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CHARACTERISTICS OF SPLAT-COOLED $SnBi_5Pb_x$ ALLOYS

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Sn-5wt.%Bi binary master alloy was prepared by melt spinning. Ternary alloys with different Pb contents of 0.5 to 2.5 wt.% were prepared by the same technique. All alloys were irradiated with 1.2 MGy γ-radiation at room temperature. The internal friction, thermal diffusivity and Young's modulus were measured at room temperature, before and after irradiation by applying the resonance technique. DTA thermograms and X-rays diffraction patterns were obtained for the tested alloys. The results show a remarkable dependence of the measured properties on both the Pb content and irradiation doze. The observed changes are attributed to the defects induced by irradiation and to the uncontrolled dispersion of Pb content in the matrix which leads to the composition inhomogeneity and density fluctuations.

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1. Introduction

The amount and type of elements added to binary alloys produce alloys with new properties [1]. The addition of 0.5wt.%Zn to Cu-5wt.%Sn alloy decreased the saturation levels of resistivity change in the temperature range 573 – 773 K and increased the flow stress needed for Cu-Sn-Zn samples to attain the same amount of strain as in Cu-Sn samples under the same conditions [2]. This was attributed to both the strong tendency of Zn atoms to segregate on deformed grain boundaries which retards softening due to slowing down of the initial rate of precipitate formation and due to the grain refining effect of Zn which improves the mechanical properties of Cu-Sn-Zn alloy [2].

Indium atoms (0.21 wt.%), which have a low solubility in Al and have a strong tendency to segregate on deformed grain boundaries [3], raised the strength parameters of Al-0.21 wt.%Au alloy due to their large effect on the distribution of vacancy clusters and modifying the structure of h-precipitate in Al-Au alloy [4].

In the ternary bearing alloy Sn-Sb-Ag, marked changes in the elastic stiffness and finer-grained structures were observed after adding Cu up to 2.5 wt.% and rapid quenching from the melt [5]. The ductility of the Bi-Sn eutectic alloy significantly improved [6] by adding small amount of Ag (less than 0.5 wt.%).

Electrical resistivity of melt-spun Pb-Sn alloys showed a strong dependence on microadditions [7]. It was suggested that alloying additions may interface with nucleation event by changing the precipitate characteristics and/or boundary properties [8].

Tin-bismuth alloys attracted attention because of their good properties as solders for some delicate electronic tools. Creep tests of Sn-5wt.%Bi revealed a decomposition of the alloy at 328 K into a solid solution and pure Bi. Both the strain rate sensitivity parameter changes and the values of the activation energy obtained before and after precipitation of the Bi phase were attributed to a grain boundary sliding mechanism [9]. A decrease in the steady state creep rate and an increase in the activation volume were obtained [10] with increasing grain size for Sn-0.5 at.% Bi alloy. This was interpreted as being due to the segregation of the solute atoms (Bi) in the vicinity of the grain boundaries as well as on the moving dislocations.

Ionizing radiation is known to be one of the major sources of altering the internal structure and properties of materials [11]. The experimental data obtained for irradiated rapidly solidified metallic materials revealed that the radiation-induced defects could be classified into vacancy-type defects and extended defects [12].

The Sn-Bi-Pb alloys, due to a formation of very heterogeneous and complexed structures, seem to be promising and interesting. The present work aims to identify the effect of Pb addition and irradiation with gamma rays on the mechanical and thermal properties of Sn-Bi alloys rapidly solidified from the melt.

2. *Experimental procedure*

In the present study Sn–5wt.%Bi–$x$wt.%Pb alloys, with $x = 0$, 0.5, 1, 1.5, 2 and 2.5, were prepared from high-purity Sn, Bi and Pb (99.99%). The proper amounts of the used elements were melted in a porcelain crucible kept in an electric furnace adjusted at constant temperature. Melt-spinning technique was carried out by using single roller aluminium wheel of 180 mm in diameter and an electric motor with 2800 rpm to produce ribbons of 6 mm wide and 0.1 mm thick.

The mechanical behaviour of the melt-spun alloys was studied before and after γ-rays irradiation using the dynamic resonance technique based mainly on the theory of free vibrations of solid bodies [13].

The low level alternating stress used in the dynamic resonance method does not permit anelastic processes, such as creep or elastic hysteresis, to take place. This represents an advantage for the resonance method over the static methods used for measuring elastic moduli. Measurements were obtained by using a vibrator as external source for the applied driving periodic force, $f = f_0 e^{i\omega t}$, where f_0 is the amplitude of this force and ω is the frequency. In the dynamic tests with the cyclic deformation of a specimen, the frequency of the oscillations plays the role of the time factor.

The internal friction, Q^{-1}, dynamic modulus, Y, and thermal diffusivity, $D_{\rm th}$, were obtained from the resonance curves of the samples by using the following relations [13]

$$Q^{-1} = \frac{\Delta F}{\sqrt{3} F_0} = 0.5773 \tan\delta\,, \tag{1}$$

where F_0 is the resonance frequency at which the peak damping occurs, ΔF is the full width at half-maximum amplitude of the resonance curve and $\tan\delta$ is the mechanical loss

$$\left(\frac{Y}{\rho}\right)^{1/2} \frac{K}{2\pi} = \frac{L^2 F_0}{Z^2}\,, \tag{2}$$

where ρ is the density of the sample under test, L is the vibrating sample length, K is the radius of gyration and Z is a constant depending on the mode of resonance (for the fundamental mode of resonance Z assumes [13] the value 1.875)

$$D_{\rm th} = \frac{2t^2 F_0}{\pi}\,, \tag{3}$$

where t is the thickness of the sample [14].

The X-ray diffraction patterns were recorded with a conventional Bragg-Brentano DP-D1 Shimadzu powder diffractometer equipped with a graphite monochromator. The wavelength λ was that of CuKα_1 (0.15406 nm) and the scanning speed was 4 degrees per minute. The degree of crystallinity is defined as the concentration of the crystalline portion existing in a certain sample. Measurements of crystallinity degree, x or CD, in terms of the equation

$$x = \frac{1}{1 + K\dfrac{I_a}{I_{cr}}}\,, \tag{4}$$

in which I_a and I_{cr} are the intensity of the diffracted beam from the amorphous and crystalline portions, respectively, were obtained by using the DP-D1 system option software crystallinity calculation for XD-D1 (P/N 215 - 00171), published by Shimadzu corporation, Surface Analysis and Semiconductor Equipment Department (Hadano), Kyoto, Japan.

The crystallite size, D, was calculated from the relation [15]

$$D = \frac{S\lambda}{B\cos\Theta}\,, \tag{5}$$

where S is the Scherrer‘s constant, which is taken as unity, and B is the broadening of diffraction line (full width at half maximum intensity of the peak) at Bragg‘s angle Θ. The correction for the instrumental broadening was not performed.

The prepared samples were irradiated with gamma-rays with the doze of 1.2 MGy from a ^{60}Co source, with a dose rate of 143 Gy /min at room temperature, in air, for 139.8 h.

The differential thermal analysis was carried out using Shimadzu thermal analyzer DT-30. A specimen having about 20 mg was used and heating started from room temperature to 500 °C with a heating rate of 10 K min^{-1}. The specific heat under constant pressure C_p was obtained from the relation [16]

$$C_p = \frac{Q}{M\Delta T}\,, \tag{6}$$

where Q is the energy transferred to the sample, M is the mass of the sample and ΔT is the temperature change of the sample.

3. *Results and discussion*

Figure 1 shows the dependence on Pb concentration of: (a) internal friction, Q^{-1}, (b) thermal diffusivity, $D_{\rm th}$ and (c) dynamic elastic modulus, Y, as deduced from the resonance curves obtained for Sn-5 wt.%Bi base alloy samples before and after irradiation. It shows that Q^{-1} increased when adding 0.5 wt.%Pb for all samples and then decreased with further increase of Pb. It is well known that elastic vibrations in a solid are damped even in the absence of external force. Also, whenever a dislocation moves through a crystal at finite speed, energy is radiated as phonons and this is the basis of the stress independent, and hence the strain amplitude, dynamic loss which dominates at high frequency [17].

In the tested rapidly solidified specimens, the condensation of the excess quenched-in vacancies leads to the formation of dislocation loops within few seconds after quenching [18]. In this case, the surface energy is converted to the strain energy and contributes to the internal hardening in the specimens (see Fig. 1c). In the Pb-free alloy, the quenched-in vacancies might be annihilated at dislocations to form jogs, or pin the slowly moving dislocations, or the dislocations which have just stopped moving, as these appear to be much more efficient sinks for vacancies than stationary ones [19]. The atoms of the small Pb content (0.5wt%) interact with vacancy clusters forming Pb-vacancy pairs. These pairs constitute elastic dipoles and this lowers the local symmetry of the lattice and give rise to anelastic deformation [20]. This causes an increase in Q^{-1} (see Fig. 1a) and Y (see Fig. 1c), and keeps $D_{\rm th}$ nearly at the level of the Pb-free specimen (see Fig. 1b). Under the effect of the applied vibrational force, two sources of loss may operate: 1) the frequency-independent breakaway loss, due to dislocations being pulled away from their pinning points, and 2) the frequency-dependent relaxation loss based on the existence of defects with several alternative geometrical configurations, each having the same formation energy and, therefore, with equally populated states but being separated by a maximum of free energy. This can account for the maximum value of Q^{-1} (Fig. 1a) and suggests the equality of the jump frequency for configuration changes and the applied frequency. In spite of this state, Pb addition in general, raises the strength level of the alloy (Fig. 1c), due to the local strains generated by the added Pb atoms. With a further increase of the Pb fraction, the inhomogeneous distribution of Pb atoms in the alloy, and their increased precipitation on the mobile dislocations forming pinning points, lower the density of the mobile dislocations, which decreases the mechanical loss as observed in Fig. 1a and causes a continuous increase of strength (Fig. 1c). Higher values of Q^{-1} and $D_{\rm th}$ (Fig. 1a,b) and lower values of Y values (Fig. 1c) for irradiated samples in relation to those of the unirradiated samples might be due to the increased γ-ray-irradiation-induced vacancies and interstitial defects which increase the possibility of pair formation. Besides, the rearrangement of the internal components of the alloy, involving defect distribution and perhaps defects annihilation, increases the vacancy-aided diffusion of the impurity atoms.

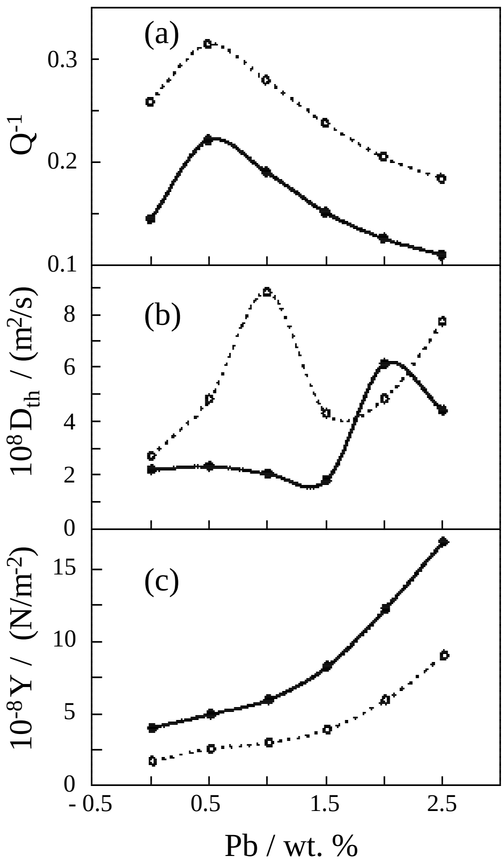

Fig. 1. The Pb *concentration dependence of: a) internal friction Q^{-1}, b) thermal diffusivity $D_{\rm th}$ and c) dynamic elastic modulus Y, for* Sn-5 *wt.%*Bi *based alloys before (full lines) and after irradiation (dotted lines).*

Thermograms of melt-spun alloys with different Pb content were obtained in the temperature range from 293 K to 773 K (20 – 500 °C), with a heating rate of 10 °C/min. Representative examples of these thermograms are given in Fig. 2a for both the binary alloy and the ternary alloy with 0.5 wt.% Pb. The peak associating the fusion of the sample seems to be sensitive to its composition. This is clear from the variations of the liquidus temperature, T_L, and the solidus temperature, T_S, with Pb content, shown in Fig. 2b. Both the liquidus temperature, T_L, at which the alloy liquefies and the solidus temperature, at which Bi crystals liquefy but Sn is still as solid crystals, increased slightly with 0.5 wt.%Pb addition, then decreased with a further increase of Pb addition.

It seems that the added low content (0.5 wt.%) of Pb highly modified the distribution of the internal defects. This can lead to a certain degree of improved internal ordering, reflecting the existence of a polycrystalline structure. Such a state is supported by the following observations: i) retarding liquefication of the binary alloy components as is clear from the increased T_S and T_L values (Fig. 2b), ii) the de-

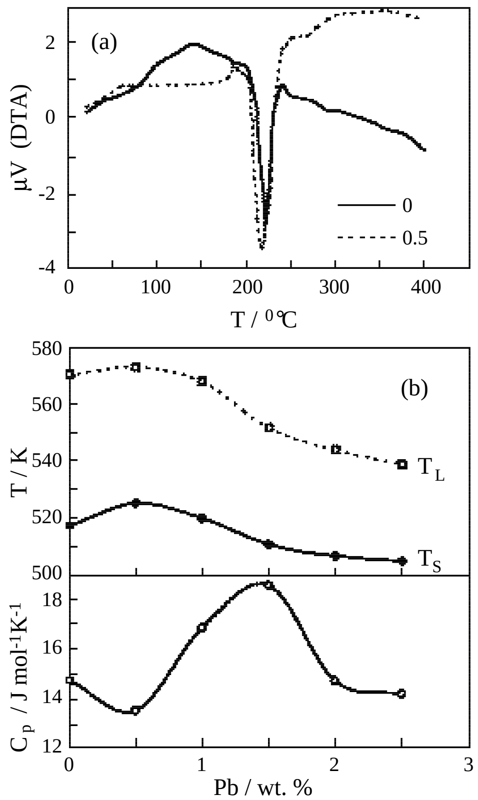

*Fig. 2. a) A representative example for the thermograms of the binary (*Sn-Bi5*, full lines) and the ternary alloy (with 0.5 wt.%* Pb *dotted lines). b)* Pb *concentration dependence of the solidus temperature, T_S, liquidus temperature, T_L, and specific heat, C_p, for* Sn-Bi5 *based melt-spun alloys.*

creased value of C_p (Fig. 2b), iii) the increase of the degree of crystallinity (CD), shown in Fig. 4a as deduced from the X-rays diffraction patterns of the tested samples, of which Fig. 3 is a representative example and iv) the decreased mean crystallite size, D, shown in Fig. 4b.

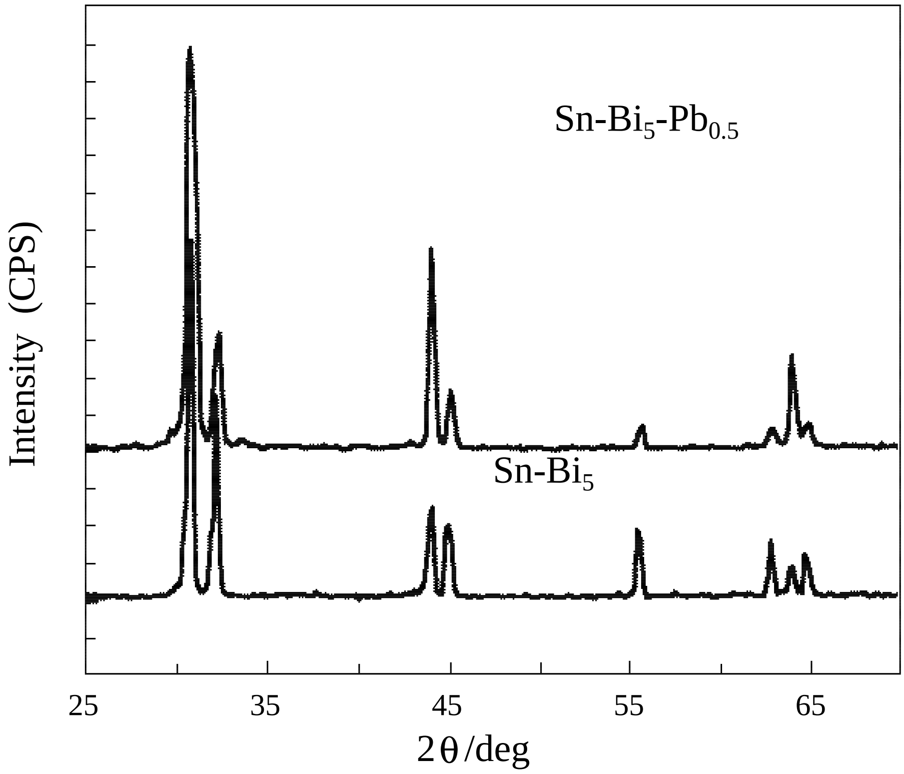

*Fig. 3. Representative X-ray diffraction patterns of the binary (*Sn-Bi5*) and the ternary alloy (with 0.5 wt.%* Pb*).*

The irregular variations of the crystalline characteristics of the tested alloys, presented in Fig. 4, can be rendered mainly to the modifying effect of Pb, showing itself by the high polycrystalline nature of the formed ternary alloys, the absence of preferred orientations in a medium of considerable inhomogeneous composition and the irregular coarsening or growth inhibition that may take place in the presence of different amounts of Pb with uncontrolled dispersion behaviour in the base alloy. From Fig. 2b it is clear that the value of C_p reaches maximum for 1.5 wt.%Pb. This suggests a high corresponding internal self-energy acquired by such alloy components.

The excess specific heat ΔC_p obeys the experimental law [21]

$$\Delta C_p = A \left(\frac{NE^2}{RT^2} \right) \exp \left(\frac{-E}{RT} \right) , \tag{7}$$

where N is the number of atoms displaced from the equilibrium position, E is the activation energy of the thermally activated ordering, R is the universal gas

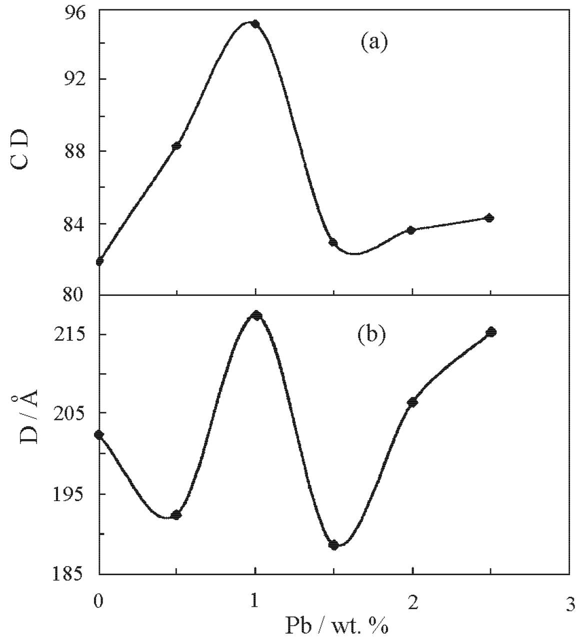

Fig. 4. Pb *concentration dependence of: (a) crystallinity degree* CD*, and (b) the mean crystallite size* D*.*

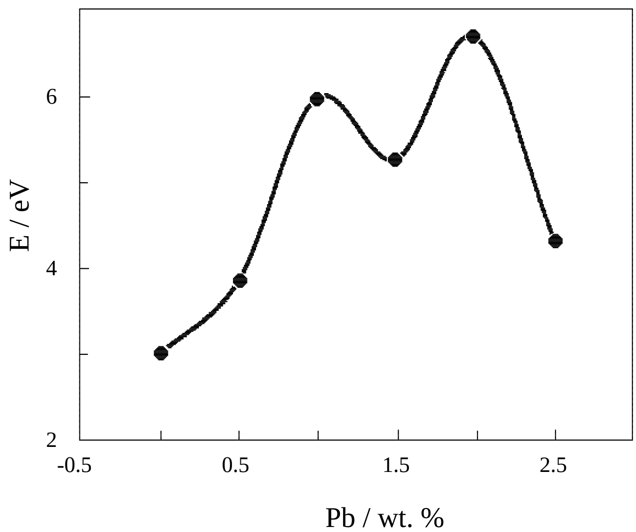

Fig. 5. Variation of the activation energy with Pb *content.*

constant and A is the coordination number i.e. the number of the nearest equidistant surrounding atoms. According to Eq. (7), the relation between $\ln(\Delta C_p T^2)$ and 1000/T is a straight line. From the slope of this line, the energy E, activating the thermally induced process taking place in a certain composition of the alloy, can be obtained. The dependence of the obtained activation energy E on the Pb content is shown in Fig. 5. The irregular behaviour observed for E again proves the suggested existing inhomogeneous composition, density fluctuations and the different nature of the phases induced due to the effect of the existing amount of Pb added to the alloy [22]. The drop of the activation energy at 1.5 wt.%Pb in Fig. 5 is expected since the value of C_p is maximum for this amount of Pb added, as is clear from Fig. 2b.

4. *Conclusion*

We require a Conclusion-section for regular articles. Please, write a short one.

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ZNAČAJKE LEGURA $SnBi_5Pb_x$ DOBIVENIH PRSKANJEM

Pripremali smo osnovnu dvokomponentnu leguru Sn-5wt.%Bi kao i trokomponentne legure s dodacima Pb od 0.5 do 2.5 tež.% metodom prskanja na aluminijski valjak. Sve smo uzorke također ozračili na sobnoj temperaturi γ-zračenjem do doze 1.2 MGy. Mjerili smo unutarnje trenje, toplinsku difuznost i Youngov modul na sobnoj temperaturi, prije i nakon ozračivanja, rezonantnom metodom. Za ispitane uzorke dobili smo DTA termograme i rentgenske difrakcijske snimke. Ishodi mjerenja pokazuju jaku ovisnost mjerenih svojstava o sadržaju Pb i dozi ozračivanja. Opažene se promjene tumače defektima izazvanim zračenjem odnosno neupravljanom disperzijom Pb u matrici legure koji dovode do nejednolikosti sastava i promjenljivosti gustoće.