研 究 速 報

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AGEING CHARACTERISTICS OF Pb-Sb ALLOYS

Pb-Sb 合金の時効について

by Seiichi NISHIKAWA* and Kazuo TSUMURAYA*

西 川 精 一・円 谷 和 雄

I. Introduction

Age hardening chracteristics of Pb-Sb alloys with minor additional elements of B sub-group were investigated by one of authors[1], and it was made clear that even a small amount of As had some outstanding unique effects.

In the present investigation, for the purpose of quantitatively clarifing this trace element effect of As on the precipitation kinetics and morphology of Pb-Sb system, electrical resistivity measurements and calorimetry have been performed. Some interesting results are described in the following brief note.

II. Experimental procedures

Alloys were prepared from 99.99% electrolytic lead, six-nine super pure antimony for semiconductor and commercial grade arsenic metal. Mother alloys of 10% Sb and 0.2% As were used. Melting was in graphite crucible and casting was into permanent mould. Ingots were hot extruded into wire of 1 mm, 3 mm and 4 mm in diameter. They were homogenized at 240°C for 48 hours after extrusion and quenched into iced water. The changes of specific electrical resistivity of the quenched alloys during ageing and reversion were measured by D-C potentiometer.

On the other hand, specimens for Takagi-Nagasaki type calorimetry were extruded and cut into cylinders, 20 mm in diameter and 30 mm in height. They were solution treated and aged as above mentioned. Specific heat vs. temperature curves of heat treated samples were obtained at a heating rate of about 1°C/min.

The chemical analysis of the alloys are shown in Table 1.

Table 1 Chemical composition of specimens.

Specimen	Chemical composition (wt%)	
	Sb	As
10	1.14	——
1A	1.14	0.01
20	1.70	——
2A	1.78	0.009

III. Results and Discussion

(1) Changes of electrical resistivity during ageing

In Fig. 1 and 2 specific electrical resistivity vs. ageing time curves of the alloys aged at various temperatures (20°C~100°C) are shown. When these alloys were aged at these temperatures, an

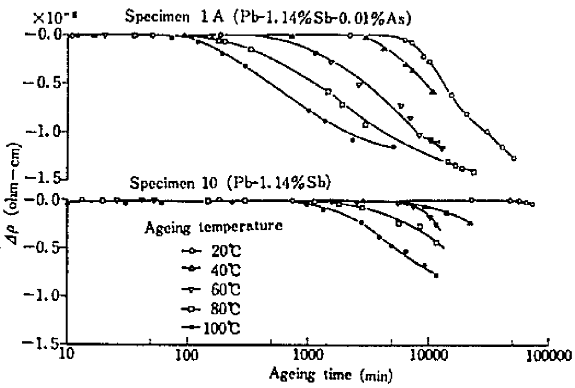

Fig. 1 Specific resistivity versus time curves of Pb-Sb alloys aged at various temperatures after quenching from 240°C into iced water.

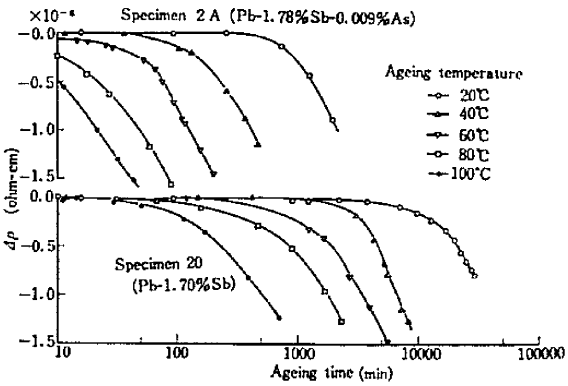

Fig. 2 Specific restivity versus time curves of Pb-Sb alloys aged at various temperatures after quenching from 240°C into iced water.

* Dept. of Industrial Chemistry and Metallurgy, Inst. of Industrial Science, Univ. of Tokyo

initial abnormal resistivity increase which is often found in other age hardening alloys[2),3)] was not observed. Only monotonous resistivity decrease curves were obtained. There was a large difference in precipitation kinetics between two alloys containing 1% Sb and 2% Sb, which seems to indicate the fact that there is an abrupt solid solubility change in this composition range. A small amount of arsenic, as already reported[1)], increased the rate of precipitation rapidly.

Assuming that these specific resistivity vs. ageing time curves fit to the Johnson-Mehl[4)]-Avrami[5)] equation;

$$f = 1\text{-}\exp(-(k\,t)^n)$$

the value of time exponent n was determined. In Fig. 3, the results of this calculation are summerized for 2% Sb alloys. The value of exponent n decreased with increasing ageing temperature. This ageing temperature dependence of n may be explained as follows; at lower ageing temprature, non-steady nucleation rate lives long and deforms the precipitation kinetics over the range of later precipitation stage. On the basis of long range diffusion controlled growth, the experimentally determined values of n between 1 and 2 can be considered for the case of next conditions; one dimensional ($n=3/2$) or two dimensional ($n=2$) growth of needle or plate under constant nucleation rate, or two dimensional ($n=1$) or three dimensional ($n=3/2$) growth under zero nucleation rate. By microscopic observations, it was found that the shape of precipitaes was plate-like or nearly rod.

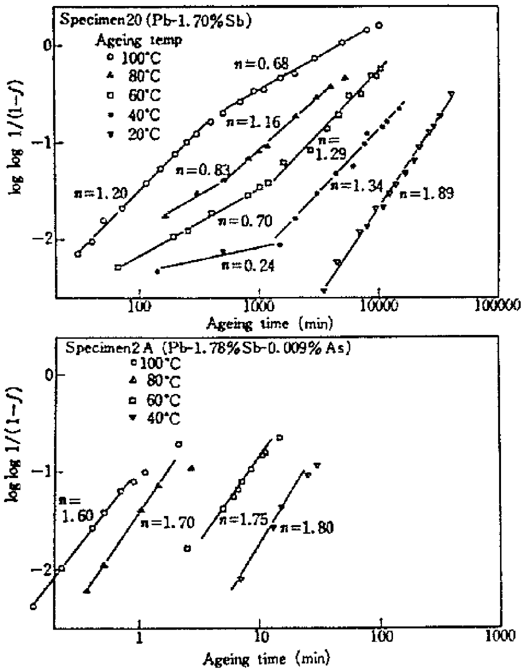

Fig. 3 Ageing kinetics of Pb-Sb alloys.

The specimen containing a small amount of arsenic showed only a small temperature dependence of n. From this and the results of isothermal ageing curves (Fig. 1, 2), it is supposed that a small amount of arsenic operates as nucleus for Sb rich precipitate from supersaturated soild solution of Pb-Sb alloys.

(2) Specific heat measurement

The specific heat vs. temperature curves (S-T curves) of the 10, 20 and 2A alloys which were quenched from 240°C and aged for various periods are shown in Fig. 4. The specimen 10 with about 1% Sb did not show any remarkable heat change but only heat absorpition R due to dissolution of stable precipitate after long ageing. This may be

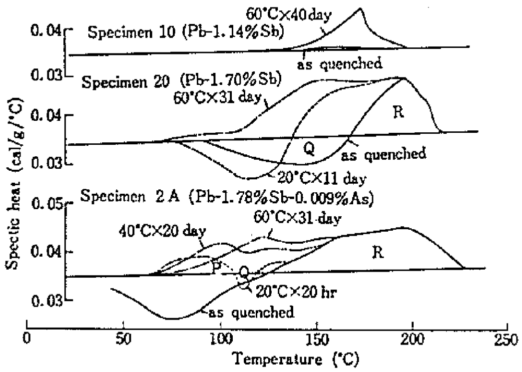

Fig. 4 Specific heat versus temperature curves of Pb-Sb alloys.

attributed to the fact that 10 alloy has too low supersaturation to show any precipitation tendency during calorimetric mesurement by heating rate of 1°C/min. In the case of 20 alloy with about 2% Sb both heat evolution Q due to precipitation and heat absorption R due to dissolution were observed even when calorimetry was performed immediately after quenching. In 2A alloy, another heat absorption peak P appeared at low temperature prior to heat evolution Q. This absorption peak P seems to be correlated with the reversion energy, i.e. the energy required for re-dissolution of such a metastable product formed during low temperature aging as observed in Al-Cu[6)], Al-Zn[7)] and Al-Ag[8)] alloys. As shown in Fig. 4, this re-dissolution reaction has a tendency to move to higher temperature side with ageing temperature. The thermal behaviour of this low temperature precipitate well resembles to that of solute atom aggregates, i.e. G.-P. zones.

(3) Reversion kinetics of low temperature precipitate

Fig. 5 shows the change of resistivity during reversion of low temperature precipitate. This re-dissolution reaction seems to take longer periods than the so called reversion reaction of G.-P. zones in other alloy systems[9),10)] and moreover, complete reversion was not observed. A small

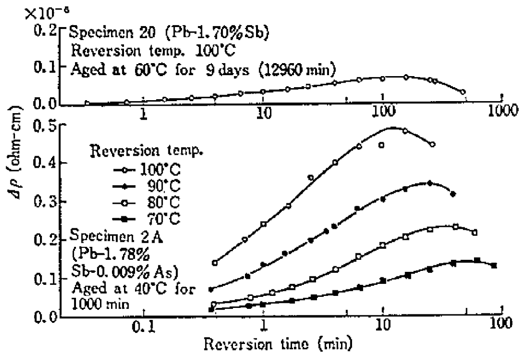

Fig. 5 Specific resistivity reversion of Pb-Sb alloys

amount of specific resistivity increase caused by reversion was observed in 20 sample free of arsenic after long ageing. Looking from the shape of S-T curves shown in Fig. 4, a faint trace of reversion of 20 sample seemed to take place at higher temperature (about 140°C) near to heat absorption peak R.

From these experimental results, the effects of a small amount of As in Pb-Sb alloy are summerized as follows;

1) The quantity of reversible precipitate in simple Pb-Sb binary system is very small, but increases very much by addition of a small amount of As (~0.01 wt. %).

2) This low temperature precipitate gives a remarkable increase of mechanical property to Pb-Sb alloy system[1)], but does not induce any initial anomalous increase in electrical resistivity vs. ageing time curve.

3) The thermal stability of this low temperature precipitate increases with ageing temperature, and becomes nearly as stable as equilibrium phase after long and high temperature ageing.

A brief note is presented concerning the low temperature precipitate which tends to appear in Pb-Sb alloy system with a small amount of As. In future, much more efforts must be devoted to determine the size of this metastable precipitate and its relation with an equilibrium phase, and moreover, the role of As in nucleation and growth mechanism. (Manuscript recieved (July 29, 1969.)

Reference

1) S. Nishikawa; Rep. Inst. Sci. Tokyo Univ. **92** (1960)
2) H. Kimura and R. R. Hasiguti; Act Met. **9** (1961) 1076
3) A. Kelly and R. B. Nicholson; Peogr. Mater. Sci. **10** (1963) 151
4) W. A. Johnson and R. F. Mehl; Trans. A. I. M. E. **135** (1939) 416
5) M. Avrami; J. Chem. Phys. **7** (1939) 1103
6) K. Hirano and H. Iwasaki; Trans. J. I. M. **5** (1964) 162
7) K. Hirano; J. Phys. Soc. Japan. **10** (1955) 995
8) K. Hirano; J. Phys. Soc. Japan. **8** (1953) 603
9) K. Asano and K. Hirano; Trans. J. I. M. **9** (1953) 24
10) W. Koster and F. Braumann; Z. Metallk. **43** (1952) 193