4</sub>Ti, Cu<sub>3</sub>Ti<sub>2</sub>, Cu<sub>4</sub>Ti<sub>3</sub>, CuTi and CuTi<sub>2</sub>, which indicates that

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Ti is an attractive candidate to develop high-strength copper alloys by precipitation hardening. Bismuth and titanium are commonly used in the modern time, but the Ti–Bi phase diagram is known approximately [11,12]. The knowledge of the Ti–Bi system would benefit the development of lead-free alloys in the cases when they contain both elements. Moreover, few literatures available reported the influence of Ti addition on the microstructure and properties of lead-free machinable brass containing bismuth, which is worth to be investigated. The research is a part of a project whose scope was to investigate the engineering properties of new commercial alloy formulations based on the Cu40Zn duplex phase brass, with the primary purpose to explore the possibility of a new cost-effective high-strength, high-conductivity and easy machinability lead-free copper alloys, combining the properties of precipitation hardening response of Ti. The mechanical properties and microstructure were investigated by powder metallurgy, and by employing novel spark plasma sintering (SPS).

### 1.1. Experimental procedure

As-received water atomized alloy powder Cu-40wt.%Zn (denoted as BS40), Cu-40wt.%Zn-2.2wt.%Bi (denoted as BS40-2.2Bi) (Nippon atomized metal powders Co.) and Ti pure powder were used as raw materials. To understand the effect of Ti contents on the mechanical properties and machinability of BS40-2.2Bi brass, the powders of BS40-2.2Bi + xTi ( $x = 0.3, 0.5$  and  $1.0$  wt.%) were also prepared, by premixing BS40-2.2Bi powder and Ti powder for 2 h using a ball milling machine. For sintering, 300 g powder was loaded into a cylindrical graphite die and sintered using the DR.Sinter/SPS-1030 system (Sumitomo Coal Mining, Japan). The sintering temperature and pressure were set at 1053 K and 40 MPa. After holding at the desired temperature for 600 s, the power was turned off and the sample was cooled in the chamber to less than 423 K.

The sintered billets were extruded with a pressure of 2000 kN by the hydraulic press machine (SHP-200-450, Shibayama Machine Co.). Before extrusion, the billets were preheated at 928 K for 30 min in a nitrogen gas atmosphere, and the final diameter after extrusion was of 7 mm. The thermal cycle of the experimental procedure used in preparing examples is shown in Fig. 1. The extruded round bar was machined into tensile test samples with 3 mm diameter in accordance with ICS 59.100.01. Tensile strength was conducted on a universal testing machine (Autograph AG-X 50kN, Shimadzu) with a strain rate of  $0.5 \times 10^{-4}$ /s. The strain was recorded by a CCD camera accessorized to the machine. Three samples at the same conditions were prepared

for the tensile strength test in order to evaluate an average value and the variation.

The machinability of the alloys was evaluated by a drilling test using a drill machine (EX-SUS-GDS: OSG Co.), having a 4.5 mm diameter tool, under dry conditions. The rotation speed of the drill was 900 rpm, and the applied load during drilling was 14.7 N. The drilling time to make a hole with a 5 mm depth was recorded. After repeating this drilling test 10 times, the average drilling time was used as a machinability parameter of the samples.

The phase compositions in the samples were identified by using X-ray diffraction (Labx, XRD-6100, Shimadzu) referenced to the standard ICDD PDF cards available in the system software. In addition, the microstructure evolution of the raw powder and the extruded samples with the transversal and longitudinal cross section to the extrusion direction, including the fracture surface were conducted by using a field-emission scanning electronic microscope (FE-SEM, JEM-6500F, JEOL). The phases were examined by the energy-dispersive X-ray spectrometer (DES) equipped by the SEM.

## 2. Results and discussion

### 2.1. As-received powder characteristics

The compositions of the raw powders are shown in Table 1. The FE-SEM micrographs of the raw powders are depicted in Fig. 2. The BS40-2.2Bi particles showed an irregular shape with a mean size of 164  $\mu\text{m}$ , and Ti powder showed narrow particle size distribution with a mean size of 30  $\mu\text{m}$ . Fig. 3 shows the XRD diffractography of the as-atomized powder of BS40 and BS40-2.2Bi. It can be observed that the raw powders show predominantly  $\beta$  phase peak at  $43.28^\circ$ ,  $62.87^\circ$  and  $79.39^\circ$ . Furthermore, a minor peak at  $27.33^\circ$  can be observed in BS40-2.2Bi, which is the main peak of Bi. The analysis result is agreeable with the status that the raw powder was prepared by the water atomized rapid solidification method, rapid cooled from the  $\beta$  phase field retains a single  $\beta$  phase in the powders, referring to the Cu–Zn binary phase diagram.

### 2.2. X-ray diffraction analysis of extruded alloys

The X-ray diffractography of the extruded BS40-2.2Bi and BS40-2.2Bi + xTi ( $x = 0.3, 0.5$  and  $1.0$  wt.%) samples prepared by SPS are shown in Fig. 4. It can be observed that peaks appeared at  $42.32^\circ$ ,  $49.27^\circ$  and  $72.24^\circ$  besides  $\beta$  phase peaks in all the samples, which are  $\alpha$  phase peaks. It indicates the phase transformation from  $\beta$  to  $\alpha + \beta$  duplex phase structure after sintering at 1073 K, preheating at 923 K and extrusion at 673 K, and subsequent pressing deformation. In addition, the minor peaks in extruded BS40-2.2Bi sample are detected at  $27.280^\circ$ ,  $38.110^\circ$  and  $39.768^\circ$  by the narrow scan method as shown in Fig. 5, which are considered to be the main peaks of Bi. The main peaks of Bi become broader when the extruded BS40-2.2Bi + 0.3Ti sample is concerned, which implies that the Ti additive shows a crystal refinement effect on Bi. The diffraction pattern of extruded BS40-2.2Bi + 0.5Ti is different from that of BS40-2.2Bi and BS40-2.2Bi + 0.3Ti, additional minor peaks besides Bi peaks can be observed at  $31.178^\circ$ ,  $33.606^\circ$ ,  $37.515^\circ$ ,  $38.698^\circ$  and  $40.138^\circ$ . When the Ti additive is increased to 1.0 wt.%, the Bi main

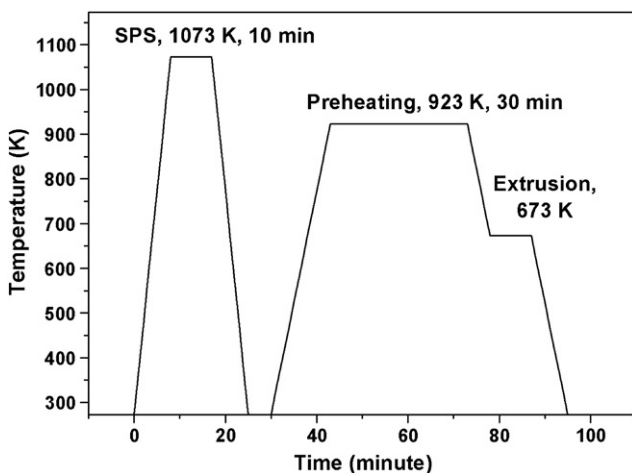


Fig. 1. Thermal cycle of the experimental procedure used in preparing samples.

Table 1  
Chemical compositions of the BS40 and BS40-2.2Bi alloy powders.

Powders	Particle size ( $\mu\text{m}$ )			Mass%		
	Median size	Mean size	Zn	Bi	O	Cu
BS40	248	279	40.00	–	0.05	Bal.
BS40-2.2Bi	139	164	40.19	2.2	0.21	Bal.

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