Microstructure Changes of Cu-Pb Alloy by Mechanical Grinding

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A high energy type ball-milling machine for mechanical grinding (MG) was used to examine its effectiveness of redistributing solute in water atomized Cu-Pb alloy powders and the process of the structure deformation of the Cu-Pb powders was discussed. The Cu-Pb powders were deformed and pulverized sequentially from their surfaces to the inner parts and pulverizing of the powders were completed after MG periods of 10 h. The structures of the sufficiently pulverized powders were composed substantially from the crystallites the diameter of which was a minimum of 50 nm and also in some parts from an amorphous-like phase. It was suggested that the crystallites are produced from an amorphous-like phase while it is unstable at ambient temperatures of the ball-milling machine. The results of DSC measurements carried out on these MG powders showed the stored energy in the MG powders was about one order of magnitude lower than the mixing free energy of the supercooled liquid Cu-Pb alloy and not enough to amorphize completely this alloy.

(Received April 18, 1991)

Keywords: mechanical grinding, ball-milling, copper-lead alloy, immiscibility, water-atomized powder

I. Introduction

Cu-Pb alloys are customarily used for sliding bearings for the lubrication ability of lead in the copper matrix. However, owing to the immiscibility of lead phase in copper, the lead may act sometimes as a kind of inclusions. It is safely presumable that if the lead phase is more finely distributed in the matrix, the load capacity of this bearing alloy can be increased.

In the present study, a high energy type ball-milling machine for mechanical alloying, the processing of which is recently established for making amorphous alloys, was used to examine its effectiveness of redistributing lead in copper. When mechanical alloying (MA) or mechanical grinding (MG)⁽¹⁾ is applied to the Cu-Pb alloys the mutual solutionizing of the both constituents will be expected as in the ordinary cases where the solid state diffusion are promoted by mixing ultra-fine particles having fresh surfaces, a large amount of point defects and dislocations⁽²⁾⁻⁽⁵⁾. However, it could be surely said that there are few examples of applying MA to the Cu-Pb alloys excepting for A. N. Patel and S. Diamond's work⁽⁶⁾. They employed a high energy milling machine for prealloyed rapidly solidified Cu-Pb-Sn bearing alloy and showed a remarkable refinement of the microstructures of this alloy by MA or MG but its details is unknown. The authors also have reported the microstructural changes in water atomized Cu-30 mass%Pb alloy powders by MG process and concluded that mutual solid solutionizing between Cu and Pb hardly take places excepting their microstructural refinement⁽⁷⁾. The present study was aimed to reveal and discuss further the process of structural deformation of the Cu-Pb alloys by MG.

II. Experimental Method

A material used for MG processing was water atomized Cu-Pb powder alloy of about 30 μm in diameter and its chemical composition is shown in Table 1. Mechanical grinding were carried out by using a ball-mill of high energy type (Mitsui-Miike, MA1D-X); bearing steel balls of 3/8" in diameter and the Cu-Pb alloy powders were mixed in the ratio of 3.5:1 by volume and stirring was continued for a maximum period of 50 h in argon gas atmosphere. MG treated powders were subjected to X-ray diffraction and differential scanning calorimetry (DSC) analyses, and scanning electron microscopic (SEM) and transmission electron microscopic (TEM) observations.

III. Experimental Results and Discussion

The immiscible phase of Pb in the water atomized Cu-Pb alloys is segregated in the dendritic cell boundaries of the copper matrix as shown in Fig. 1. The dimension of the dendritic cells depends on atomized powder size. The smaller the powder size is, the smaller the cell size is, because of its heat transfer efficiency across the surface of the powders. The cell structures of the powders having average size of 30 μm , vary from fine columnar at the surface side to coarse equiaxed one in the central region of the powders as often seen in the conventional chill castings. When these powders were ball-milled for various periods of time, the microstructures changed with the milling periods as representatively shown in Fig.

Table 1 Chemical composition (mass%) of water-atomized Cu-Pb alloys.

Cu	Pb	Sn	Fe	Zn	Ni	Sb
bal.	31.6	0.91	<0.03	<0.05	<0.05	<0.05

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Fig. 1 SEM microstructures of water-atomized Cu-30 mass%Pb alloy powders. Pb rich regions are colored with white.

Fig. 2 Change in the microstructures of water-atomized Cu-Pb alloy powders ball-milled for 3 h, "a": plastically deformed and flattened zone, "b": laminated zone.

2 that corresponds to the structures of MG powders ball-milled for a period of 3 h. It can be seen that the spherical shape of the powders was plastically deformed and flattened. In the area (marked with "a") of this deformed powder, the dendritic cells were elongated along the flattened surface of the powder and thus Pb segregated in the cell boundaries was not dispersed throughout the matrix. The area "a" is also surrounded by a layer marked with "b". This layer has an indefinite structure, which might safely be formed by severe plastic deformation corresponding to the fracture strain of the matrix during ball-milling. The formation of such a layer structure suggests that each of the atomized powders around the average size is not crushed and pulverized all at once but sequentially from its surface during ball-milling. When the thickness of the layer exceeds a critical value, these layers are detached from and stuck on the powders and the region "a" becomes so small that it cannot be identified by any way. In this process, kneading effect should be prominent⁽⁸⁾⁽⁹⁾. After ball-milling of about 10 h almost all of the atomized powders were pulverized as shown in the region "b".

Prolonging ball-milling time up to 50 h, which should guarantee the complete pulverizing, gave a structure (by TEM) as shown in Fig. 3. The samples for TEM observations were prepared by dipping up the MG powders by a mesh coated with carbon film. Figure 3(a) shows an irregular shape of the MG powders that can be observed as dark shadows under a low magnification. Selecting extremely small one from these powders could allow one to observe the structures of MG powders as shown in Fig. 3(b), in which the MG powder is constructed from fine grains of about 50 nm in diameter as supported by Debye rings of the reflections from Cu and Pb lattice planes. Under TEM observations, occasionally the instantaneous formation of these fine grains could be recognized in the other powders which have an amorphous-like

Fig. 3 TEM microstructures of MG powders ball-milled for 50 h; (a) low magnification picture of dispersed MG powders, (b) high magnification picture of aggregated small MG powder.

Fig. 4 TEM dark field image of MG powder ball-milled for 50 h, showing amorphous-like structure with fine dispersed grains.

structure with fine crystalline phases as suggested from the haloes of the selected area diffraction pattern (Fig. 4). The haloes are appreciably different in the hierarchy of the Debye rings of the Cu and Pb as the haloes appear only near $(111)_{\text{Pb}}$ and $(200)_{\text{Cu}}$ or $(220)_{\text{Pb}}$ Debye rings. Such an amorphous-like particle could not be so frequently observed as the polycrystalline particles did and these TEM observations lead us to judge that the Cu-Pb alloys should be amorphized by MG but the amorphized phases are thermally less stable.

Another interesting powder structure could be seen on the MG powders ball-milled for 50 h as shown in Fig. 5. The powder takes almost square shape and its size just over 100 nm. Also some stripes (marked A and B) which lie in the direction of the square axis can be emphasized. Diffraction pattern inserted in the figure shows the (100) plane of copper and each reflection spot have streaks

Fig. 5 TEM microstructure of a single crystal in MG powders ball-milled for 50 h. Mark A and B show stripes lying in the direction parallel to the streaks of the reflection spots in the insert.

parallel to $\langle 100 \rangle$ which coincides with the direction of the stripes. Thus, the streaks may have been caused by the stripes and if it is the case the stripes are stacking faults.

Now then, as the stacking fault energy of pure Cu is high it is difficult for pure Cu to form such a defect. However, when the elements having higher valence numbers than Cu are added to Cu, the stacking fault energy of Cu decreases with their concentration and the stacking faults are likely to form⁽¹⁰⁾⁻⁽¹²⁾.

The valence number of Pb is 2 and hence the Cu-Pb alloy lowers its stacking fault energy if Pb dissolves into Cu. The above consideration should lead us to have an idea that MG process by means of the ball-milling has an ability to increase the solid solubility of Pb in Cu though its solid solution is less stable as in the case of the amorphous-like phase (Fig. 3).

X-ray diffraction analyses (Fig. 6) which were carried out to reveal the structural changes of the MG powders with ball-milling period⁽⁷⁾ could hardly prove the formation of amorphous-like phase as shown in Fig. 4 even though there were some broadening and intensity change in the back ground near $(111)_{\text{Pb}}$ reflections. Thus, there should be not so much amorphous-like particles in volume as the TEM observations of these MG powders could demonstrate their presence. In viewing the above results, the water atomized Cu-Pb alloys could be crushed to extremely fine pieces enough to form the amorphous-like alloys followed by mechanical alloying but these MG powders could not keep themselves in such an unstable state for a acceptable period; that is, they are most likely to crystallize during and/or after ball-milling. Estimated crystallite sizes of Cu and Pb from the half-value width of X-ray reflections were from 10 to 30 nm⁽⁷⁾ and consistent in terms of the magnitude with the TEM observations. It is noticeable here that there is a small amount of tetragonal PbO in the atomized powders and its X-ray reflections, particularly from the lattice planes intersecting c-axis, shift their reflection angles to higher values leading a decrease in their intensities with ball-milling period. Table 2 shows the change in the lattice spacing of $(101)_{\text{PbO}}$ and $(110)_{\text{PbO}}$ as well as calculated c/a with ball-milling periods. An apparent decrease in the lattice axial ratio (c/a) of tetragonal PbO can be recognized and suggests the formation of a nonstoichiometric oxide like a $\text{Pb}_x\text{O}_{1-x}$ in MG processing.

MG processing also gives the Cu-Pb powders an excess energy as well as the structure changes mentioned above. Such an energy can be estimated from exothermic or endothermic heats by means of a DSC (differential scanning calorimetry) measurement. Fig. 7 shows some results of DSC thermograms of the MG powders, measured in the atmosphere of Ar gas, as a parameter of ball-milling period. Heat-flow is defined here as "J/s/g". The lowest heat release is in the as-atomized powders (0 h) and a sharp endothermic peak due to eutectic reaction at 599 K⁽¹³⁾ can be seen there. Increasing the ball-milling periods the heat-flow rates increase as the energies of MG

Fig. 6 Change in X-ray diffraction profiles of MG powders with ball-milling periods: (a) as-water-atomized, (b) 1 h, (c) 3 h, (d) 10 h, (e) 25 h, (f) 50 h.

Table 2 Interplaner lattice spacing (nm) and axial ratio of PbO.

MG periods (h)	d_{101}	d_{110}	c/a
0	0.3129	0.2812	1.275
1	0.3122	0.2812	1.268
10	0.3103	0.2812	1.248
25	0.3077	0.2812	1.221
50	0.3055	0.2812	1.200

powders given by the ball-milling increase. These stored energies that might be kept in the forms of the lattice defects, strain and/or the increased grain boundary area as well as surface of the MG particles are mostly released during heating up to about 773 K.

Apparent exothermic peak due to the crystallization of amorphous phase could not be recognized in the DSC curves as was predicted in the results of X-ray diffraction

Fig. 7 DSC thermograms of MG Cu-Pb alloys: given MG times are ball-milling periods (heating rate: 5 K/min). Marked arrow indicates the weak exothermic peak.

analyses (Fig. 6); nevertheless, a very weak exothermic peak (marked with an arrow) the intensity of which increases with increasing the ball-milling periods can be seen at about 623 K. So as to inquire into the cause of this peak, the MG powders ball-milled for 50 h were annealed for 1 h at several temperatures and the line profiles of X-ray diffraction were measured on these annealed samples. The half-value widths (B) of the $(111)_{\text{Cu}}$ reflection were calculated from the line profiles by a Brill's method⁽¹⁴⁾ and also plotted against the temperatures in Fig. 7. A pronounced decrease in the half-value widths can be seen at a temperature of about 573 K to which the weak exothermic peak temperature corresponds well. Such a decrease in the half-value widths should have been due to the recrystallization of Cu and hence the same to the weak exothermic peak.

Total released energies in the temperature range from 373 to 773 K were estimated from the area surrounded by both of the DSC curves of the as-atomized powders and of the ball-milled powders. These released energies were 2.09, 2.39 and 3.91 kJ/mol for the ball-milling periods of 1, 3 and 50 h, respectively.

After Schwartz and Johnson⁽¹⁵⁾ the definition of solid state amorphizing involves a large negative enthalpy of mixing as well as the fast diffusion of one component. In Cu-Pb alloy⁽¹⁶⁾⁽¹⁷⁾, the enthalpy of mixing has positive values over the whole composition range to be considered and gives a value of 2.9 kJ/mol to the Cu-30 mass%(11.6 at%)Pb alloy at 1473 K. The entropy of mixing of this alloy is 3.8×10^{-3} kJ/mol·K at the same temperature. If this liquid alloy is undercooled to an ambient temperature of 300 K with negligible small changes in the enthalpy of fusion of Cu and Pb⁽¹⁸⁾, the free energy of this supercooled alloy gives a positive value of about 10 kJ/mol referring to the mechanical mixture of Cu and Pb at the solid state. Chemical driving force to form amorphous alloys is thus lacked in this alloy and it is suggested that the amorphization of the Cu-Pb alloys will need an energy more than 10 kJ/mol by MA or MG as suggested in the Cu-Ta system the mixing enthalpy of which is positive⁽¹⁹⁾.

In the present experiment, the stored energies within the MG powders may be kept substantially in high-angle grain boundaries of Cu, as pointed out by Y. Seki and W. L. Johnson⁽²⁰⁾. The average grain sizes of the MG powders of the Cu-Pb alloys were estimated to be 10 to 30 nm after 50 h ball-milling⁽⁷⁾ and the corresponding grain boundary areas of these grains which were calculated according to an approximate method for truncated octahedral grains⁽²¹⁾ were 168 and 84 m²/mol, respectively. Using the experimentally determined grain boundary energy value of about 625 mJ/m²⁽²²⁾⁽²³⁾, the grain boundary energy of the MG particles is calculated to be 105 J/mol and 53 J/mol for the grain size of 10 and 30 nm, respectively. These values are at least one third of the total released energy of the MG powders. Thus, almost all of the released energies are suggested to be the contributions from the lattice defects, strain and the surface of the particles and maybe very small from

the amorphous-like phases.

Also the endothermic peak due to the eutectic reaction decreases its intensity with increasing the ball-milling periods and fades away in the MG powders milled for 50 h. In this connection, endothermic heats (essentially the enthalpy of fusion of Pb) at the eutectic reaction temperature were 0.058, 0.053, 0.018 and nearly 0 kJ/mol for the ball-milling periods of 0, 1, 3 and 50 h, respectively. Such a decrease in the enthalpy of fusion of the component is reported also on a ball-milled Ge-Sn alloy by Koch⁽²⁴⁾ and its cause has been considered to be due to disordering or amorphizing of Sn at the interface of the Ge/Sn. In the case of the Cu-Pb powders, the quantity of chemically analyzed Pb in the ball-milled powders was nearly equal to that in these starting materials, so the decrease in the enthalpy of fusion may not be due to the loss of Pb under the milling process but the preferential amorphization of the Pb phase as indicated in the Ge-Sn alloys; however, it is not the case because the halos as shown in Fig. 4 rather contain a few reflection spots from the Pb. Thus, the most probable source for the decrease in the enthalpy of fusion may be from the oxidation of Pb during handling the MG powders in atmosphere. Such a presumption is supported by the reflection intensity changes between PbO and Pb in the X-ray profiles (Fig. 6) where the intensity ratio of $(311)_{\text{Pb}}$ to $(103)_{\text{PbO}}$, for instance, tends to decrease with the ball-milling period.

IV. Conclusions

The water atomized Cu-Pb powders are deformed and pulverized sequentially from their surfaces to the inner parts by mechanical grinding. Pulverizing of the atomized powders are completed after the ball-milling or MG period of about 10 h.

The structures of the sufficiently pulverized powders by the ball-milling are composed substantially from the crystallites the diameter of which is a minimum of 50 nm and also in some parts from an amorphous-like phase. There is a probability that these crystallites are produced from an amorphous-like phase while it is unstable at ambient temperatures of the ball-milling machine.

Stored energy in the ball-milled powders is about one order of magnitude lower than the free energy of the supercooled liquid Cu-Pb alloy and not enough to amorphize this alloy.

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