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Citation	Transactions of JWRI. 2011, 40(2), p. 59-62
Version Type	VoR
URL	https://doi.org/10.18910/3776
rights	
Note	

Fabrication of High-strength Cu40ZnSnTi Brass via Powder Metallurgy and Hot Extrusion†

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Abstract

The super-saturated solid solution of Ti in water-atomized BS40-1.0Ti (Cu-40wt%Zn1.0wt%Ti) brass powder creates a high chemical potential for the precipitation reaction. However, Ti readily segregates in the primary particle boundaries at elevated temperatures, which detrimentally affectes the mechanical properties of the extruded BS40-1.0Ti brass via powder metallurgy (P/M). Accordingly, Sn was proposed as an additive in BS40-0.6Sn1.0Ti (Cu-40wt%Zn0.6wt%Sn1.0wt%Ti) to inhibit Ti segregation. Consequently, the Ti precipitates were retained as $CuSn_3Ti_5$ compound in both interior grains and grain boundaries rather than in the primary particle boundaries. This result demonstrates that Sn addition can effectively obstruct Ti segregation in the primary particle boundaries, and showed a significant grain refinement and mechanical strengthening effect on BS40-0.6Sn1.0Ti brass.

KEY WORDS: (Brass) (Powder metallurgy) (Extrusion) (Microstructure) (Mechanical property)

1. Introduction

Solid-solution strengthening and precipitation hardening are the primary methods used for the development of high-strength brasses [1-3]. Our previous study [4, 5] involved the addition of Ti to Cu-40wt%Zn brass, which favored grain refinement by increasing the formation rate of nucleation and recrystallization centers and by retarding the subsequent grain growth by fine precipitates. Unfortunately, precipitation strengthening effects continue to weaken with increased processing temperature because of segregation and the coarsening of Ti precipitates in the primary particle boundaries by the powder metallurgy route. In this study, Sn was proposed as an additive for the Cu40Zn-1.0wt%Ti brass from the viewpoint of alloy designation and processing method. The addition of Sn to brass is expected to impede the segregation of Ti and to stabilize the mechanical properties of Ti brass at high processing temperatures via powder metallurgy.

2. Experimental

The as-received water-atomized BS40-1.0Ti (Cu-40wt% Zn 1.0wt%Ti), BS40-0.6Sn1.0Ti (Cu-40wt% Zn 0.6 wt% Sn1.0wt% Ti) and BS40 (Cu-40wt%Zn) pre-alloyed powders (Nippon Atomized Metal Powders.) were used

as the raw materials. The chemical compositions of the raw powders are shown in **Table 1**. For sintering, 300g of raw powder was loaded into a cylindrical graphite die and sintered by SPS (DR.Sinter/SPS-1030; Sumitomo Coal Mining) at 400 °C – 600 °C with an interval of 100 °C. The obtained sintering billets with 41 mm diameter were subsequently extruded, using a hydraulic press with a load of 2000 kN (SHP-200-450; Shibayama Machine). Before hot extrusion, the billets were preheated to 650 °C for 1.8 ks under a nitrogen gas atmosphere. The final diameter after extrusion was 7 mm. The extruded round bar was machined into test samples with diameter of 3 mm in accordance with ICS 59.100.01. Tensile tests were conducted on a universal testing machine (Autograph AG-X 50kN; Shimadzu) with a strain rate of 5×10^{-4} s^{-1}.

The phase compositions of the samples were identified using X-ray diffraction (Labx, XRD-6100; Shimadzu). The microstructure evolutions were conducted using a field-emission scanning electronic microscope (FE–SEM, JEM-6500F; JEOL) and a transmission electron microscope (TEM; JEM-3010, JEOL). The phases were examined using an energy-dispersive X-ray spectrometer (EDS) equipped with the SEM. Crystal orientation information, which contained grain size and phase information, was analyzed by the electron backscatter diffraction (EBSD) technique. EBSD was performed using a TSL (TSL DigiView IV; EDAX) instrument

attached to the FE-SEM, which was operated at 20 kV.

Table 1. Particle size and chemical compositions of BS40, BS40-1.0Ti and BS40-0.6Sn1.0Ti alloy powders.

Powders	Particle size(μm)		Composition (wt%)				
	Median size	Mean size	Zn	Ti	Sn	O	Cu
BS40	248	279	40.00	-	-	0.05	Bal.
BS40-1.0Ti	206	250	41.19	0.99	-	0.23	Bal.
BS40-0.6Sn1.0Ti	256	285	40.09	1.03	0.65	0.19	Bal.

3. Results

3.1 X-ray diffraction

The X-ray diffraction data of the raw powders and the SPS compacts of BS40-1.0Ti and BS40-0.6Sn1.0Ti are presented in **Fig. 1**. For BS40-1.0Ti SPS compacts prepared at 400 °C, α peaks appear at 32.324°, 49.52°, and 72.54°, which indicate that the α phases precipitate and the parts of β' phases are transformed to the α phases after being subjected to thermal impact at 400 °C during sintering. The phase volume fractions of the α and β phases in the samples prepared at different temperatures are calculated using the XRD diffraction peak intensities. The α-phase ratio in the sintered BS40-1.0Ti compact increases from 50.7% to 55.9% when the temperature is increased from 400 °C to 500 °C, then decreases to 54.2% as the temperature is increased to 600 °C. For the sintered BS40-0.6Sn1.0Ti compact, the α-phase ratio shows a trend similar to that of the BS40-1.0Ti SPS compact, increased from 50.5% to 52.3%, then decreased to 50.5% as the temperature is increased from 400 °C to 600 °C. The α-phase ratio reaches a maximum value of 55.9% for BS40-1.0Ti and 52.3% for BS40-0.6Sn1.0Ti at 500 °C. The shift of the maximum value of the α-phase ratio from 55.9% in BS40-1.0Ti to 52.3% in BS40-0.6Sn1.0Ti verifies that the addition of 0.6 wt% Sn is favorable to the formation of β-phase. Because the intermetallic β-phase exhibits higher hardness and better hot workability compared to the α-phase, the appropriate increment of β-phase volume fraction created by the addition of Ti and Sn alloying elements is favorable to the mechanical properties of the brass alloys.
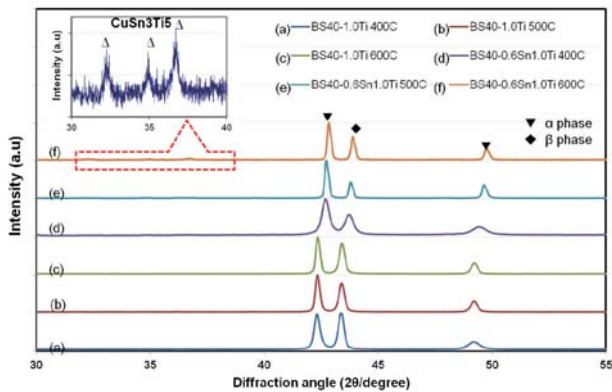

Fig. 1 X-ray diffractograms of the BS40-0.6Sn1.0Ti and BS40-1.0Ti raw powder and SPS compacts prepared at different temperatures in the range of 400 °C – 600 °C.

In addition, minor peaks at 37.3°, 38.1° and 39.26° are observed in the XRD patterns of BS40-0.6Sn1.0Ti SPS compacts sintered at different temperatures as shown in **Fig. 1**. These peaks are indexed by spacings 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 the Cu-Sn-Ti system [6-8]. The ternary compound $CuSn_3Ti_5$ is in equilibrium with a liquid at 900 °C and evolves during cooling [6]. The peak intensity of $CuSn_3Ti_5$ increases with increased sintering temperatures, which indicates that the volume of $CuSn_3Ti_5$ increases with temperature from 400 °C to 600 °C.
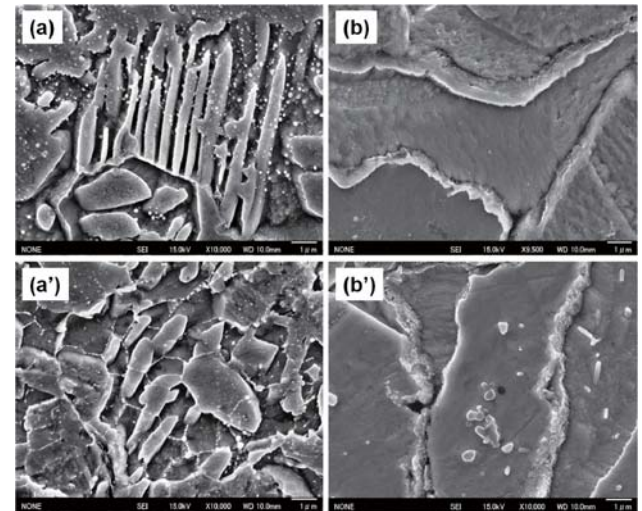
Microstructure

Fig. 2 SEM micrographs of BS40-1.0Ti and BS40-0.6Sn1.0Ti SPS compacts sintered at different temperatures. (a) BS40-0.6Sn1.0Ti, 400 ℃; (b) BS40-0.6Sn1.0Ti, 600 ℃; (a') BS40-1.0Ti, 400 ℃; (b') BS40-1.0Ti, 600 ℃.

The SEM micrographs of the BS40-1.0Ti and BS40-0.6Sn1.0Ti SPS compacts sintered at different temperature are shown in **Figs. 2**. The BS40-1.0Ti samples sintered at 400 ℃ contains ultrafine precipitates distributed evenly throughout the structure, as shown in **Fig. 2(a)**. The laminar-structured α phase coalesced and formed large island structures in the β-phase matrix. The Ti precipitates concentrated and formed a layered structure in the primary particle boundaries. Few precipitates were observed in the interior of the α and β phases in the BS40-1.0Ti compact sintered at 600 ℃ (**Fig. 2(b)**). In the BS40-0.6Sn1.0Ti compact sintered at 400 ℃ (**Fig. 2(a')**), ultrafine, nano-scale-sized Ti precipitates dispersed at grain boundaries and formed net-like structures, and a partial α phase grew that passed through the grain boundaries. After the compact was sintered at 600 ℃ (**Fig. 2(b')**), Ti precipitates were observed to grow coarser and were retained inside the particles instead of completely segregating completely in the primary particle boundaries. The precipitates were confirmed to be $CuSn_3Ti_5$ IMC according to their XRD pattern, as shown

in **Fig. 1**. **Figures 3** depict the TEM micrographs of the BS40-0.6Sn1.0Ti SPS compact sintered at 400 °C. Titanium precipitates with a size of 50 nm were observed in the interiors of grains and at grain boundaries, as shown in the bright field (BF) image of **Fig. 3(a)**. These precipitates were also discernible in the dark-field (DF) image of **Fig. 3(b)**.
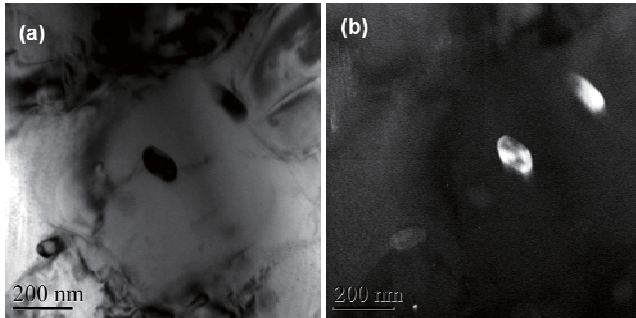

Fig. 3 Transmission electron micrographs of a BS40-0.6Sn1.0Ti SPS compact consolidated at 600 °C; (a) bright-field image; (b) dark-field image.

2.2 Mechanical properties

Figure 4 presents the true stress versus true strain curves of the extruded BS40, BS40-1.0Ti and BS40-0.6Sn1.0Ti brasses, which are consolidated at different temperatures in the range of 400 °C – 600 °C. All depictions involving mechanical properties represent the extruded materials. The average values of the ultimate tensile strength (σ_{UTS}), the yield strength (σ_{YS}), and the elongation are summarized in **Table 2**. For the samples sintered at 400 °C, the σ_{UTS} of the BS40-1.0Ti is 617 MPa, which is 23.4% higher than that of the BS40 prepared under identical conditions. When the sintering temperature is increased from 400 °C to 600 °C, The σ_{UTS} shows a dramatic decreasing trend, that is, a decrease of 19.2% from 617 MPa to 498 MPa, as shown in **Fig. 4**; this latter value is approximately the same as that of BS40 at 600 °C. The σ_{UTS} of the BS40-0.6Sn1.0Ti exhibits a distinctly different tendency than does the BS40-1.0Ti; it presents almost the same σ_{UTS} value as BS40-1.0Ti at 400 °C, shows a slight decreasing trend when the sintering temperature is increased from 400 °C to 600 °C, decreasing by 2.8% from 615 MPa to 598 MPa showing that the addition of elemental Sn has a significantly positive effect on the prohibition of the the degradation of the σ_{UTS} of BS40-0.6Sn1.0Ti at elevated temperatures.

The values of σ_{YS} for all brasses decrease gradually when the sintering temperature is increased. The σ_{YS} value of 390 MPa and 392 MPa are obtained for BS40-1.0Ti and BS40-0.6Sn1.0Ti sintered at 400 °C, respectively, which are 28.7% and 31.3% higher than the 303 MPa σ_{YS} value of BS40. These results verify that the addition of Ti makes a valuable contribution to the yield strength of brass, whereas the addition of Sn does not. The behavior of BS40-1.0Ti is, interestingly, different from that of BS40-0.6Sn1.0Ti prepared at an elevated sintering temperature. The σ_{YS} of BS40-1.0Ti exhibits a rapid drop from 390 MPa to 248 MPa, in which 36.4% of the σ_{YS} is

lost when the sintering temperature is increased from 400 °C to 600 °C. This result indicates that BS40-1.0Ti shows approximately the same σ_{YS} value as that of BS40. In contrast, the σ_{YS} value of BS40-0.6Sn1.0Ti exhibits a moderate reduction of 20.8%. The decreased rate of the σ_{YS} degradation at elevated temperatures is clearly attributable to the addition of Sn.
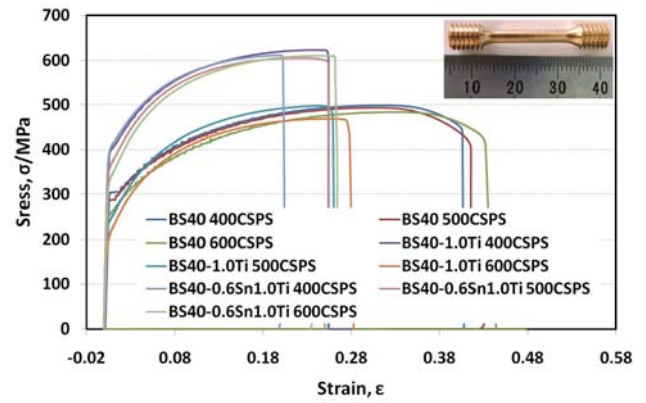

Fig. 4 True stress–strain curves of extruded BS40, BS40-1.0Ti and BS40-0.6Sn1.0Ti brasses; the billets are prepared by SPS at different temperatures of 400 °C – 600 °C. The inset shows a photograph of tensile test sample.

Table 2 Mechanical properties of extruded BS40, BS40-1.0Ti and BS40-0.6Sn1.0Ti brasses prepared using SPS in temperature range of 400 °C – 600 °C.

Materials	Temp /°C	YS /MPa	Devi.	UTS /MPa	Devi.	Elong. /%	Devi.
BS40	400	303.3	0.58	500.1	0.99	41.4	1.5
	500	288.0	1.66	493.7	0.27	39.7	3.76
	600	251.3	1.09	483.4	1.37	41.9	1.36
BS40-1.0Ti	400	390.2	12.94	617.0	12.55	26.6	2.72
	500	292.5	12.24	530.7	32.71	26.1	4.11
	600	247.8	11.27	498.6	34.42	26.5	2.62
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

4. Discussion

The Sn element is completely soluble in copper and forms solid solutions with copper. A super-saturated solid solution of 1.03 wt% Ti in BS40-0.6Sn1.0Ti raw powder is formed by the water-atomization method. The difference in atomic radii between Ti, Sn, Cu, and Zn provides a strain field, which is favourable for the solid solution strengthening. Furthermore, rapid cooling from high temperatures is one method for applying stress to cause dislocation motion [9] and thereby creating a high dislocation density and a high precipitation potential in the raw powder. The higher dislocation density of the microstructure provides more sites for precipitation, which provides a thermo-kinetic advantage for the precipitation reaction [10]. A super-saturated solution of Ti in the brass matrix creates a high chemical potential for

the 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 precipitates in the form of an ultrafine dispersoid of $CuSn_3Ti_5$ with the addition of Sn during sintering. The precipitates distribute in grain boundaries and act as a pinning effect, which increases resistance to grain boundary slip and produces marked work-hardening effects. However, the tiny $CuSn_3Ti_5$ precipitates induce significant refinement of the microstructure, which hinders the movement of dislocations so that stronger mechanical properties and higher hardness are achieved at lower sintering temperatures. The BS40-0.6Sn1.0Ti sintered at 600 °C exhibits a yield strength of 315 MPa, a tensile strength of 598 MPa and a micro-hardness of 216 Hv. These values are much higher than those of BS40-1.0Ti. The results show that the addition of Sn has remarkable positive effects. Sn increases hard strengthening by increasing the volume fraction of the harder β phase. Furthermore, it also can sustain the Ti precipitate strengthening by retaining the Ti precipitates in the interior of grains and at grain boundaries in the form of $CuSn_3Ti_5$ compound, as opposed to allowing them to segregate at the primary particle boundaries.

5. Conclusion

The Ti precipitates in the form of $CuSn_3Ti_5$ at grain boundaries in BS40-0.6Sn1.0Ti, rather than segregating at primary particle boundaries; this result demonstrates significant grain refinement and mechanical strengthening effects on brass BS40-0.6Sn1.0Ti. The results confirm that the introduction of Sn to BS40-1.0Ti brass can effectively impede the segregation of Ti and stabilize the mechanical properties at high processing temperature via powder metallurgy.

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