Development of precipitation strengthened brass with Ti and Sn alloying elements additives by using water atomized powder via powder metallurgy route

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Abstract

Effect of Ti and Sn alloying elements on microstructure and mechanical properties of 60/40 brass has been studied via the powder metallurgy (P/M) route. The water-atomized BS40-0.6Sn1.0Ti (Cu40wt%Zn-0.6wt%Sn1.0wt%Ti) pre-alloyed powder was consolidated at various temperatures within range of 400°C-600°C using spark plasma sintering (SPS) and hot extrusion was carried out at 500°C. Effects of extrusion temperature on microstructure and tensile strength were investigated by employing SEM-EDS/EBSD, TEM, XRD and tensile test. Results indicated that super-saturated solid solution Ti and Sn elements created high chemical potential for a precipitate reaction in rapidly solidified brass powder, which showed significant strengthening effects on the extruded sample consolidated at lower temperature. Solid solubility of Ti in brass matrix decreased with increasing of sintering temperature, thus resulted in degradation of mechanical properties. Consequently, lower hot processing temperature is necessary to obtain excellent mechanical properties for BS40-0.6Sn1.0Ti during sintering and extrusion. An yield strength of 398 MPa and ultimate tensile strength of 615 MPa were achieved, they respectively showed 31.3% and 22.9% higher values than those of extruded Cu40Zn brass.

Keywords: Brass; powder metallurgy; spark plasma sintering; extrusion; precipitation strengthening; solid solution; phase transformation.

1. Introduction

Brasses are extensively used in many applications because of their attractive properties such as excellent electrical and thermal conductivities, outstanding corrosion resistance, ease of fabrication, and good strength [1-3]. Widely used $\alpha+\beta$ brasses have the best combination of high technological and service properties. Solid solution strengthening and precipitation hardening are the primary methods used for developing high-strength brasses, by introducing alloying elements and impurities to improve the mechanical properties of $\alpha+\beta$ brasses [4-6]. Binary phase diagrams of copper alloys [7] show that Cr, Fe, Ti, Zr, Mg, Sn, etc. can serve as candidate alloying elements for precipitation strengthening to develop high-strength copper alloys, because the solid solubility of these alloying elements in copper decreases sharply with decreasing temperature. The solubility of Ti in copper is very low and virtually insoluble in copper, even higher than 0.2 wt% of Ti can give precipitation. According to Kumar et al. [8], the phase diagram shows five intermediate phases in the Cu-Ti system: Cu_4Ti , Cu_3Ti_2 , Cu_4Ti_3 , CuTi and CuTi_2 . Such a large number of phases imply Ti as an attractive candidate element and may be expected to develop high-strength brasses by precipitation hardening. Additionally, as a conventional alloying additive for copper alloys, Sn is completely soluble in copper and forms solid solution with copper which can significantly increase strength and corrosion resistance. From the other side, the interactions of binary systems Cu-Ti [9-11], Ti-Sn [12] and Cu-Sn [13] as well as the Cu-Ti-Sn [14, 15] are interesting topic in the prospect of joining materials by means of the transition liquid phase method. The introduction of Sn to brass is believed to enhance the solid solution strengthening effect of Zn on Cu by substituting some Sn for Zn, and

expected to impede the segregation of Ti [16, 17] and stabilize the mechanical properties of brass with Ti additive at high processing temperature via powder metallurgy (P/M) route.

Powder metallurgy process is more flexible than casting and forging techniques, and possible to fabricate components which otherwise would decompose or disintegrate in direct alloying of fused materials [18]. Rapid solidification, i.e., high cooling rate can lead to super-saturated alloying elements solid solution in the brass matrix. Upon heat treatment very fine dispersoids of the second phase are precipitated in the matrix, as a result, the precipitation hardening effect is greatly intensified. On the other hand, the technological and service properties of $\alpha+\beta$ brass are determined by their phase composition, i.e., by the presence of two main phases: an fcc α solid solution of zinc alloying element in copper and the bcc β phase based on the intermetallic compound CuZn. It is interesting to study the properties of microstructure and phase transformations in these materials, which are caused by both chemical compositions of brass and heat treatment conditions.

In this study, Ti and Sn were proposed as alloying elements additives to the Cu40Zn brass in viewpoint of alloy designation and processing method by powder metallurgy. The microstructure, phase transformation, precipitation behavior and mechanical properties of the Cu40Zn with Ti and Sn pre-alloyed P/M materials were investigated in detail.

2. Experimental

The as-received water atomized BS40-0.6Sn1.0Ti (Cu40wt%Zn-0.6wt%Sn1.0wt%Ti) pre-alloyed powder (Nippon Atomized Metal Powders) was used as the raw material. To elucidate the effects of Ti and Sn additions on properties of brass, as-received water atomized BS40 (Cu40wt%Zn) brass powder was used for comparison. Chemical

compositions of the raw powders are shown in Table 1. A thermal analysis system (DTG-60/60H; Shimadzu) was used with the combination of thermo-gravimetry (TG) and differential thermal analysis (DTA) to examine the physical properties of the as-atomized powders.

Table 1. Particle size and Chemical compositions of the BS40 and BS40-0.6Sn1.0Ti alloy powders.

Powders	Particle size(μm)		wt%				
	Median size	Mean size	Zn	Ti	Sn	O	Cu
BS40	248	279	40.	-	-	0.05	Bal.
BS40-0.6Sn1.0Ti	256	285	40.09	1.03	0.65	0.19	Bal.

For sintering, 300 g raw powder was loaded into a cylindrical graphite die and consolidated by spark plasma sintering equipment (DR.Sinter/SPS-1030; Sumitomo Coal Mining) at 400°C, 500°C and 600°C for 1.8ks, with pressure of 40 MPa. The sintered billets with 41 mm diameter were extruded using 2000 kN hydraulic pressing (SHP-200-450; Shibayama Machine). Before extrusion, the billets were preheated at 500°C for 1.8 ks in nitrogen gas atmosphere. Then the final diameter after extrusion was of 7 mm. The extruded round bar was machined into tensile test samples with 3-mm diameter in accordance with ICS 59.100.01. Tensile test was conducted on a universal testing machine (Autograph AG-X 50kN; Shimadzu) with a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The strain was recorded using a CCD camera accessorized to the machine. Three samples were prepared in identical conditions for the tensile strength test to obtain the average value. The micro-hardness was measured by a Vickers micro-hardness tester (HMV-2T, Shimadzu), and 30 measurements were conducted to obtain an average value.

The phase compositions in samples were identified using X-ray diffraction (Labx, XRD-6100; Shimadzu) referenced to the standard ICDD PDF cards available in the system

software. The microstructure evolution of the raw powder and samples with the transversal and longitudinal cross-section to the extrusion direction were carried out using a field-emission scanning electronic microscope (JEM-6500F; JEOL) and a transmission electron microscope (JEOL-JEM 3010, JEOL). Phases were examined using an energy-dispersive x-ray spectrometer (EDS) attached with the SEM equipment. Crystal orientation containing grain size and phase information was analyzed by electron backscatter diffraction (EBSD) technique, which was performed using TSL instrument attached to the FE-SEM operating at 20 kV. The transversal and longitudinal cross-section of the extruded samples were mechanical ground to 5 μm silicon carbide paper finish, and vibratory polished for 30 min to remove any remaining surface damages. The electron beam moved in 0.2 μm steps in an area 50 $\mu\text{m} \times 50 \mu\text{m}$.

3. Results and discussion

3.1 Characteristics of the raw powders

The DTA and TG profiles of the raw powders BS40 and BS40-0.6Sn1.0Ti are presented in [Fig. 1](#). An exothermic peak is visible at 280°C for BS40 powder, which suggests that the phase transformation of unstable β' to α occurred, based on the fact that the raw powders were prepared using water atomization. The high-temperature phase β of the bcc structure was transformed to ordered β' structure, and it was retained in the raw powders at rapid cooling condition. Nevertheless, no marked exothermic peak is visible near 280°C for BS40-0.6Sn1.0Ti powder, which means that the phase transformation of β' to α was slow and successive because the copper content was reduced to 58.4 wt% in BS40-0.6Sn1.0Ti when 1.0 wt% Ti and 0.6 wt% Sn were pre-alloyed with Cu40Zn brass, which retarded the

progress of the phase transformation from β' to α . At 455°C, an endothermic peak was obviously detected in both of the powders, indicating the phase transformation of β' to β , referring to the Cu-Zn binary phase diagram [7]. The gravimetric analysis curve indicated that the weight decreased concomitantly with increasing temperature over 672°C for BS40, and 625°C for BS40-0.6Sn1.0Ti powder, respectively. It suggests that Zn vaporization in BS40-0.6Sn1.0Ti powder occurred prior to BS40 powder and showed a higher vaporization rate than that of BS40. Actually, 37.3 wt% mass was lost when temperature increased to 1000°C, indicating that nearly all the Zn vaporized at 1000°C for the BS40-0.6Sn1.0Ti powders.

Fig. 1 Differential thermal analysis (DTA) and thermogravimetry (TG) of the as-atomized powders were analyzed from 20°C to 1000°C protected by argon at 450 mL/min.

3.2 X-ray diffractography

The X-ray diffractography data of the extruded BS40-0.6Sn1.0Ti are presented in Fig. 2. The raw powder was produced by rapid solidification method: cooling from the β field retained a single β' phase state in the powder. For sample sintered at 400°C, α peaks appeared at 32.324°, 49.52°, and 72.54°, indicating parts of β' phase were transformed to α phase after being subjected to thermal impact at 400°C during sintering and hot extrusion. The quantitative analyses of different phases in the samples can be calculated according to the diffraction peak intensity [19]. The phase volume fractions of α and β in samples were calculated according to the following equation.

$$V_{\alpha} = \frac{I_{\alpha(111)} + I_{\alpha(200)} + I_{\alpha(220)}}{I_{\alpha(111)} + I_{\alpha(200)} + I_{\alpha(220)} + I_{\beta(110)} + I_{\beta(200)} + I_{\beta(211)}} \times 100\% \quad (1)$$

In the equation (1), V_α stands for the α phase ratio, I_α denotes the intensity of α diffraction peak, and I_β signifies the intensity of the β diffraction peak. The α phase volume fraction in extruded BS40-0.6Sn1.0Ti increased from 50.5% to 52.3%, with the elevated temperature from 400°C to 500°C, then decreasing to 50.5% as the temperature increased to 600°C. The α phase ratio reached an maximum value of 52.3% at 500°C, which is also congruent with the Cu–Zn binary phase diagram [7]. The volume fraction of β phase showed corresponding balance variation with that of α phase. As comparing materials, the α phase volume fraction in extruded BS40 showed a much larger value, 82.6% at 400°C, 84.9% at 500°C and 80.8% at 600°C. The addition of alloying elements changes the boundaries of phase fields in the phase diagram: an increase in the content of any additions except for nickel shifts the β phase field toward low zinc content [20]. The intermetallic compound β phase has higher hardness and excellent hot workability than those of α phase, the appropriate increment of β phase volume fraction is believed to favor the mechanical properties of brass. However, β phase ratio varies only 1.8% at different temperature, which suggests that phase ratio has limited effect on extruded BS40-0.6Sn1.0Ti at present study. In addition, minor peaks at 37.3°, 38.1° and 39.26° can be observed in the samples sintered at different temperature, which can be indexed by spacing characteristic of the ternary compound CuSn_3Ti_5 . Two ternary compounds CuSn_3Ti_5 and CuSnTi and their crystal structure data have been reported in Cu-Sn-Ti system [14, 15, 21]. The ternary compound CuSn_3Ti_5 is in equilibrium with a liquid at 900°C and evolves during cooling [14].

Fig. 2 X-ray diffractography of the BS40-0.6Sn1.0Ti prepared by SPS at different temperatures.

3.3 Mechanical properties

Figure 3(a) presents the true stress versus true strain curves of the extruded Cu40Zn-0.6Sn1.0Ti and BS40 brasses, which were consolidated at different temperatures using SPS. A photograph of the tensile sample used in the present study is portrayed in Fig. 3(a). All depictions involving mechanical properties are referred to the extruded materials. The average values of the ultimate tensile strength (σ_{UTS}), the yield strength (σ_{YS}), and elongation are presented in Table 2. Compared with the BS40 prepared in identical conditions, for example that sintered at 400°C, σ_{UTS} of the BS40-0.6Sn1.0Ti was 615 MPa, which is 22.9% higher than that of the BS40. When the sintering temperature increased from 400°C to 600°C, σ_{UTS} showed a slight decreasing trend, decreasing 2.8% from 615 MPa to 598 MPa as shown in Fig. 3(b). By contrast, σ_{UTS} of the BS40 showed similar tendency as that of BS40-0.6Sn1.0Ti with elevated temperature, i.e., the strengthening effects by Ti and Sn alloying elements were not significant degraded by elevated sintering temperature.

Fig. 3 Mechanical properties of the extruded BS40-0.6Sn1.0Ti and BS40 brasses, the billets are prepared by SPS at different temperatures. The inset shows a photograph of the tensile test sample. (a) The true stress–strain curves of the extruded brasses. (b) Yield strength as a function of sintering temperature. (c) Ultimate tensile strength as a function of sintering temperature. (d) Elongation as a function of sintering temperature.

Table 2 Mechanical properties of the extruded BS40-0.6Sn1.0Ti and BS40 brasses prepared using SPS at different temperatures of 400–600°C.

Materials	Temp./°C	Y.S/MPa	Deviation	UTS/MPa	Deviation	Elongation/%	Deviation
BS40	400	303.3	0.58	500.1	0.99	41.4	1.5
	500	288	1.66	493.7	0.27	39.7	3.76
	600	251.3	1.09	483.4	1.37	41.9	1.36
BS40-0.6Sn1.0Ti	400	398.4	5.43	615.1	5.15	21.5	1.87
	500	355.2	24.84	601.4	27.98	21.9	2.45
	600	315.2	15.57	597.7	10.96	25.5	0.81

Simultaneously, excellent σ_{YS} values of 398 MPa are obtained for the sample sintered at 400°C, which is 31.3% higher than 303 MPa of BS40, manifesting significant work hardening effect of Ti and Sn additions. Then σ_{YS} decreased to 315 MPa, 26.4% of σ_{YS} was lost with increasing the sintering temperature from 400°C to 600°C as shown in Fig. 3(c). On the other hand, Ti and Sn addition showed an adverse influence on elongation of BS40-0.6Sn1.0Ti, which degraded the ductility, remaining 48.2% lower than that of BS40 at 400°C, as shown in Fig. 3(d). The primary reason for the drop off of ductility was considered as the reduction of the ductile α phase volume fraction as shown in section 3.2. In addition, the elongation decreased slightly at 500°C instead of increasing concomitantly with the increase of temperature for BS40. Nevertheless, the ductile α phase volume increased to the maximum 52.3% at 500°C, as calculated using equation (1). It was presumably attributable to the variation of the chemical composition of β phase, which was designated as an intermetallic compound. The chemical composition of the intermetallic compound β can usually have stoichiometric ratios of 45-49% Zn at 500°C [2]. The rise of the Zn element content in β phase was regarded as depressing ductility because the α phase reached a maximum value at 500°C.

3.4 Microstructure

The FE-SEM micrographs of the BS40-0.6Sn1.0Ti compacts sintered at different temperatures are shown in Figs. 4(a)-4(c). In contrast, the conventional BS40 compacts were prepared under the same conditions, as shown in Figs. 4(a')-4(c'). The raw powders prepared by water atomization consisted of fundamentally equiaxial grains of β' phase. After sintering at 400°C for 1.8 ks, the α phase was observed to precipitate along the boundaries of the initial β' phase, which was surrounded by a matrix of deeper etching β' phase, visible as fine island-like structures emanating from the primary particle boundaries. For BS40 compacts, large β' grains contained typical Widmanstätten structures of α phase, which grew larger rapidly with elevated temperature. Compared with that of BS40 compacts, BS40-0.6Sn1.0Ti showed considerably finer grains than those of the binary alloy, as depicted in Fig. 4(a), since Sn addition showed no-effective grain refinement effect on yellow brass [22], which marks Ti as a beneficial element for grain refinement. The increased volume fraction of α phase during exposure at 500°C accompanied the coarser microstructure. The ultrafine precipitates grew coarser after sintering at 500°C (Fig. 4(b)). The microstructure of the BS40-0.6Sn1.0Ti sample sintering at 600°C (Fig. 4(c)) showed a different morphology from that of samples sintered below 600°C. The α phase grows larger and shows an island shape in the β' matrix. The Ti precipitates grew coarser continuously, and the population decreased after sintered at 600°C. Furthermore, the Ti precipitate was found to be readily concentrated in the primary particle boundaries rather than grain boundaries when the temperature increases to 600°C as shown in Fig. 4(c).

Fig. 4 SEM micrographs of BS40-0.6Sn1.0Ti (a) 400°C, (b) 500°C, (c) 600°C and BS40 (a') 400°C, (b') 500°C, (c') 600°C compacts prepared by SPS.

The SEM micrographs of the SPS compact sintered at 400°C with high magnification image are shown in Figs. 5(a)-5(b). It can be observed that the constrained Ti in the super-saturated solid solution of the raw powder precipitated as ultrafine precipitates that were distributed evenly throughout the structure as shown in Fig. 5(a). In the higher resolution image as shown in Fig. 5(b), ultrafine Ti precipitate with nano-scale size concentrated at grain boundaries and formed net-like structure, partial α phase grew passing through grain boundaries. The microstructural changes before and after hot extrusion was studied by TEM and result was shown in Fig. 6(a)-6(b). In BS40-0.6Sn1.0Ti SPS sample sintered at 400°C, Ti precipitates with size of 50 nm can be observed in the interior of grains and at grain boundaries as shown in Fig. 6(a). In contrast, dislocation density was found increased after hot extrusion as shown in Fig. 6(b), increasing the dislocation density increases the yield strength which results in a high shear stress required to move the dislocations, the process is easily observed while working a material.

Fig. 5 FE–SEM micrographs of BS40-0.6Sn1.0Ti SPS compacts after sintering at 400°C for 1.8 ks: (a) lower magnification at $\times 5000$ resolution, (b) higher magnification at $\times 20000$ resolution.

Fig. 6 Transmission electron micrographic of BS40-0.6Sn1.0Ti (a) SPS compact consolidated at 400°C, (b) sample extruded at 500°C.

Figure 7(a)-7(d) present the electron backscatter diffraction (EBSD) micrographs of extruded BS40-0.6Sn1.0 consolidated at different temperatures. The grain boundaries can be identified by the lines, and the phase boundaries can be identified by colors. The green (light gray in monochrome) area represents α phase, and the red (dark gray in monochrome) area represents β phase. The α phase precipitates along the β phase boundaries, and forms

net-like structure after sintered at 400°C as shown in Fig. 7(a). After extruded with extrusion ratio of 37, the BS40-0.6Sn1.0Ti microstructure is characterized by discrete α phase elongation along the extrusion direction with corrugated boundaries (Fig. 7(b)). At the lower sintering temperatures, α phase is defined as fine globules distributed along a different band after extrusion. It means that recrystallization occurred in both α phase and β phase, and typical twins can be observed in α phase, which are the feature for dual brass. The Ti precipitates present as tiny third phase particles dispersed uniformly throughout the microstructure (Fig. 7(b)). Such a microstructure is expected to be very helpful in increasing the mechanical properties of brass alloys. The morphology of the extruded sample sintered at 600°C (Fig. 7(c)) differs greatly from these sintered at lower temperature. The α phase became progressively coarse and elongated successively along the extrusion direction as the sintering temperature increases to 600°C (Fig. 7(d)). Ti precipitate distributed not only along the plastic flow line between α/β phase bands, but also in the interior of grain. This microstructure is explainable by the tendency of partial Ti precipitates to be segregated at the primary particle boundaries as the sintering temperature increases (Fig. 4(c)), which consequently constrains the grain growth. Ti precipitates were redistributed with the flow of the large plastic deformation of the soft brass matrix by the high extrusion pressure during the subsequent hot extrusion.

Fig. 7 The grain and phase boundaries of BS40-0.6Sn1.0Ti (a) SPS compact sintered at 400°C and longitudinal cross section of the extruded sample prepared at (b) 400°C (c) 500°C, (d) 600°C using SPS reveals by EBSD technique.

Fig. 8 The grain boundaries maps of (a) BS40 (b) BS40-0.6Sn1.0Ti SPS compact sintered at 400°C reveals by EBSD technique.

The grain boundaries maps of BS40 and BS40-0.6Sn1.0Ti SPS compact sintered at 400°C detected by EBSD technique are shown in Fig. 8(a)-8(b). The distinct grain refinement can be noticed in BS40-0.6Sn1.0Ti SPS compact (Fig. 8(b)), which showed an average grain size of 1.97 μm , much smaller than 3.15 μm of BS40 (Fig. 8(a)). The grain size in the longitudinal direction of the extruded BS40-0.6Sn1.0Ti and BS40 as function of sintering temperature are shown in Fig. 9. The extruded BS40-0.6Sn1.0Ti showed much smaller grain size values than that of extruded BS40 at different sintering temperature. According to the grain size in the longitudinal direction of the extruded samples detected by EBSD, the relationship between yield strength and grain size, so-called Hall-Petch relationship is plotted in Fig. 10. The correlations between YS and grain size for the extruded BS40 showed good linear fit relationship, indicating an ideal grain size controlled strengthening mechanism for BS40. However, the R-squared value for BS40-0.6Sn1.0Ti showed a little lower fitness, which illustrated that YS of BS40-0.6Sn1.0Ti was not strictly controlled by grain size. In order to manifest the strengthening mechanism besides grain refinement and dual phase strengthening, the solid solubility of Ti and Sn in BS40 matrix at different temperatures were detected by SEM-EDS, which was shown in Fig. 11. Ti solid solubility in β phase reduced from 0.87 wt% to 0.35 wt% at 500°C sharply, and retained 0.32 wt% and 0.31 wt% solubility in α and β phase at 600 °C, respectively. While Sn in α phase and β phase illustrated relative complementary variations at different temperature, showed a few decrease totally in BS40 matrix, because of Sn is completely soluble in brass. Based on the results mentioned above, strengthening effect was weakened by the decrease of Ti solid solubility with increasing of temperature.

Fig. 9 The grain size in the longitudinal direction of the extruded BS40-0.6Sn1.0Ti and BS40 as function of sintering temperature.

Fig. 10 Hall-Petch relationship between the yield strength and the grain in the longitudinal direction of the extruded BS40-0.6Sn1.0Ti and BS40 at different sintering temperature.

Fig. 11 Solid solubility of Ti and Sn in BS40-0.6Sn1.0Ti matrix at different temperature.

4. Discussion

Super-saturated Ti and Sn elements on Cu40Zn brass matrix were found from this study to show marked strengthening effects from solid solution and precipitation reactions. A high cooling rate engenders the formation of a more refined microstructure and extended solid solubility and even metastable phases [23, 24]. The rapid cooling rate retained single β' phase in the water atomized Cu40Zn brass powders. Super-saturated solid solubility of 1.03 wt% Ti in BS40-0.6Sn1.0Ti raw powder is formed. The difference in atomic radius between Ti, Sn, Cu, and Zn provides a strain field, which is beneficial to the solid solution strengthening. Furthermore, rapid cooling from a high temperature is one method for applying stress to cause dislocation motion [25]. It was well known that when dislocations encounter obstacles such as grain boundaries, the dislocation's motion is impeded; causing the required stress to continue the deformation process to increase [26]. Dislocations may be pinned due to stress field interactions with other dislocation and solute particles, or physical barriers from grain boundaries and second precipitates. Introducing individual or combinational of these mechanisms which prohibit the mobility and propagation of dislocations is primary method to enhance a material's mechanical properties.

Super-saturation of Ti solid solution was achieved by water atomization in BS40-0.6Sn1.0Ti raw powder. Thereby high dislocation density and high precipitation potential

were created in the raw powder. The higher dislocation density of the microstructure provided more sites for precipitation, which provided a thermo-kinetic advantage for the precipitation reaction [27]. Super-saturated Ti element in the brass matrix creates a high chemical potential for precipitation reaction of Ti. The dislocation density increases gradually with increasing deformation strain during hot extrusion, which supplies more potential nucleation sites for Ti precipitation. In fact, Ti precipitated in the form of ultrafine dispersoid of CuSn_3Ti_5 during sintering and consequent hot extrusion, which distributed in grain boundaries serving as a pinning effect, increasing resistance to grain boundary slipping and producing marked work-hardening effects.

On the other hand, the tiny CuSn_3Ti_5 precipitates hinder the movement of dislocations so that higher hardness is obtained at lower sintering temperature. However, the possible recovery or dynamic recrystallization induced by hot deformation at higher temperature might reduce the dislocation density [28, 29]. Recrystallization of α phase occurred at higher sintering temperature induces a decrease of dislocation density, which has strong effects on the precipitation behaviors of CuSn_3Ti_5 particles, thereby engendering segregation of Ti precipitates at primary particle boundaries, resulting in decrease of the hardness. BS40-0.6Sn1.0Ti sintered at 400°C achieved yield strength of 398 MPa, tensile strength of 615 MPa, which are much higher than those of BS40. Sun et al. [30] established a model (SMJ model) for the nucleation of MnS particles near boundaries and dislocations in which all atoms in the boundaries, and dislocation were presumed to be the potential nucleation position. The model can be used to interpret the precipitation mechanism of Ti in this study. The consumption of Cu and Sn atoms around Ti atoms in the boundaries or

dislocations engenders CuSn_3Ti_5 nucleus formation and growth. The high-angle boundaries between matrix grains are the rapid diffusion channels at high temperature. These favor the coarsening of CuSn_3Ti_5 particles in the boundaries, which, in turn, weakens the pinning effects against the boundary migration. Therefore, the mechanical properties continue their weakening as a result of the coarsening and clearing away of CuSn_3Ti_5 particles. It is apparent that in order to develop high strength brasses to satisfy requirements for new applications during service period, more detailed studies and systematical analysis must be undertaken to elucidate the interactions between Ti precipitation behaviors and segregation mechanisms in the brass matrix.

5. Conclusion

Microstructure, phase transformation, precipitation behavior and mechanical properties of $\text{Cu}_{40}\text{Zn}-0.6\text{Sn}1.0\text{Ti}$ brass at different sintering temperature were studied. The remarkable strengthening effect of Ti and Sn addition on mechanical properties of brass was achieved by powder metallurgy processing. The super-saturated solid solution Ti element in water atomized brass Cu_{40}Zn powder created high chemical potential for precipitate reaction. Ti and Sn precipitated in the form of CuSn_3Ti_5 particles, demonstrated significant grain refinement and work-hardening effects on brass Cu_{40}Zn . Consequently, the outstanding strengthening effects obtained with yield strength of 398 MPa, ultimate tensile strength of 615 MPa. They respectively showed 31.3% and 22.9% higher values than those of extruded Cu_{40}Zn brass.

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Captions

Fig. 1 Differential thermal analysis (DTA) and thermogravimetry (TG) of the as-atomized powders were analyzed from 20°C to 1000°C protected by argon at 450 mL/min.

Fig. 2 X-ray diffractography of the BS40-0.6Sn1.0Ti prepared by SPS at different temperatures.

Fig. 3 Mechanical properties of the extruded BS40-0.6Sn1.0Ti and BS40 brasses, the billets are prepared by SPS at different temperatures. The inset shows a photograph of the tensile test sample. (a) The true stress–strain curves of the extruded brasses. (b) Yield strength as a function of sintering temperature. (c) Ultimate tensile strength as a function of sintering temperature. (d) Elongation as a function of sintering temperature.

Fig. 4 SEM micrographs of BS40-0.6Sn1.0Ti (a) 400°C, (b) 500°C, (c) 600°C and BS40 (a') 400°C, (b') 500°C, (c') 600°C compacts prepared by SPS.

Fig. 5 FE-SEM micrographs of BS40-0.6Sn1.0Ti SPS compacts after sintering at 400°C for 1.8 ks. (a) lower magnification at $\times 5000$ resolution, (b) higher magnification at $\times 20000$ resolution.

Fig. 6 Transmission electron micrographic of BS40-0.6Sn1.0Ti (a) SPS compact consolidated at 400°C, (b) sample extruded at 500°C.

Fig. 7 The grain and phase boundaries of BS40-0.6Sn1.0Ti. (a) SPS compact sintered at 400°C and longitudinal cross section of the extruded sample prepared at (b) 400°C (c) 500°C, (d) 600°C using SPS reveals by EBSD technique.

Fig. 8 The grain boundaries maps of (a) BS40 (b) BS40-0.6Sn1.0Ti SPS compact sintered at 400°C reveals by EBSD technique.

Fig. 9 The grain size in the longitudinal direction of the extruded BS40-0.6Sn1.0Ti and BS40 as function of sintering temperature.

Fig. 10 Hall-Petch relationship between the yield strength and the grain in the longitudinal direction of the extruded BS40-0.6Sn1.0Ti and BS40 at different sintering temperature.

Fig. 11 Solid solubility of Ti and Sn in BS40-0.6Sn1.0Ti matrix at different temperature.

Figure(1)

Figure(2)

Figure(3)

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Graphical abstract

The Ti and Sn alloying elements additions showed significant grain refinement on Cu40Zn-0.6Sn1.0Ti brass (Fig. (b)) as comparing with that of the conventional Cu40Zn brass (Fig. (a)), detected by electron backscatter diffraction (EBSD) technique.

Figure The grain boundaries maps of (a) BS40 (b) BS40-0.6Sn1.0Ti SPS compact sintered at 400°C reveals by electron backscatter diffraction (EBSD) technique.