

Thermomechanical, plastic deformation and quenching effects on precipitation in Pb-17.4 wt. % Sn alloy

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The use of various experimental techniques as X-ray diffraction with Rietveld analysis, differential scanning calorimetry (DSC) and micro-hardness measurements shows their importance and their complementarity in the study of the ageing process in Pb-17.4 wt. % Sn alloy. Actually, their sensitivity to various precipitation stages is different and can give more information to describe the evolution of the structure, the nature and the morphology of the precipitated phase's particles which is not yet well established. However, no effect on the precipitation mode has been observed during the low and high deformation. Moreover it has been shown that the phase's transformations kinetics (precipitation or recrystallization) is very fast.

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1. Introduction

Pb-Sn alloys are the most popular solders and their properties are extensively investigated. However, due to health and environmental concerns, the European Union has made resolution prohibiting Pb usage in the electronic products [1], and the electronic industries are now shifting to Pb-free solders [2–4].

In this paper we discuss briefly how the cellular reaction is affected, and examine in detail the reaction in a Pb-17.4 wt. % Sn alloy. The cell boundary is known to be a grain boundary of the large angle type. Presumably, with both lower activation energy, smaller correlation factor for diffusion, it is suitable for fast mass transport and is highly mobile [5]. Cellular precipitation in several substitutional alloys has been found to be dominated by grain boundary diffusion [6-12]. This is also true for a cellular dissolution reaction whenever the dissolution temperature is relatively low so that boundary diffusion still predominates [13,14].

When a heterogeneous nucleation problem is considered, we usually assume that the heterogeneity such as a grain boundary is stationary. In Pb-5.5 at. % Sn alloy after nucleation, in order to transform the whole specimen, a kinetic process must follow the formation of these heterogeneously formed nuclei and proceed from there to reach all of the untransformed regions [5]. The activation

energy of lattice diffusion of tin in lead has been measured to be 26 kca/mole. Taking this value, we estimate that the diffusivity at room temperature is about 10^{-20} cm²/s, which means it will take more than 10^5 s for a tin atom to make a single jump in the lattice of lead [15].

2. Experimental methods

The alloy containing Pb-17.4 wt. % Sn was prepared using high purity lead and tin (99.99%) by melting in a vacuum of 1.5 mPa. (10^{-5} Torr). The ingots were homogenized in vacuum at 200 °C for 100 h and quenched in water to obtain supersaturated solid solution α_0 . We have prepared a disk shape of 3 mm diameter and 1mm thick for differential scanning calorimetry (DSC) analysis. The DSC measurements were performed with a NETZSCH 200 PC DSC. The X-ray diffraction analysis is performed by "PAN Alytical X' Pert PRO" diffractometer using CuK α radiation, scanned at a speed of 0.9 deg. /min. Structure and microstructure characterization of the different samples have been made by employing Rietveld whole profile fitting method using the MAUD 2.044 software [16]. The instrumental broadening was evaluated with a sample of LaB6 calibrated against a sample of NIST SRM-640b and provided by the Gem Dugout Company. The Vickers

micro-hardness was measured with an AFFRI hardness testing machine.

The chemical analysis of the Pb-17.4 wt. % Sn alloy is presented in Table 1:

Table 1. Chemical composition of Pb-17.4 wt. % Sn alloy.

Element	Pb	Sn	Si	Fe
wt. %	82.57	17.4	0.02	0.01

3. Results and discussions

3.1 X-ray diffraction analysis

Although main emphasis in the present work relies on the metallographic investigation. It was found necessary to investigate certain points by means of X-ray method. Figs. 1, 2 and 3 depict the diffraction patterns of prepared samples under different conditions and treatments. Table 2 gives the refined structural parameters obtained from Rietveld analysis applying the MAUD program [16]. Inspecting the percentage of the Sn, β -precipitate phase resulting from quantitative analysis, one found that it is different from that intended during preparation for all samples; some Sn atoms have been incorporated in the Pb (α -matrix). Rietveld analysis showed that (a) part of Sn atoms is incorporated substitutionally in the α -matrix, lattice replacing Pb atoms forming solid solution. During analysis, the sites occupancies of the atoms Pb and Sn in α -matrix were refined keeping the overall occupancy of the site 4a constrained to 1.0. Fig. 1d depicts the pattern fitting resulting from Rietveld quantitative phase analysis for the sample of (Fig. 1b). For all samples, correlating the refined occupancies with the phase percentages of Sn (β -precipitate), we find that they do not correspond to the weight ratio considered during preparation; few Sn are missed. For example, the Sn occupancy in α -matrix in (Fig. 1c) should be 0.126 instead of 0.099 to balance for the

resulting β -precipitate phase percentage. This will lead us to suppose that (a) part of Sn dopants is diffused on the grain boundary surface or interstitially in the Pb (α -matrix) lattice. These methods were employed in order to determine the lattice parameter of the parent matrix, the depleted matrix to investigate their changes during precipitation as well as to identify the precipitate phases and to examine the crystallographic orientation of the precipitate.

3.1.1- Thermomechanical treatment effect

To highlight the effect of the thermomechanical treatments on the development of the discontinuous precipitation in Pb-17.4 wt. % Sn alloy, we show a state reference of our samples submitted to homogenization at a temperature of 200 °C during 2 hours then quenched in water and deformed to 40 % (Fig. 1a), aged at 60 °C during 20 minutes, (Fig. 1b), 35 hours (Fig. 1c) and (Fig. 1d) which correspond to Fig. 1a developed by the Rietveld analysis method. The X-rays diffraction spectrum of this sample shows peaks of α matrix and β phase. This analysis provides us with information about the plastic deformation effect and the ageing temperature on the discontinuous precipitation kinetics. One observes relative intensity variations treatments and variations in voluminal fraction of phases. New peaks showing the β precipitate, come out with the maintaining time increase, because peaks from (200) β and (101) β type planes become more intense.

The Fig. 1 showed strong preferred orientation [200] for α matrix, leading to anisotropic grain size. The phase percentage of β precipitate is bigger for the quenched (Fig. 1a) and decreases by aging for (Fig. 1b) and (Fig. 1c). The lattice parameter of α matrix decreases depending on the amount of Sn (145 pm) substituting Pb (180 pm) in the matrix. Examining Table 2, one can see the increase of the average grain size from 139 nm for (Fig. 1a) to 321 nm for (Fig. 1c) due to the effect of aging temperature. Also, the lattice microstrain is reduced from 0.001132 to 0.000305.

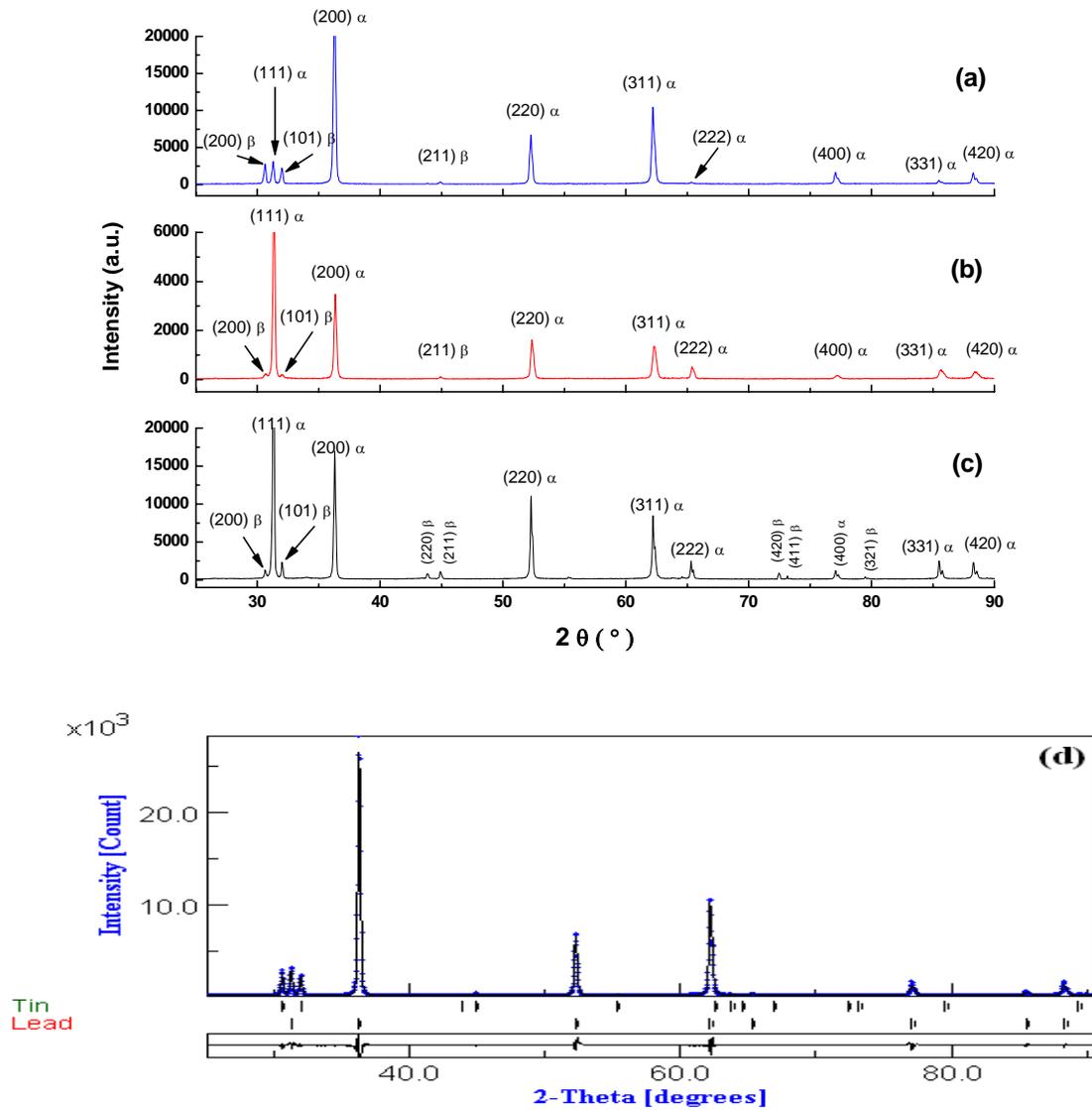


Fig. 1. X-Ray Diffraction Spectrum of Pb-17.4 wt. % Sn alloy, homogenized during 2 hours at 200 °C, water quenched and deformed 40 % (a, d), aged during 20 minutes (b) and 35 hours (c) at 60 °C.

Table 2. The refined lattice parameter a (Å), the relative occupancy of Sn in α -matrix, the phase percentage of β -precipitate, Average Grain size (nm), microstrain obtained from Rietveld analysis of the XRD patterns of Pb-17.4 wt. % Sn.

	Cell parameter a (Å)	β %	Sn Occ.	Average grain size (nm)	Average microstrain (10^{-3})
Fig. 1a	4.94564(20)	14.7	0.045	139	1.132
Fig. 1b	4.94129(9)	05.3	0.156	159	0.791
Fig. 1b	4.94521(7)	10.5	0.099	321	0.305
Fig. 2a	4.94694(20)	16.0	0.022	250	0.019
Fig. 2b	4.94758(17)	10.5	0.097	224	0.016
Fig. 2c	4.94808(19)	12.2	0.075	224	0.108
Fig. 2d	4.94723(20)	15.1	0.018	230	0.059
Fig. 3a	4.94592(29)	0.0	0.279	300	0.012
Fig. 3b	4.94314(22)	7.1	0.077	304	0.324
Fig. 3c	4.94058(12)	3.8	0.175	90.2	1.191

Table 3. Lattice parameter as a function of the quenching temperature.

Sample state	at 200 °C	Iced water quenching	N ₂ liquid quenching
Lattice parameter (Å)	4,9459	4,9431	4,9406

3.1.2 Plastic deformation effect

The X-Ray Diffraction Study is based on Pb-17.4 wt. % Sn alloy samples spectrum; homogenized during 2 hours at 200 °C, quenched (a) then deformed $\epsilon = 30$ % (b); $\epsilon = 50$ % (c); $\epsilon = 70$ % (d) and ageing at 60 °C during 35 hours (Fig. 2).

This analysis shows the relative variation of samples intensities and variation in phase's voluminal fraction. Nevertheless, no change has been observed, during the ageing, in β phase intensity. This means where the increase of the reduction rate by lamination has no effect on peaks represents β precipitate.

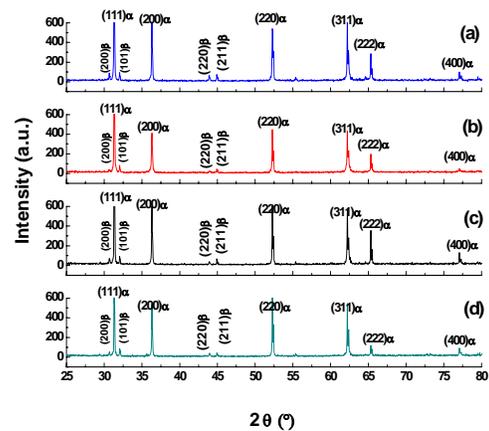


Fig. 2. X-ray diffraction spectrum of Pb-17.4 wt. % Sn alloy, homogenized 2 hours at 200 °C, quenched (a) deformed $\epsilon = 30$ % (b), 50 % (c) and 70 % (d) and ageing at 60 °C during 35 hours.

3.1.3 The quenching effect

Highlighting the quenching effect on the evolution of the discontinuous precipitation of Pb-17.4 wt. % Sn alloy, homogenized at 200 °C (single-phase domain) during 2 hours (Fig. 3a), requires the X-ray diffraction spectrum display for the following cases:

- 1- Iced water quenching after homogenization at 200°C during 2 hours (Fig. 3b).
- 2- Quenching in nitrogen liquid after homogenization at 200°C during 2 hours (Fig. 3c).

The X-ray Diffraction spectrum of Pb-17.4 wt. % Sn sample at 200 °C (Fig. 3a) detects only solid solution peaks (α single-phase domain). The experimental value of the calculated crystalline parameter ($a = 4,945 \text{ \AA}$) is tightly close of the theoretical one ($a = 4.950 \text{ \AA}$) [17].

For quick iced water and liquid nitrogen quenching (Fig. 3b,3c), one can observe phases peaks (α_0 and β). These spectra are practically identical to those of Figure 3a (peaks position number). One notes that peaks of the α_0 saturated solid solution basically of lead (Pb) are moved towards great angles with regards to those of the sample at 200 °C.

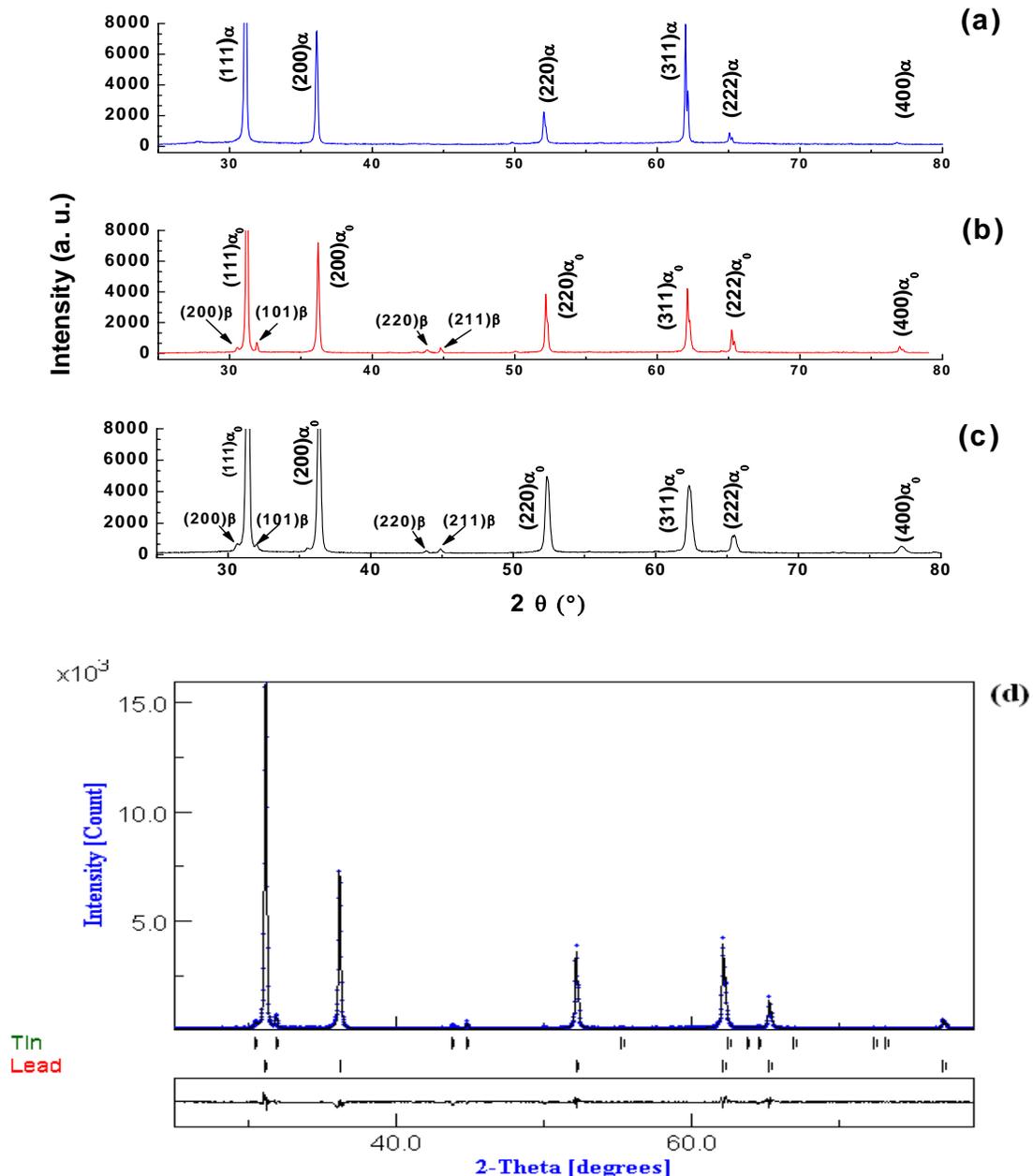


Fig. 3. Samples X-ray diffraction spectra of Pb-17.4 wt. % Sn alloy, matured during 2 hours at 200 °C (a), iced water quenched (b, d) then liquid nitrogen quenched (c).

The crystalline mesh parameter at quenching are lower than those of lattice of the sample at 200 °C ($a = 4.945\text{Å}$). The quenching state (at iced water and liquid nitrogen) of the sample is at the state of contraction because of the solution setting of 17.4 % mass in α solid solution (solution containing lead) at homogenization temperature. The insertion of all the tin atoms in the lead crystal lattice leads to this contraction (the atomic ray of lead 1.801 Å being higher than that of tin 1.405 Å).

One can clearly observe crystalline parameter change, which confirms a second β precipitate phase occurrence.

Moreover, XRD spectra show β phase peaks (containing tin) of the same intensity for the previous quenching cases. Thus, one concludes that the precipitation reaction is prompt and the β phase appears just after a rapid liquid nitrogen quenching.

One may point out that the study on the discontinuous precipitation kinetics of Pb-Sn alloy shows that the growth speed of the cell is controlled by the diffusion in the grain boundary and the concentration of the cell increases with the reduction in the temperature and the deformation [18].

One notes that a study of Josef [19], on a Pb-12, 13 and 15 wt. % Sn alloys, shows that the reaction of discontinuous precipitation is very fast starting from the supersaturated solid solution. In addition, [20] showed on the Pb -7.5 wt. % Sn alloy, for polycrystalline samples, that time τ needed for isothermal half-precipitation is a function of time, temperature of homogenization as well as predeformation before the homogenization. The cells growth is made during a constant and short time [21].

3.2 Micro-hardness measurements

The micro-hardness variation of samples of the Pb-17.4 wt. % Sn alloy, homogenized during 2 hours at 200 °C subjected to a plastic deformation by cold rolled of 10, 30, 50 and 70 % respectively, followed by an ageing at 60 °C is represented in Fig. 4.

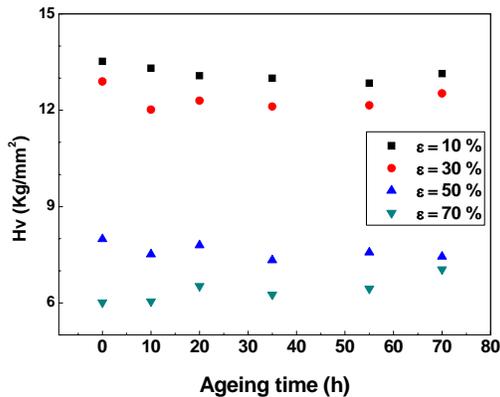


Fig. 4: Micro-hardness variation as a function of ageing time of various samples of Pb-17.4 wt. % Sn alloy aged at 60 °C.

The obtained curves have practically the same shape, that is, a slight reduction in the micro-hardness right after the first ageing times then a slight increase and finally stabilization when the maintaining time (state of equilibrium). One concludes that phase's transformations kinetics (precipitation or recrystallization) is very fast. This variation is in good agreement with work of Sharma [22] and Hilger [23].

3.3 DSC measurement

The DSC (differential calorimetric analysis) tests confirm the speed of precipitation reaction ; just after iced water quenching, while heating from 25 °C to 200 °C with a speed of 5 °C/min, the curve of the DSC presents an anomaly within the temperature interval [130 °C - 195 °C] with a minimum located around $T_m=170$ °C (Fig. 5). This anomaly is an endothermic effect characterizing a dissolution reaction of the β phase formed during quenching and heating. The increases in the deformation result in the increase of dissolution peaks amplitude.

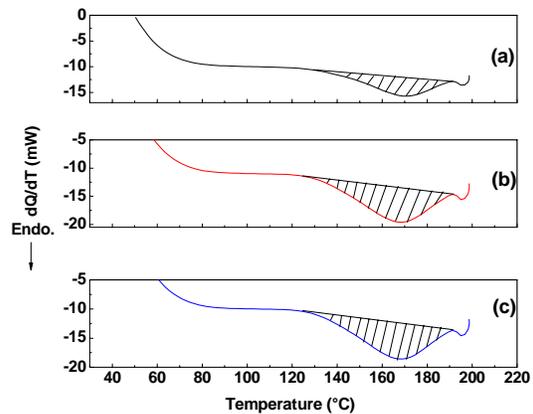


Fig. 5: DSC curves of Pb-17.4 wt. % Sn alloy homogenized during 2 hours at 200 °C, quenched with iced water (a), deformed at 20 % (b) and 30 % (c). (heating rate 5°C/min)

4. Conclusion

In Pb-17.4 wt. % Sn alloy, the increase of the deformation has no effect on peaks representing β precipitate. According to XRD spectra, the micro-hardness measurements and DSC tests we have concluded that:

The precipitation reaction in this alloy is discontinuous.

The change in crystalline parameter confirms the occurrence of a second β precipitate.

The precipitation reaction is very fast and the precipitate β phase occurs just after a rapid quenching with nitrogen liquid.

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